ABSTRACT

AN ABSTRACT OF THE THESIS OF


Title: Effects of Selected Minor Alloying Additions on the Structure and Deformation Characteristics of Beryllium

Abstract approved: [Redacted]

William D. McMullen

Solid solution alloying was employed in an attempt to produce some relatively ductile form of beryllium. If the c/a ratio could be significantly altered, it was felt new or different slip systems could be activated. The following elements were selected on the basis of atomic size, melting point, crystal structure and density for adding to beryllium in amounts of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 atomic percentages: boron, manganese and titanium. All samples were non-consumable arc melted, machined and sectioned for wet chemical, spectrographic, X-ray diffraction and metallographic analysis as well as for mechanical (compression) testing.

These tests showed all alloy samples exceeded the solubility limits in each respective system. Be$_{4.5}$B, Be$_8$Mn and Be$_{12}$Ti were identified as
the second phases in the individual systems. Beryllium-boron alloys exhibited an eutectic or peritectic reaction and the eutectic composition in the beryllium-manganese system was established at 22.0 weight percent manganese.

The samples Be/0.5B, Be/1.0Mn and Be/0.5Ti gave yield strengths of 47, 200 psi, 56, 600 psi and 81, 250 psi respectively in compression testing. These same specimens yielded work hardening rates of $1.07 \times 10^6$ psi, $1.3 \times 10^6$ psi and $1.52 \times 10^6$ psi respectively.

Long wide twins in pure beryllium were accompanied by large amounts of cross-slip. The boron sample displayed long wide twins and also very short narrow twins, no cross-slip and extensive areas with microcracks present. Shorter and narrower twins characterize the manganese specimens. The beryllium-titanium alloys exhibited extremely small twins emanating from particles of second phase Be$_{12}$Ti; however, the majority of the twins in this system are long, extremely narrow and are seen to be internally constricted along the length of the twin. These constrictions have been ascribed to a strain relief process which further prevented the twin from growing parallel to its shorter dimension.

The near total absence of cross-slip in the three alloy systems was attributed to a lessening of the stacking fault energy as a result of increasing the solute concentration. The drop in the stacking fault energy
decreases the probability for cross-slip, makes extensive deformation difficult and explains higher yield strengths and work hardening rates.

Evidence presented suggests slip occurs prior to gross twin propagation. The relationship between twinning shear and twin shape suggests for the beryllium-titanium alloys twinning on higher order planes (e.g., \(\{11\bar{2}1\}\) or \(\{11\bar{2}2\}\)) rather than the \(\{10\bar{1}2\}\) twinning normally observed.
Effects of Selected Minor Alloying Additions on the Structure and Deformation Characteristics of Beryllium

by

George Joseph Dooley III

A THESIS submitted to Oregon State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

June 1969
APPROVAL SHEET

APPROVED:

____________________________
Associate Professor of Mechanical Engineering

____________________________
Head of Department of Mechanical Engineering

____________________________
Dean of Graduate School

Date thesis is presented May 7, 1969

Typed by Joyce McInnis for George J. Dooley III
ACKNOWLEDGMENTS

The author would like to express his gratitude to the U.S. Bureau of Mines, Albany, Oregon and to Oregon State University, Corvallis, Oregon, whose cooperative agreement made this research work possible. Although many Bureau of Mines' personnel were helpful throughout the course of this work, particular thanks must be extended to members of the Metals Processing branch under the direction of Mr. Robert Beall, to members of the Materials Science branch under the direction of Mr. Hal Kelly and to Mr. Jim Wilderman of the drafting section for his work on the figures and drawings. Mrs. Joyce McInnis, typist and secretary, deserves more praise than thanks for her efficiency, assistance and good nature during the author's stay at the Bureau of Mines.

The majority of the technical guidance for this piece of research was provided by Dr. William McMullen of Oregon State University. His unique personality coupled with technical competence provided the latitude necessary for carrying through a research project of this type. His suggestions and guidance gave more directionality to the work and saved many hours time when the author's efforts would perhaps have proceeded along other avenues of approach. The author's sincere appreciation is extended to him for his aid and cooperation.
The greatest debt of any must be paid to the author's wife for her patience, hard work and encouragement throughout this somewhat trying period of life. Her willingness (and often insistence) of putting academic and research efforts on the part of the author before their personal and family obligations was indicative of the continuing support received while working as a graduate student. Without her aid the work would have been less enjoyable, less meaningful and certainly much less rewarding.
TABLE OF CONTENTS

INTRODUCTION.................................................. 1
THEORETICAL BACKGROUND..................................... 8
REVIEW OF LITERATURE......................................... 30
MATERIALS....................................................... 97
APPARATUS AND EXPERIMENTAL PROCEDURES.................. 102
  Weighing and Compacting................................... 102
  Nonconsumable Arc Melting.................................. 103
  Machining and Sectioning.................................... 108
  Metallographic Analyses.................................... 109
  X-ray Diffraction Analysis.................................. 110
  Chemical and Spectrographic Analyses..................... 112
  Compression Testing........................................ 113
EXPERIMENTAL RESULTS......................................... 116
  X-ray Diffraction........................................... 116
  Metallography............................................... 118
  Mechanical Deformation...................................... 124
  Slip and Twinning.......................................... 128
DISCUSSION AND CONCLUSIONS.................................. 151
SUMMARY....................................................... 169
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS (Continued)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUGGESTIONS FOR FUTURE WORK</td>
<td>172</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>175</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Planes in an hexagonal lattice with a common ${\bar{1}2\bar{1}0}$ direction</td>
</tr>
<tr>
<td>2</td>
<td>Important planes and directions in an hexagonal close packed metal</td>
</tr>
<tr>
<td>3</td>
<td>Crystallographic directions and planes in hexagonal close packed beryllium</td>
</tr>
<tr>
<td>4</td>
<td>Slips, fracture and twin planes in beryllium</td>
</tr>
<tr>
<td>5</td>
<td>Effect of temperature on the critical stress for (0001) slip and (10\bar{1}0) slip</td>
</tr>
<tr>
<td>6</td>
<td>The compounds of beryllium</td>
</tr>
<tr>
<td>7</td>
<td>Nonconsumable arc melting button furnace</td>
</tr>
<tr>
<td>8</td>
<td>Second phase Be$_{4-5}$B in beryllium-boron alloys</td>
</tr>
<tr>
<td>9</td>
<td>Eutectic phase in Be/4.0Mn</td>
</tr>
<tr>
<td>10</td>
<td>Be$_8$Mn phase in Be/1.0Mn</td>
</tr>
<tr>
<td>11</td>
<td>Be$_{12}$Ti phase in Be/0.5Ti</td>
</tr>
<tr>
<td>12-A</td>
<td>Microstructure of deformed pure beryllium</td>
</tr>
<tr>
<td>12-B</td>
<td></td>
</tr>
<tr>
<td>12-C</td>
<td>Typical deformation twins in pure beryllium</td>
</tr>
<tr>
<td>13</td>
<td>Straight slip lines in pure beryllium</td>
</tr>
<tr>
<td>14</td>
<td>Cross slip in pure beryllium</td>
</tr>
<tr>
<td>15</td>
<td>Slip lines crossing twins in pure beryllium</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>16</td>
<td>Typical deformation twins in Be/0.5B</td>
</tr>
<tr>
<td>17</td>
<td>Microcracks in Be/0.5B</td>
</tr>
<tr>
<td>18</td>
<td>Curved twins in Be/0.5B</td>
</tr>
<tr>
<td>19</td>
<td>Representative deformation twins in Be/1.0Mn</td>
</tr>
<tr>
<td>20</td>
<td>Very narrow twins in Be/1.0Mn</td>
</tr>
<tr>
<td>21</td>
<td>Twin intersections in Be/1.0Mn</td>
</tr>
<tr>
<td>22</td>
<td>Extensive twinning in Be/1.0Mn</td>
</tr>
<tr>
<td>23</td>
<td>Short twins and second phase in Be/0.5Ti</td>
</tr>
<tr>
<td>24</td>
<td>Narrow twins in Be/0.5Ti</td>
</tr>
<tr>
<td>25</td>
<td>Slip lines in Be/0.5Ti</td>
</tr>
<tr>
<td>26</td>
<td>Irregular twins in Be/0.5Ti</td>
</tr>
<tr>
<td>27</td>
<td>Slip crossing twins in Be/0.5Ti</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Modes of slip in hexagonal metals</td>
<td>22</td>
</tr>
<tr>
<td>II</td>
<td>Beryllium deformation behavior</td>
<td>40</td>
</tr>
<tr>
<td>III</td>
<td>Microstructure of binary beryllium alloys as melted</td>
<td>74</td>
</tr>
<tr>
<td>IV</td>
<td>Beryllium starting material analysis</td>
<td>100</td>
</tr>
<tr>
<td>V</td>
<td>Alloying element analysis</td>
<td>101</td>
</tr>
<tr>
<td>VI</td>
<td>Alloy compositions after arc-melting of samples used in compression testing experiments</td>
<td>124</td>
</tr>
<tr>
<td>VII</td>
<td>Work hardening rates and yield strengths for beryllium alloys</td>
<td>127</td>
</tr>
</tbody>
</table>
EFFECTS OF SELECTED MINOR ALLOYING ADDITIONS
ON THE STRUCTURE AND DEFORMATION
CHARACTERISTICS OF BERYLLIUM

INTRODUCTION

The potential of the metal, beryllium, has been recognized for some time. Its notable characteristics are low density, high elastic modulus and its high strength-to-weight ratio (61). Its density (1.848 grams per cubic centimeter) approaches that of magnesium, yet beryllium melts some 600° C higher than magnesium. Its elastic modulus is approximately 140 percent that of iron, however, it is less than one-fourth as heavy. Its electrical conductivity is approximately 40 percent that of pure copper (2). But, use of pure beryllium in industrial applications has never significantly materialized. Beryllium has not realized its full potential in industrial applications because of its lack of so-called third-dimensional ductility. The term "third-dimensional ductility" infers that plates and sheets of beryllium can be successfully fabricated, but these structures are incapable of supporting any bending or any significant forces perpendicular to their major plane of symmetry. Efforts to fabricate beryllium by conventional means of fusion, casting and extrusion, have been only partially successful. It is possible to limitedly manipulate the ductility of beryllium, but each particular application requires a careful study of the fabrication methods so as to produce optimum ductility in a specific direction by a
compromise of the ductilities in the other directions. This fact is physical evidence for the known anisotropy of beryllium.

Beryllium has other features not related to the ductility aspect which make it a valuable material. These will not be of interest in this work; however, they should be mentioned for the sake of completeness. Beryllium is characterized by some outstanding nuclear properties. It has an extremely low neutron capture cross section and a high neutron scattering cross section which make it useful as a moderator and reflector for thermal nuclear-power reactors. During the last few years emphasis in the application of beryllium has shifted from nuclear applications to so-called "space applications" and the latest development of beryllium has been in connection with the various rocket, missile, and aircraft projects. Nevertheless, two main factors have delayed a wider application of beryllium in industry. The first of these, the relatively low ductility of the metal, is directly related to this present work. The second factor is the high price of beryllium. A third reason - the danger in handling beryllium on account of its toxicity - has been overcome almost completely.

The question has been raised as to just how great a deterrent is beryllium's lack of ductility (21). Of the three above-mentioned problems limiting its use as a common structural material, the lack of ductility is the most serious problem. Most of the work directed toward solving the ductility problem has taken one of two possible approaches. The first of these is that
the metal is inherently non-ductile or that it is unlikely to be made ductile in the near future. Under this approach, effort is aimed at optimizing the usefulness of beryllium by understanding the nature of the brittleness in designing metallurgical procedures to minimize the problems encountered in the use of the metal. Now, the other point of view is that beryllium is inherently ductile. In this instance, attempts are made to purify the metal and to ascertain the impurity or impurities responsible for the lack of ductility.

"Commercial" beryllium is not a reasonably pure metal as are commercially pure copper, nickel, titanium, etc. It is a very complex alloy with many individual impurities in solid solution and in the form of stable and unstable precipitates and dispersed phases. Consequently, some investigators feel research on "commercial" beryllium will not produce any significant improvements in desirable properties or lead to an understanding of its behavior (9). Today the most widely held opinion is that a severe ductility problem exists in beryllium and there should be no question but that the problem is a most severe one. There is a need to recognize, and in some way design around, its adverse properties in order to take advantage of the favorable attributes.

Aside from the brittleness problem, beryllium is not employed in many potential applications because its use is simply too costly. It is felt the price of the metal could be reduced most significantly if the producers could operate more efficiently, which could be done by a greater rate of production. In this regard it is interesting to note that an improvement in ductility,
desirable, is not of itself a prerequisite to many uses (39). Thus, the ever-present implication that unless the "brittleness-problem" is solved, the use of beryllium will be very limited is not always true. It should be better appreciated that in the environments of the Atomic Energy Commission and the Department of Defense, there is an assured expanding role for beryllium regardless of its brittleness and toxicity. Improvements are necessary indeed, but they are chiefly related to reliability and uniformity of product.

A major part of the efforts to increase the ductility of beryllium have taken the so-called purification route. It is felt that if the majority of the impurities can be removed from the metal, as has been shown to be the case for many other metals, the ductility of the metal should be improved. Depending on the process used to produce the beryllium, the major impurities present are usually carbon and oxygen.

The objective of this present study is also to increase the ductility of beryllium from a different but by no means unique technique. The method decided upon was that of alloying beryllium with certain selected elements. The initial reasoning was that if the c/a ratio (1.567) in beryllium could be significantly altered from this present value, then some new and/or different slip systems could be initiated in beryllium and, hopefully, these new slip systems would tend to increase beryllium's ductility.
The idea of a beryllium alloy is not new. As far back as the mid-1920's, various concerns such as Union Carbide and the Beryllium Corporation of America were investigating alloying beryllium with copper, nickel, gold, iron, and aluminum (61, p. 9). Of these alloys, beryllium-copper, and beryllium-iron have enjoyed the widest reputation. The first beryllium-copper alloy was used for springs and diaphragms, but during the early development of the industry, the largest use of beryllium-copper alloys was in the manufacture of nonsparking safety tools. And even at the present time, contrary to the somewhat popular belief, the major use of beryllium is still in beryllium-copper alloys. This use accounts for 80 percent or more of all beryllium extracted from the ore. It should be noted, however, that many of the beryllium alloys in use today contain the non-beryllium element as a major constituent. In this present study the major component is to be the beryllium instead. The selected alloying additions are to be present only in minor atomic percentages or mole percentages. But even the beryllium alloys which did not have beryllium as a major component were only developed after the discovery that extraction of pure beryllium was a difficult and costly process and that the metal was hard to fabricate even after purification attempts, and that due to its lack of ductility and its coarse grain size even cast metal could not be machined (14).

In some of the beryllium alloy studies mentioned above, the purpose was admittedly not to increase the ductility of beryllium. For example,
beryllium is able to precipitation-harden copper. In aluminum- and magnesium-base alloys, beryllium is used to prevent oxidation. In nickel-base and iron-base alloys, beryllium finds use as a potent strengthening or hardening agent. Again in the magnesium-base alloys it was found that small traces of beryllium markedly inhibited the oxidizing tendencies and inflammability of magnesium and magnesium alloys. But here again, the emphasis is on the component other than beryllium.

Assuming that significant ductility cannot be obtained in the pure metal, the widespread possibilities of a beryllium alloy, with beryllium as the major constituent, are immediately obvious. The high melting temperature, the high tensile strength, the low density, the high modulus of elasticity, and the high strength-to-weight ratio of beryllium would be retained. Often overlooked is the fact that the thermal expansion of beryllium is considerably less than that of magnesium and aluminum, the other two light metals to which it is frequently compared. Of major importance is the fact that the specific heat of beryllium is almost twice as large as the specific heat of these two metals (25). Thus, efficient heat dissipation would be another advantage of beryllium.

The fact is well recognized that impurities play a very significant role in affecting the ductility and other mechanical properties of beryllium. Their effect is more pronounced due to the small size of the beryllium atom and the
extreme reactivity of the material. As stated by Bunshah (9) a few years ago, future research trends for beryllium would develop into two main areas:

1. Improvements on commercial beryllium, and 2. Production of super-purity beryllium. In the first area, that of improving commercial beryllium, the major objective was to produce a commercial material with a minimum amount of precipitates and second phases, of about 99.5 percent purity, the 0.5 percent representing desirable alloying elements, in order to test its mechanical properties. In the second area, producing super-purity beryllium, it was felt the major efforts should be directed toward the production of alloys (from the super-pure beryllium) without contaminants. It was in thoughts and beliefs of these types that this study received its inception.
THEORETICAL BACKGROUND

As early as 1950, Kaufmann (32) concluded there was no obvious evidence that impurities were responsible for the lack of ductility in beryllium. This observation was based on the facts that (a) the common impurities in beryllium such as aluminum, silicon, oxygen, carbon, and nitrogen appeared to have a negligible solid solubility in beryllium, and hence, could not embrittle the metal by solution hardening. (b) No metallographic evidence was uncovered of inclusions or precipitated phases in appreciable amounts which might cause this lack of ductility. (c) Beryllium from different sources having varying degrees of impurity content was unable to be fabricated even though they possessed essentially the same values for physical constants.

It is well known that slip occurs in beryllium single-crystals on both (0001) basal planes and (10I0) prismatic planes at all temperatures between room temperature and at least 700° C. The manner in which textures and preferred orientations are developed in extrusion, rolling, and cross rolling at temperatures of 1,000 to 1,100° C suggests both these modes are still operative in this temperature range. The slip direction has been established as <1120> for both slip planes. These directional and planar relationships are represented graphically for an equivalent set of planes and directions in Figure 1.
FIGURE 1. Planes in an hexagonal lattice with a common [1210] direction
Basal slip is characterized by the formation of relatively straight slip lines, by having a critical stress which is about one-fifth that for prism slip at room temperature, by the formation of \(\{11\bar{2}0\}\) kink-bands both in tension and compression, by the development of cracks associated with these kink-bands, and by the fact that the resolved shear stress for basal slip is apparently higher at 500° C than it is at room temperature. The resolved shear stress for basal slip in tension has been measured to be 2,000 psi ± 500 psi at room temperature increasing up to about 2,500 psi ± 300 psi at 500° C. Lee and Brick (61, p. 380) found values of the critical resolved shear stress for basal slip in compression of 4,600 psi at room temperature, 4,060 psi at 300° C, and 6,460 psi at 500° C.

One of the most important deformation features in beryllium was not identified until 1951. This deformation mechanism was the occurrence of slip on \(\{10\bar{1}0\}\) planes found in single crystals at room temperature. This is normally referred to as prismatic slip. When basal planes are parallel to the tension or compression axis, an effect of orientation on room temperature prism slip and ductility exists, which depends on whether a Type 1, \((10\bar{1}0)\), or Type 2, \((11\bar{2}0)\), prism plane is perpendicular to the stress axis. When the applied stress is normal to a \((10\bar{1}0)\) plane, as is shown in Figure 2B and in Figure 3, simultaneous slip can occur on two \(\{10\bar{1}0\}\) planes which are 30 degrees to the stress axis; the duplex slip in specimens of this orientation
FIGURE 2. Important planes and directions in an hexagonal close packed metal.
FIGURE 3. Crystallographic directions and planes in hexagonal close-packed beryllium.
acts as a self-aligning feature which maintains the original degree of axiality with respect to the stress system; furthermore, the average orientation will remain constant during deformation by virtue of equal and opposing reorientations on the two slip planes. When the applied stress is normal to a (\(11\bar{2}0\)) plane, as is shown in Figure 3 and Figure 4B, slip begins on one or the other of the \(\{10\bar{1}0\}\) planes which were at 60 degrees to the stress axis. Because of the reorientation accompanying this slip the active slip plane located toward the stress axis tends to increase the resolved shear stress on the initial or active slip plane and to reduce it on the second \(\{10\bar{1}0\}\) plane which was also originally at 60 degrees. This leads to fracture on the \(\{11\bar{2}0\}\) plane perpendicular to the stress axis.

The critical stress for slip on \(\{10\bar{1}0\}\) planes together with those for basal slip in the temperature range of -196° to 700° C are shown in Figure 5. In this figure the stress values shown for slip are twice the value of the critical resolved shear stress, \(\tau\); that is, they represent the critical minimum applied stress, \(\tau\) which will cause slip to occur. The critical resolved shear stress \((\tau)\) for \(\{10\bar{1}0\}\) slip is measured to be 9,500 psi ± 500 psi at room temperature.

Because of the high ratio of the critical resolved shear stress for prism slip to the critical resolved shear stress for basal slip at room temperature, prism slip is restricted to orientations in which the basal planes are
A Basal (0001); slip and fracture plane
Prism type 1 (10\{10\}); slip plane
B Prism type 2 (11\{20\}); fracture plane
C Pyramidal (10\{12\}); twin plane
D Atomic sites in the hexagonal cell and important
directions (in brackets)
E Pyramidal (10\{11\}); slip plane at elevated temperature

FIGURE 4. Slip, fracture, and twin planes in beryllium
FIGURE 5. Effect of temperature on the critical stresses for (0001) slip and \{10\overline{1}0\} slip (Ref. 61)
within a few degrees of being parallel to the stress axis. For this reason, (0001) slip is the dominant plastic process at room temperature. In Figure 5 the bottom of the band represents the first apparent departure from linear, elastic stress-strain behavior while the upper boundary of the band represents the stress level at approximately 0.5 percent offset.

The possibility exists that the decrease recorded for the critical stress of (10\overline{1}0) slip as a function of increasing temperature may be partially the result of slip occurring on other planes of the (10\overline{1}X) family and may not be attributable to a lowering of the critical stress for slip on the (10\overline{1}0) plane. In Figure 5, the dotted lines for (11\overline{2}0) fracture, (0001) basal cleavage, and (10\overline{1}2) twinning are not meant to imply that actual critical stresses exist for these phenomena but merely to give an indication of the applied stress levels below which these deformation modes have not been observed.

As Kaufmann (61, p. 383) has pointed out, it is surprising the critical stresses for basal slip should be one-quarter to one-fifth those for prismatic slip at room temperature since beryllium, because of its low c/a ratio, has a larger spacing between (10\overline{1}0) prism planes than between (0001) basal planes. Thus, prism slip should be increasingly favored with decreasing c/a. This is true for the elements Cd through Y, but beryllium reverses the trend. This
is not an impurity effect, for beryllium shows increasing preference for basal slip with increasing purity. This anomaly could be caused by the marked anisotropy of the elastic constants of beryllium (16). However, magnesium also has much lower shear stresses on basal planes than on other planes. The fact that slip is apparently easier in titanium and zirconium on \{10\overline{1}0\} prism planes than it is on basal planes, indicates that factors other than the c/a ratio (e.g., the electronic configuration) may be important in determining slip behavior. In beryllium single-crystal specimens where only (0001) slip occurred, or where there was slip on only one (10\overline{1}0) slip plane, relatively little strain hardening occurs, but where duplex (10\overline{1}0) slip is observed, the strain hardening is quite marked.

For polycrystals, under conditions of primarily tensile stress or where large extension occurs in one direction, the beryllium crystals are reoriented during deformation in such a way as to cause (0001) planes to become parallel to the tension axis or direction of greatest extension. This means, that even if basal slip does occur (and is not interrupted by fracture), reorientation will tend to lead to an orientation where prismatic or pyramidal slip will become active.

It has been noted that wavy slip occurs in connection with slip on \{10\overline{1}0\} planes in beryllium single crystals and this waviness increases with temperature. This waviness is also always observed to be much more prominent in
non-basal slip than in basal slip. The degree of waviness of slip lines in the beryllium also increases with the strain or degree of work hardening. The effect of strain is to change the apparent slip-behavior since waviness occurs between original slip lines which are relatively straight.

One of the most important deformation modes in beryllium as far as this present research work is concerned is twinning. Twinning in beryllium has been reported as early as 1928 (61, p. 389). Twinning takes place on \(\{10\overline{1}2\}\) planes as shown in Figure 2D, Figure 3 and Figure 4C and it is generally agreed that only \(\{10\overline{1}2\}\) twinning occurs in beryllium between \(-190^\circ\) and \(700^\circ\) C. All other hexagonal close-packed metals exhibit additional twinning modes. The twinning direction in \(\{10\overline{1}2\}\) twinning has been established as \(<10\overline{1}1>\). Much of the planar and directional relationships about twinning in beryllium has been obtained on compression specimens in which a \(<10\overline{1}0>\) axis was parallel to the compression axis and the square sides of the compression specimens were respectively parallel to \((0001)\) planes and a \(\{11\overline{2}0\}\) plane. No marks were observed on the \(\{11\overline{2}0\}\) faces while the \((0001)\) faces had prominent twin markings parallel to the compression surface. Depending on orientation, most authors agree that twinning is operative from room temperature to at least \(850^\circ\) C.

Despite earlier suppositions that there was no unique critical shear stress at room temperature on the \(\{10\overline{1}2\}\) twin plane at which twinning would occur, a resolved stress on the twinning plane of approximately 8,000 psi is now recognized. The similarity of this value to the critical shear stress for
\{10\bar{1}0\} slip at room temperature could cause competing between these two modes of deformation in compression tests parallel to the basal plane in which \{0001\} slip is inhibited. It can be said if twinning starts before \{10\bar{1}0\} slip in a compression specimen in which \langle10\bar{1}0\rangle direction is parallel to the compression axis, the first twin that forms creates an effective barrier for subsequent \{10\bar{1}0\} slip in the matrix since two of the \langle11\bar{2}0\rangle slip directions in the matrix in which \{10\bar{1}0\} slip could occur have been destroyed within the body of the twin. The new \langle11\bar{2}0\rangle directions which are created within the twin are essentially parallel to the plane of compression and hence cannot contribute to slip.

In beryllium there are indications twinning occurs more easily in the compression perpendicular to prism planes than in tension perpendicular to basal planes. One reason for this may be that under conditions of compression there is a slight decrease in volume strain energy within the body of the twin arising because of the difference in elastic moduli parallel and perpendicular to the c-axis, while in tension perpendicular to basal planes there is a slight increase in volume strain energy. Other possible reasons for the predominance of twinning in compression are: (a) there is a much larger area of the total surface in which twinning is possible in compression and (b) the \langle10\bar{1}0\rangle texture which may be developed during extrusion causes twinning to be a much more probable process in compression parallel to the prior extrusion axis than in tension.
In simple body-centered cubic and face-centered cubic metals (these are called single-lattice structures), parent and twin structures are related by a homogeneous shear. This is not so in double lattice structures, such as hexagonal close pack, (which contain two atoms per lattice point), where additional small atom displacements are required in a direction different from the lattice shear. These atom movements are called shuffles.

Twinning in \(\{10\bar{1}2\}\) planes occurs in all hcp metals; this twinning mode has the lowest shear and involves simple shuffles in the plane of shear. Unfortunately, it is difficult to obtain quantitative information on other observed more complex twinning modes such as \(\{10\bar{1}1\}\) because of the large amount of deformation associated with the twins and a detailed explanation of these twinning modes is not yet available. For \(\{10\bar{1}2\}\) type twins, the shear is a maximum in beryllium, but is still small compared with other types of twins in hcp metals.

For a short summary as far as slip and twinning are concerned, prismatic slip on \(\{10\bar{1}0\}\) planes in \(<1\bar{1}\bar{2}0>\) directions occurs in both tension and compression. Unlike other hexagonal metals, this slip system is the important one when beryllium undergoes appreciable amounts of tensile elongation. Basal plane slip occurs at a relatively low value (2,000 psi as compared with 9,500 psi for \(\{10\bar{1}0\}\) slip) of resolved shear stress in tension at room temperature. After small amounts of (0001) slip in tension, fracture occurs, normally on the (0001) plane, although it is sometimes found on the \(\{11\bar{2}0\}\) planes. Fairly large
amounts of (0001) slip can be accommodated in compression. The critical shear stress for basal slip increases slightly with temperature up to approximately 2,500 psi at 500° C, while that for \( \{10\overline{1}0\} \) slip decreases markedly to a similar value of 2,500 psi at 500° C. Twinning, on the other hand, occurs only on the \( \{10\overline{1}2\} \) planes and is observed both under tension and under compression. In order to obtain twinning in tension there must be a major component of the tensile force parallel to the c-axis; for twinning in compression there must be a major component of the compressive force perpendicular to the c-axis. Twinning has been found to be operative at all temperatures between -190° and 850° C, although at elevated temperatures, because of the relative ease of operation of other deformation modes (e.g., \( \{10\overline{1}0\} \) slip), \( \{10\overline{1}2\} \) twinning is thus apparently less active.

The von Mises criterion states that at least five independent slip systems are required in order to insure extensive ductility in polycrystalline aggregates. The criterion deals only with slip, and excludes twinning and fracture. A number of possible modes of slip in hexagonal metals are given in Table I. The first four modes have been detected experimentally (although certainly not all of them in beryllium) and the last two are shown merely to indicate additional possible, but yet undetected, modes. By the \( \{0001\} <11\overline{2}0> \) systems contribute only two independent modes since the third Burgers vector lying in the basal plane is equal to the sum of the other two and conse-
TABLE I. - Modes of slip in hexagonal metals

<table>
<thead>
<tr>
<th>Number</th>
<th>Burgers vector type</th>
<th>Slip direction</th>
<th>Slip plane type</th>
<th>Slip plane</th>
<th>Number of independent systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>&lt;12\bar{1}0&gt;</td>
<td>Basal</td>
<td>{0001}</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
<td>&lt;12\bar{1}0&gt;</td>
<td>Prismatic first type</td>
<td>{10\bar{1}0}</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>&lt;\bar{1}2\bar{1}0&gt;</td>
<td>Pyramidal first type</td>
<td>{10\bar{1}1}</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>c+a</td>
<td>&lt;11\bar{2}3&gt;</td>
<td>Pyramidal second type</td>
<td>{11\bar{2}2}</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>c</td>
<td>&lt;0001&gt;</td>
<td>Prismatic second type</td>
<td>{10\bar{1}0}</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>c</td>
<td>&lt;0001&gt;</td>
<td>Prismatic third type</td>
<td>{11\bar{2}0}</td>
<td>2</td>
</tr>
</tbody>
</table>
sequently does not provide an independent mode. Twinning may provide additional modes in one direction on each plane but basal slip plus twinning permits only a few percent strain before fracture takes place since the shear strains due to twinning are limited. Prismatic slip by the (10\(\bar{1}\)0) <11\(\bar{2}0\>) systems provide three modes of deformation but only two of these are independent. Consequently, simultaneous basal and prismatic slip provides four modes of deformation and does not allow for shear straining parallel to the c-axis. The basis of the problem, as far as beryllium is concerned, is that simultaneous action of only the first three modes depicted in Table I does not provide for shearing parallel to the c-axis. Consequently, they must be supplemented by relatively easy action of one or more of the last three modes in order to provide extensive ductility. Twinning can assist only in a limited way in providing some of the needed shear strains parallel to the c-axis. Thus, objections to counting twinning modes as contributing to an increase in ductility can be raised. Stress concentrations, for example, at the intersections of slip bands or twin lamallae with grain boundaries, eliminate the possibility of twinning aiding ductility in "notch sensitive" materials. Whether such stress concentrations prove catastrophic depends on the cleavage strength of the material, the size of the stress concentrations, and the speed with which they are formed. Also, only a limited amount of deformation can be achieved even when the entire volume has been twinned. The strain is not limited, however, if twinned volumes may re-twin or re-slip, as has been observed.
It might be argued twinning in polycrystals occurs in only one direction only so that it can accommodate either $c$-extension or $c$-contraction but not both. The especially large ductility of materials such as rhenium, titanium and zirconium must be due to a profusion of twinning systems. If both "positive" and "negative" twinning occur, the independent deformation modes provided by twinning are exactly the same as those from $(c+a)$ pyramidal slip, that is, all five. But no twinning mode has been seen to give $c$-contraction. Of the five independent deformation modes available, only two are "full" modes, the other three are unidirectional. The conclusion is that compatibility can be maintained, for some considerable amount of strain at least, by fewer than five full modes. The unidirectionality of twinning appears to be of little importance.

These observations point out the lack of ductility in beryllium polycrystals, where basal slip plus unidirectional twinning is observed, cannot be due to a lack in the number of independent modes. Conrad and Perlmutter (3, p. 326) suggest that, while unlimited ductility is only possible with five full, independent deformation modes, the absence of some modes, especially unidirectional ones, only decreases the degree of ductility and, if brittleness is observed, it must be due to other causes such as a sensitivity to stress concentrations.
It is still questionable how the compatibility conditions on macroscopic plastic strains can be fulfilled in a polycrystal with less than five independent deformation modes. If a particular grain had five independent deformation modes available, it could accommodate any strain conditions imposed on it by the surroundings. If there is a particular strain component the grain cannot provide, it will in turn impose conditions on its surroundings. The surrounding grains should be able to accommodate this condition fairly well when there is only one mode missing, less well when there are two missing, etc. If only a unidirectional mode is missing, half the surrounding grains will, on the average, be able to fulfill any condition whatsoever. If a series of grains can be found all of which are unable to fulfill a particular prescribed strain component, only then should a sample be brittle in the true sense of the word.

Beryllium's ductility is more limited than most common metals and beryllium is more sensitive to prior mechanical and thermal treatment. This behavior is attributed to several factors, foremost of which is the deformation behavior of the single crystal itself which is severely anisotropic with respect to its mechanical properties. In polycrystalline beryllium, grain orientation and grain size are highly influential upon the mechanical properties. Impurity or alloy content is also of great importance to the ductility behavior of beryllium mainly because impurities may alter the deformation behavior of the single crystal and further may possibly produce ageing effects of
some significance in the polycrystalline material. Although some hexagonal metals and alloys often exhibit unique and desirable engineering properties, they are not particularly noted for their high strength. On the other hand, there is no theoretical reason why hexagonal alloys of high strength cannot be developed (16). The major problem in increasing the strength of these hexagonal metals and alloys concerns maintaining adequate ductility. This problem is much more difficult to solve in hexagonal metals than in cubic metals which always have an adequate number of operative slip systems to satisfy the von Mises condition.

Two factors of interest concerning the physical configuration of the unit cell of beryllium are: First, the c/a ratio of the unit cell is less than ideal. This ratio for beryllium is 1.567, as compared to the ideal value of 1.633. (The a-axis length is 2.285 angstroms, and the c-axis is 3.583 angstroms at room temperature.) The second factor of interest is the unusually small size of the beryllium unit cell. On the basis of the first factor mentioned above, the relative basal plane spacing and prism plane spacing is such that atoms in the prism plane should be more closely packed than atoms in the basal plane. According to the general rule that slip is favored on planes in which atoms are most closely packed, slip should occur most readily on prism planes. The observed fact is for beryllium slip occurs most readily on the basal plane. Thus at the present time for the beryllium crystal there is no clear relationship between slip behavior and the c/a ratio.
The reasons behind these c/a ratio considerations are quite critical. It might be expected that whereas crystals having a large c/a ratio should slip with relative ease on the basal plane, those having lower c/a ratios might exhibit more facile slip on the prismatic or pyramidal planes. This trend appears to be observed as the c/a ratio decreases from 1.861 for zinc to 1.571 for yttrium, but beryllium with its axial ratio of c/a = 1.567 is an exception to this expectation. It is not known whether the strong elastic anisotropy of beryllium might be responsible for this anomaly. The critical resolved shear stress in beryllium for both the <1120> {0001} and <1120> {1010} modes of slip decrease with increasing purity; the ratio of the critical resolved shear stress for prismatic slip to basal slip increased from 5 to 1 to 38 to 1 with increasing purity. Firstly, this suggests impurity hardening is very pronounced in beryllium and secondly, even high purity beryllium is an exception to the general trend that prismatic slip becomes more favorable as the c/a ratio is reduced.

In slip on close-packed planes in face-centered cubic and hexagonal close-packed crystals, the core of the dislocations in the basal plane consists of two partial dislocations separated by a stacking fault. The total dislocation width is determined primarily by the energy of the stacking fault separating the partial dislocations. Similar splitting is also possible on the prism plane of hcp crystals as dissociation into two complex partials. However, the energy of the stacking fault formed on these prism planes is expected to be
very high because of an accompanying change of the coordination number in the fault. The separation of the partials in prism planes must therefore be much smaller than that in basal planes.

If the stacking fault energy in the basal plane is low, then lowering the energy of the dislocations in this plane when they dissociate should favor basal slip. However, in spite of the importance of this parameter in explanations of the mechanical properties of metals, very little is known about the factors determining the magnitude of the stacking fault energy. It is certain preference for basal and prismatic slip in hexagonal crystals is not governed solely by elastic anisotropy; the stacking fault energy undoubtedly plays a major role.

Twins may be important in accounting for the non-ductile behavior of metals of the cleavage type. A twin, like a grain boundary, may present a strong barrier to slip and a crack can be initiated by the pile-up of slip dislocations at the twin interface. In addition, cracks may also be initiated at the intersection of twins.

Both twinning and fracture occur readily in tests at low temperature on both body-centered cubic and hexagonal close-packed crystals. The ultimate question is whether twins are nucleated by the high stress concentrations associated with fracture or that the formation of twins actually initiates the fracture. Often overlooked is the fact both effects may occur.
However, many observations point out twinning is not always essential to brittle fracture. Both phenomena depend closely on the strength of the dislocation locking. It is probably a fair generalization to say that slip is the fundamental process in metals and that both twinning and fracture occur as a result of slip. It is the slip dislocations generated immediately prior to fracture which give rise in certain regions of the crystal to microcracks, or "cavity dislocations" as they are sometimes termed. Most metals fracturing in a brittle manner, i.e. with little plastic extension, do show, when carefully examined, some evidence of plastic deformation in the region of the fracture. A brittle-ductile transition (in which the fracture changes from the completely ductile to the completely brittle as the temperature is lowered by a few degrees through a critical range) can be explained on the basis of the criterion that the material is ductile at any temperature, if the yield stress at that temperature is smaller than the stress necessary for the growth of microcracks, but if it is larger the material is brittle.
REVIEW OF LITERATURE

The wealth of material written about the metal beryllium is indeed prodigious. However, within this great quantity of material, only two main divisions are of interest here. The first major area concerns measures taken to improve the properties of beryllium itself. The second area concerns beryllium-base alloys containing minor alloying additions. Specifically included here are previous studies in which the chemical and physical properties of beryllium were attempted to be improved by means of alloying. Material written on shaping various beryllium products will be excluded.

Attempts at improving the ductility of beryllium metal itself will be treated first. These attempts are exclusive of the various attempts made through alloying. Mash (36) observed as early as 1955 that changes in the mechanical properties of beryllium could be affected by heat treatment. The early results of Mash (36) have been confirmed and further refined by subsequent investigators. It is possible to reduce the hardness and decrease the electrical resistivity of beryllium through purification, showing that minor amounts of certain alloying constituents have a hardening effect.

Klein, Perelman and Beaver (14, p. 302-315) have reported tensile tests on a 2-percent chromium alloy fabricated from powder by hot pressing at approximately 1,100° C. This alloy had an improved tensile strength over unalloyed metal but it was not as large as that shown by a 2-percent iron alloy.
These authors also indicated the tensile properties of a 2-percent molybdenum in beryllium alloy were a considerable improvement over those of the unalloyed metal, while a 2-percent tungsten alloy had properties little better than unalloyed metal. A 3-percent manganese alloy resulted in a slight increase in high temperature strength at 750° C. Iron was found to be a very potent alloying element for improving the high temperature strength of beryllium. Hot-pressed blocks of 2 and 3-percent alloys had strengths which were roughly double that of the unalloyed metal; but, 3-percent alloys fabricated by hot pressing or cast 2.4-percent alloys could not be rolled. Yans, Donaldson and Kaufmann increased the yield and tensile strength of sheet formed by cold pressing (followed by sintering) beryllium powder, mixed with up to 0.54-percent iron powder. However, the elongation fell from 22 percent for the unalloyed metal (during extrusion) to only 4 percent for the 0.54-percent alloy (14, p. 309). Klein et. al reported favorable tensile data on 3 and 5-percent cobalt in beryllium alloys fabricated by hot pressing in air. Little elongation or ductility was recorded however. Three and 6-percent vacuum hot (1,060° C) pressed powders could not be rolled.

The effects of various heat treatments on a 10-percent nickel alloy were studied by Kaufmann et. al. (32) but none of them improved the ductility. This fact is in opposition to earlier work reported by Klein et. al. who investigated the room temperature properties of 3 and 6-percent nickel alloys
fabricated by vacuum hot pressing. Microstructural examination proved the nickel was in solution in both alloys and the 3-percent alloy had better properties. Additional work on the mechanical properties of beryllium-nickel alloys has been done by Kaufmann and Corzine (61) and Yans, Donaldson and Kaufmann (14, p. 313). Klein, Perelman and Beaver found that neither cast nor vacuum-hot pressed billets containing 3-percent palladium could be rolled (14, p. 315).

Ranzetta and Scott (47) conducted an electron-probe microanalysis investigation into the effect of heat treatment on the metallographic structure of beryllium and some dilute beryllium alloys. Their objective was to study the dissemination of impurities and alloying additions in beryllium, both before and after a heat treatment to give improved ductility in the temperature range 400° C - 600° C. The reasons for their study were that a considerable amount of evidence had been accumulated in past years indicating the mechanical properties of beryllium in the temperature range 400° C - 600° C depend strongly on the composition and former history of the metal. Generally, rapid cooling of commercial purity beryllium or dilute beryllium alloys from high temperatures leads to a decrease in ductility with increasing temperatures above 400° C, reaching a minimum about 600° C. The drop in ductility can be avoided by slow cooling or annealing treatment which is usually more effective when applied to dilute beryllium alloys rather than to commercial purity beryllium (8).
The analysis of Ranzetta and Scott (47) and their experimental work was confined to beryllium with the following alloying additions: iron, aluminum, silicon, chromium, manganese, and nickel, all as minor weight percentages. There was a general enrichment of the grain boundary in iron in the beryllium-iron alloys which were found to be ductile at 600° C. This was most pronounced in the higher iron alloys. The degree of iron enrichment at the grain boundary was found to increase with time during heat treatment, indicating that iron is slowly diffusing to the grain boundaries during heat treatment. The iron content of the matrix was not found to be significantly affected by the heat treatment. There was, also, the detection of a slight enrichment of the grain boundaries in aluminum, which appears to be associated with the distribution of iron; however, not every grain boundary was enriched to the same extent.

No grain boundary enrichment was detected in the beryllium-iron specimens, which exhibited low ductility at 600° C, the iron being distributed uniformly throughout the specimen irrespective of its initial dissemination. The results demonstrated the iron segregation at the grain boundaries associated with increased ductility at 600° C is reversible. Fewer precipitates were found in these specimens but some were still present at the grain boundaries and occasionally within the grains.
Microanalysis of commercial purity beryllium (approximately 0.2 weight-percent iron) annealed at 650° C for 100 hours revealed small iron-rich areas containing iron distributed at random which were not revealed metallographically; no segregation of iron in the grain boundaries was detected.

Preliminary results by Ranzetta and Scott (47) on heat-treated specimens of a 1 weight-percent iron arc-melted alloy indicate after 168 hours at 800° C the majority of the iron was in solid solution, about 0.9 weight percent as measured in the matrix. Iron segregation had taken place to randomly distributed cavities which were produced during the manufacture of the alloy, and to the grain boundaries. A 5 weight-percent iron arc-melted alloy, also heat treated at 800° C for 168 hours, was found to contain several percent of an iron-rich phase present at the grain boundaries and within the grains. The large precipitates were found to contain approximately 31 weight-percent iron indicating this was the equilibrium zeta (Be$_{13}$Fe) phase (32.4 weight-percent iron).

Ranzetta and Scott (47) found in their work on other beryllium alloys, a 0.4 weight-percent aluminum alloy which had been extruded, contained rounded aluminum-rich particles, mainly at the grain boundaries. Thermal treatment at 700° C for 212 hours did not appear to affect the distribution of the aluminum within the sample but the elements iron and titanium were then
found to be associated with some of the aluminum-rich grain boundary precipitates. They did not feel there was a general grain boundary enrichment in the aluminum alloys similar to that found in the iron alloys. Since aluminum was not found in the matrix of any of their test specimens they concluded the solubility of aluminum in beryllium at 700° C was below their limit of detection, 0.05 weight percent.

An extruded 0.4 weight-percent silicon alloy had most of the silicon (in this same work by Ranzetta and Scott) present at the grain boundaries in the form of precipitates of several microns diameter. They reported the particles appeared to be more rounded in shape after heat treatment at 700° C for 212 hours, both silicon-rich and aluminum-rich particles being identified. More iron was then found associated with the precipitates and some titanium-rich particles were located. No general grain boundary enrichment in silicon was detected. The matrix contained approximately 0.1 weight-percent silicon.

Ranzetta and Scott (47) found numerous chromium-rich precipitates in a 0.2 weight-percent chromium alloy, mainly at the grain boundaries. No general enrichment of the grain boundary in chromium could be detected. The matrix was found to contain less than 0.02 weight percent of either chromium or iron. A 0.18 weight-percent manganese alloy, which had been heat treated for 2 hours at 800° C, gave good high temperature properties. Manganese
was found to be segregated in the form of inclusions mainly at grain boundaries. Up to 30 weight-percent manganese was measured in the larger inclusions which usually contained aluminum and silicon (approximately 4 weight percent) and occasionally iron (0.3 weight percent). No general enrichment of the grain boundaries in manganese was evident. The manganese content of the matrix was 0.1 weight percent, while 0.02 weight-percent iron was also found to be present.

Ranzetta and Scott (47) gave evidence in a 0.4 weight-percent nickel alloy that the distribution of nickel was uniform in both heat-treated (700° C for 200 hours) and as-extruded specimens.

Although the efforts of Ranzetta-Scott (47) were mostly confined to beryllium-iron alloys, the results they obtained on the other beryllium alloys which they did investigate are also meaningful. First, in their beryllium-iron alloys, they found a clear distinction between samples which gave good ductility and those which gave poor ductility at 600° C. In the samples which gave good ductility, the grain boundaries were found to be enriched with iron while, in contrast, the specimens associated with low ductility showed no grain boundary enrichment. They pointed out a second distinction in that the good ductility material, inclusions containing aluminum and silicon which were situated mainly at the grain boundaries showed iron enrichment up to a measured value of approximately 7 percent, compared with only a slight enrichment.
(approximately 0.3 weight percent) in the low ductility alloys. Thus during their annealing treatment iron diffused to the grain boundaries, precipitates and other imperfections and this segregation of iron was accompanied by an improvement in high temperature ductility. They found the minimum annealing time to improve the ductility at 600° C was found to depend on the rate at which the specimen was strained while tensile testing.

The beryllium-manganese alloy (0.18 weight-percent manganese) did not require an annealing treatment to produce good ductility at 600° C. Manganese was found to be segregated mainly to small aluminum-silicon inclusions at grain boundaries, while about 0.1 percent remained in solution. This distribution was similar to that found in the iron alloys which gave good ductility, except no general enrichment of the grain boundaries was observed. They point out however that it is possible their heat treatment (2 hours at 800° C) was not sufficient to give a detectable enrichment.

The beryllium-chromium alloys produced precipitates presumably consisting of \( \text{CrBe}_{12} \), but a trace of iron and other impurities was also present. The beryllium-aluminum and beryllium-silicon alloys had some ductility which could be increased by annealing although not to the same extent as for the iron alloys. The silicon-rich and aluminum-rich phases in the respective alloys were situated mainly at grain boundaries both before and after heat treatment. The additions of nickel to beryllium had a similar
ductility response as the addition of aluminum and silicon with respect to the heat treatment; the nickel did not segregate before or during heat treatment, remaining fully in solution in both conditions.

Ranzetta and Scott (47) discuss at the end of their paper other experimental data on beryllium alloys and the various mechanisms which have been proposed to explain the high temperature ductility of beryllium. First concern is with the matrix properties of the metal and the second with its grain boundary properties. No one simple theory appears to explain adequately all the experimental evidence and they conclude it is possible that mechanisms which take account of both matrix and grain boundary behavior are required.

Recent work at the Franklin Institute has shown zone refining may produce crystals of sufficient purity such that large shear strains can be sustained during slip on the basal plane (25, p. 180). It is apparent impurities in the lattice of commercial beryllium severely limit such a mode of deformation. Unfortunately the specific impurity or impurities that embrittle beryllium have not been identified, and the Franklin Institute continues work in this direction. To date, the room temperature mechanical properties of hot-pressed beryllium have not been improved by quench-aging treatments. As shown in the reference by Ranzetta and Scott (47) the British have been successful in increasing the elevated-temperature ductility of extruded ingot and sheet. This effect is undoubtedly associated with the precipitation of impurities in beryllium.
Beryllium-nickel alloys are of interest, since nickel renders the elevated temperature allotropic form of beryllium (body-centered cubic) stable at temperatures down to 1,065°C. A beryllium-8 atomic percent nickel alloy (22) exhibited 20-percent reduction in area when tensile tested at 1,070°C, whereas unalloyed beryllium exhibited zero reduction in area at this same temperature. Unfortunately, it has not been possible to retain the body-centered cubic phase at room temperature by quenching techniques. It seems reasonable to state that should this be possible, enhanced ductility would probably result. Copper and cobalt also expand and lower the elevated temperature phase field, but to a lesser extent than nickel. The effect on ductility of several elements with beryllium is given in Table II.

Beryllium alloys have been formulated in an attempt to surround individual grains with a ductile matrix such as silver or aluminum. The ductility and impact strength characteristics of beryllium can potentially be improved by this type of an approach, with an accompanying sacrifice in other properties. Implementation of this concept has proved to be difficult, because of many varied problems, including the formation of brittle interfaces and excessive diffusion. Liquid-phase sintering has also been investigated in an attempt to improve ductility (30). This approach involves the selection of a system in which the flow characteristics of the beryllium and matrix phase match. The beryllium and matrix powders are blended together, compacted, and sintered
TABLE II. - Beryllium deformation behavior

<table>
<thead>
<tr>
<th>Alloying or impurity material</th>
<th>Approximate material solubility</th>
<th>Deformation characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>0.92 w/o at 1,000° C</td>
<td>Good 400° C ductility displayed grain boundary enrichment up to 7 w/o iron. Poor high temperature ductility exhibited little grain boundary enrichment, only 0.3 w/o.</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;0.05 w/o at 700° C</td>
<td>Good high temperature ductility indicated general grain boundary enrichment of both iron and aluminum, never aluminum alone. Poor high temperature ductility showed no general grain boundary enrichment in aluminum.</td>
</tr>
<tr>
<td>Silicon</td>
<td>&lt;0.1 w/o</td>
<td>Never yielded ductile specimens. Non-ductile specimens contained silicon precipitates at grain boundaries, but no general grain boundary enrichment in silicon was ever detected.</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.02 w/o</td>
<td>No ductility. No general grain boundary enrichment in chromium.</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1 w/o</td>
<td>No annealing was required to give good ductility at 600° C. Manganese segregated to the grain boundary in the form of inclusions with aluminum and silicon. No general grain boundary enrichment with manganese.</td>
</tr>
<tr>
<td>Nickel</td>
<td>25 w/o at 1,065° C</td>
<td>Very good high temperature properties. Nickel enlarges the beryllium beta field and it does not segregate before or during heat treatment.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1 a/o</td>
<td>No ductility. Cobalt enlarges beryllium beta field.</td>
</tr>
<tr>
<td>Copper</td>
<td>7 a/o</td>
<td>No ductility. Copper enlarges beryllium beta field.</td>
</tr>
</tbody>
</table>

(Continued)
**TABLE II. - Beryllium deformation behavior (Continued)**

<table>
<thead>
<tr>
<th>Alloying or impurity material</th>
<th>Approximate solubility</th>
<th>Deformation characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>&lt;0.1 w/o</td>
<td>No ductility.</td>
</tr>
<tr>
<td>Carbon</td>
<td>&lt;0.3 w/o</td>
<td>No ductility.</td>
</tr>
</tbody>
</table>
at a temperature at which the matrix powder is liquid and will envelop individual solid beryllium particles. The beryllium ductile matrix alloys in general require fairly large quantities of matrix alloy, and the desirable properties of beryllium such as low density and high modulus of elasticity are usually sacrificed.

Much of the recent and more up-to-date literature on the metallurgy of beryllium is presented as the proceedings of conferences held over the past several years. The first of these meetings was an international conference organized by the Institute of Metals and held in London, England in October of 1961 (30). This work contains excellent sections on the mechanical and physical properties and on the metal preparation and fabrication of beryllium. Each large section is a composite of technical presentations by several persons in the field of beryllium research.

One of the initial works presented at this meeting by Greethan and Martin (30, p. 47) investigated the effect of purity and temperature on the critical shear stress of beryllium single crystals. They concluded, from comparison with earlier work, that further purification of beryllium could lead to a decrease in the ductile-brittle transition temperature for extruded beryllium rod.

Wilsdorf and Wilhelm (30, p. 68) have presented an excellent treatment of the behavior of dislocations in beryllium. Their investigation in-
cluded both single crystal and polycrystalline beryllium specimens of commercial and electrolytic flake purity and they concluded that glide dislocations are strongly hindered in their movements and often appeared to be pinned, possibly by small impurity clusters in beryllium of commercial purity. They observed dislocation tangles in the deformed flake beryllium; the presence of round as well as elongated prismatic dislocation loops was in evidence. In the flake material, in which obstacles were comparatively rare, the dislocations had a pronounced tendency to align along crystallographic directions, indicating a strong Peierls-Nabarro force. They also found the dislocations were always immobile at the stress created by the high intensity electron beam in the electron microscope. Lastly, they found dislocation arrays of very high density to lie in [1210].

Herman and Spangler (30, p. 75) have looked into the flow and fracture characteristics of zone-melted beryllium. Their purpose was to determine if an impurity effect was associated with the basal plane ductility of beryllium. They used a floating-zone-type zone-melting procedure both to purify and to produce their beryllium single crystals, which were then tested in tension with their orientation arranged to yield basal plane slip. The critical resolved sheer stress was observed to decrease with increased purification. Glide strain also varied, increasing with increased purification. They concluded an impurity effect did exist in their single crystal samples.
Moore, Morrow, Scott and Cheer (30, p. 112) conducted a study on precipitation-ageing and the improved mechanical properties in commercially pure beryllium and beryllium alloys. They determined the effect of small additions of iron and of binary additions of aluminum, silicon, and nickel on the tensile properties near 600° C, as a function of annealing schedules over the range 500° – 1,000° C. They showed the normal ductility minimum found at 600° C is associated with an "aged" condition that can be remedied by "over-ageing". They discussed corresponding changes in the constitution of these specimens as evident from optical and electron microscopy, X-ray diffraction techniques, as well as microbeam analyses.

Allen and Moore (30, p. 193) conducted an investigation on the ductile-brittle transition in beryllium. Their specimens, commercial-purity beryllium, were tensile tested between 20° and approximately 300° C and it was revealed that an abrupt alteration took place in both the level of ductility and in the mode of fracture at some critical temperature, T_C, which was found to vary with the grain size of the metal and also with the strain rate. They associated this behavior with the classical tough-brittle transition of the type already well established in other metals and they used their data for correlation with the various mechanistic interpretations which have been proposed for this phenomenon. They suggest the mechanical behavior of beryllium between 20° and 300° C may be complicated by thermally-induced consti-
tutional changes. Their metallographic studies showed under certain conditions fracture in polycrystalline beryllium could be associated with bend-plane splitting. General indications from their tentative analyses showed, with a mean grain size of approximately 1 - 10 microns, $T_C$ may be depressed to approximately 20° C.

Sinelnikov, Ivanov, Amonenko and Tikhinsky (30, p. 264) reported on some properties of high purity distilled beryllium. They prepared their high purity beryllium by distillation and condensation on various types of surfaces and this material was studied for texture, mechanical strength and ductility, the beta-allotropic modification, and variation of expansion coefficients with temperature. The conclusion was reached that ductility is a function of purity and texture, the texture depending upon the condensing surface used in preparation of the samples, and the body-centered cubic-phase beta structure is obtained between 1,258° C and the melting point (approximately 1,283° C).

Gelles, Pickett, Levine and Nowak (30, p. 588) performed a rather thorough investigation into the stability of the high temperature phase in beryllium and beryllium alloys. Their study involved the determination of the stability and mechanical properties of the body-centered-cubic phase which exists just below the melting point of beryllium-rich alloys. They employed standard differential thermal analysis techniques (DTA) to alloys
of beryllium in each of the following systems: chromium, cobalt, copper, iron, nickel, silicon, silver, nickel-cobalt, nickel-copper, nickel-iron, nickel-palladium, nickel-cobalt-iron, and nickel-cobalt-manganese. They claim to have established fairly well the beta-phase field in the systems of beryllium with chromium, copper, cobalt, iron, and nickel. The remaining systems had not been sufficiently defined. The phase diagrams were of two classes: enlarged beta field and closed beta field. Their primary interest was with the enlarged-field systems such as beryllium with cobalt, copper, and nickel. They found a correlation between the beta-alpha upper solvus transition temperatures and electron:atom ratios for alloys of beryllium with cobalt, copper, iron and nickel. They did not observe complete beta retention, but they did measure suppression of the beta-alpha transformation temperature by quenching. At elevated temperatures, the beta-phase structure appears to be more ductile than the alpha-phase structure. A beryllium-8 atom percent nickel alloy exhibited 20 percent reduction in area in tensile tests at 1,070° C (at which temperature the alloy is mostly beta). Unalloyed beryllium exhibited zero reduction in area at this temperature.

Beaver (30, p. 601) has presented a rather broad treatment on beryllium base alloys. The potential application of these beryllium-base alloys appeared to be of the duplex "ductile-matrix" variety, i.e. beryllium with aluminum,
silicon, silver or tin in binary or ternary combinations, possibly some of the few solid-solution types, and undoubtedly the many dispersed-phase hardening alloys available. Duplex alloys are principally characterized by another phase surrounding the beryllium grains. This phase imparts improvement in ductility or malleability at some expense of strength, stiffness-modulus, and high temperature properties. Elements forming solid solutions in beryllium generally increase strength, particularly at lower temperatures, while dispersed-phase-hardening alloys have substantially enhanced elevated temperature properties usually gained at the expense of further low temperature lack of ductility. Dispersion-strengthened alloys containing intermetallic compounds are discussed with reference to a substantial increase in the temperature of the ductile-brittle transition and the reportedly excellent accompanying elevated temperature properties.

The Conference on the Physical Metallurgy of Beryllium was held at Gatlinburg, Tennessee, on April 30 – May 1, 1963 under the auspices of the United States Atomic Energy Commission and sponsored by Oak Ridge National Laboratory (40). As evident from the title of this conference, aspects related to the physical metallurgy of beryllium were of primary interest.

The Gatlinburg Conference proceedings contain several articles on the preparation of high purity beryllium by distillation and also by vacuum distillation. The metal preparation aspects are not of direct interest here; however, the mechanical properties of this high purity metal are also reported. The
initial paper at the meeting by Levine, Tensler and Gelles (40, p. 6) discussed the characteristics of vacuum-distilled beryllium. They studied in detail the distribution of residual impurities in their distilled beryllium and they developed fabrication procedures which resulted in samples having a fine, uniform recrystallized grain structure. Their impurity studies revealed in addition to trace amounts of soluble impurities, insoluble particles containing iron and silicon did exist; and that these particles probably limited ductility severely. They reported a reduction in both soluble and insoluble impurities by performance of a second distillation. Their mechanical property studies revealed that double-distilled beryllium exhibited considerably greater three-dimensional ductility than material of lower purity.

Beasley and Moore (40, p. 29) investigated ageing effects on beryllium single crystals. Their study was made on the effect of thermal treatment on both the flow stress and the occurrence of yield point phenomena of single crystals of beryllium. This work is closely related to the work by Moore et. al. (30, p. 112) reported in the Beryllium Conference held in London in 1961.

Herman and Spangler (40, p. 48) reported on basal plane fracture of beryllium single crystals which were prepared by zone melting and tested in tension at room temperature with orientations such that basal glide was the principal deformation system. Their findings indicated fracture occurred in most cases by cleavage on the basal plane where the extent of deformation
prior to fracture was enhanced by the effect of purification. They claim the improvement in ductility resulted from lowering the critical resolved shear stress and the work-hardening characteristics and minimizing crack nucleating precipitates. They analyzed their results with respect to two theoretical treatments for the propagation of cleavage cracks in metals such as beryllium which can glide and cleave on the same crystallographic plane. Their first treatment considers the conditions for propagating a crack nucleated by the splitting of a wall of dislocations while the second one considers the case where a dislocation pile-up is responsible for the crack. Both schemes yield similar stress relationships but differ in the dependence of fracture on crystal orientation. The results of their analysis indicated the cleavage of beryllium on the basal plane during tensile testing is associated with the split-bend-plane mechanism of crack initiation and propagation.

Kaufman, Levine, Pickett and Aronin (40, p. 69) of Nuclear Metals, Inc. investigated the effect of zone refining on the purity and mechanical properties of beryllium single crystals. They concluded zone refining of beryllium did result in a large reduction in impurity content, and the ultimate level of purity attained is strongly dependent on the purity of the starting material. Critical resolved shear stresses for basal and prismatic slip were found to decrease in a regular manner with decreasing impurity content, as measured by the resistance ratio technique. The critical resolved shear stress for prism
slip was strongly temperature dependent, while critical resolved shear stress for basal slip was almost independent of temperature. Purification by zone refining greatly increased the capacity for basal glide and reduced the rate of work hardening. Fracture still occurred by basal cleavage at room temperature, but at elevated temperatures brittle fracture by cleavage was eliminated. Brittle fracture by cleavage accompanying slip on a single set of prismatic planes was eliminated in crystal purified by zone refining. The addition of iron to zone-refined beryllium resulted in lattice strengthening as measured by critical resolved shear stress for basal slip. Flow characteristics as measured by work-hardening rate were relatively unaffected. They concluded that although the ease of basal glide in zone-refined crystals had so far inhibited the appearance of deformation processes permitting c-axis contraction, it might be possible this same ease of basal glide could improve three-dimensional ductility in polycrystalline material by permitting extensive deformation by shear.

Tristen and Moore (40, p. 90) studied the effect of purification and recontamination on (0001) and (1010) slip in beryllium single crystals. They determined the critical resolved shear stresses for slip for both these planes from 20° to 600° C. Compared with corresponding work on crystals of purity lower than those used in their study, they noted a decrease in the critical resolved shear stress at 20° C in (0001) slip and a proportionally much smaller
decrease in (10\bar{1}0) slip. At higher temperatures they found both these decreases less marked. They did not determine to what extent contamination of the crystal affected prismatic slip. Purification, however, did clearly facilitate slip; but to evaluate this effect, they indicated recontamination during testing and annealing must be prevented.

Moore and Ellis (40, p. 102) have given an account of the deformation and fracture in single and polycrystalline beryllium between 20° and 450° C. These men claim to have resolved the anomaly that the acknowledged deformation modes of beryllium did not conform with the observed plasticity in the range 20° to 450° C. For some time it has been claimed beryllium has a unique slip direction \(<11\bar{2}0>\) in which (0001), (10\bar{1}0) and (10\bar{1}1) slip can occur; only at temperatures greater than 800° C has slip been noted in directions with a resolved component in the c-direction. Compression tests were performed at 165° to 280° C on single crystals oriented such that the resolve shear component in \(<hk\cdot o>\) was zero. Between 280° and 195° C these crystals appeared to slip on (10\bar{1}1) and, assuming slip occurred in the closest packed direction, \(<11\bar{2}3>\), the critical resolved shear stress for slip was determined. Pyramidal slip was not observed below 195° C but strains of approximately three percent were accommodated by twinning on (10\bar{1}2) and basal slip within the twinned regions. The appearance of (10\bar{1}2) twins in crystals compressed in the c-direction was not expected for this required extension in the c-direction.
Clearly, however, beryllium can deform in three directions mutually at right angles above 195° C, but slip appears to be restricted to \( \langle h k \cdot 0 \rangle \) directions below 195° C. The restriction is believed to be the basis of the ductile-brittle transition which occurs in the region 150° to 200° C. Their studies have shown that although prolific (0001) and (10\( \bar{1} \)0) slip occurs in \( \langle 11\bar{2}0 \rangle \), slip on (10\( \bar{1} \)1) also occurs in an unknown direction out of the basal plane. They stress the need for further confirmation in this latter work since it is believed slip on (10\( \bar{1} \)1) in \( \langle h k \cdot 1 \rangle \) occurs to relieve strains induced in neighboring grains by slip in \( \langle 11\bar{2}0 \rangle \) and on (0001) and (10\( \bar{1} \)0). Moore and Ellis postulated marked changes in the ductile-brittle transition might be expected if the difference in stress for slip in \( \langle h k \cdot 1 \rangle \) and fracture could be increased. Unfortunately there is no clear way of increasing the number and ease of deformation modes or of increasing the fracture strength without adversely affecting the deformation modes. Moore and Ellis discussed in the later sections of their paper the electron microscopy techniques which have been developed to identify Burger's vectors in beryllium thin films. They state their work has shown that homogeneous deformation in polycrystalline beryllium at 99.85 percent purity is not expected below approximately 150° C and the stress required to activate slip with a component in the c-direction is of the same order as the fracture strength at approximately 200° C.
The last paper of pertinent interest at this conference was given by Walters, VanDerWalt and Makin and their work is concerned with Burger's vectors in beryllium and their effect on ductility (40, p. 126). Thin film electron microscopy and selected area diffraction techniques were used to determine the possible Burger's vectors in beryllium. Dislocation loops and dislocations having various vectors were observed and likely slip directions were determined. Their most significant finding was that slip in directions out of the basal plane has been observed at room temperature in thin foils. They do state however these slip directions may not operate in bulk material at room temperature if the critical resolved shear stress is high. Twinning is likely to be the more favorable deformation mode. However, if the critical resolved shear stress for slip out of the basal plane is lowered by purification, the slip modes observed in thin foil experiments could operate in bulk material at room temperature.

One of the larger meetings on beryllium research was the Second International Conference on Beryllium Technology sponsored by the Non-ferrous Committee of the Institute of Metals Division, The Metallurgical Society, American Institute of Mining, Metallurgical, and Petroleum Engineers in Philadelphia, Pennsylvania, October, 1964 (38). In the period following the first International Symposium on Beryllium Technology held in England under the auspices of the Institute of Metals in the fall of 1961, the technology and
applications of the metal beryllium had moved from the nuclear power orientation, which had been prevalent at the time of this first conference, to one which now emphasized aerospace and instrumentation applications. The program of the 1964 A.I.M.E. conference was divided into four broad areas: (1) purification and alloying studies, (2) physical metallurgy, (3) mechanical and process metallurgy, and (4) design and application of beryllium structures. Only the first three of these are of direct concern here.

Tristen and Moore (38, p. 29) reported on the effect of trace impurities on the critical resolved shear stress for (0001) slip in beryllium. They used single crystals 99.975 percent pure which had been obtained from vacuum-cast and extruded Pechiney S. R. grade metal by vertical zone refining in an argon atmosphere using up to six zone passes. Originally, these high purity crystals were characterized by a critical resolved shear stress for (0001) slip of approximately 400 psi at 20° C. These crystals were then recontaminated with carbon at 1,000° C and as a result the critical resolved shear stress for (0001) slip increased to 1,770 psi at 20° C. They point out this high level of critical resolved shear stress is more characteristic of beryllium of 99.90 percent purity and emphasizes the possible importance of carbon relative to other impurity elements. Recontamination in a nitrogen atmosphere had not resulted in a significant increase in the critical resolved shear stress for slip. They concluded by considering the role of carbon both as a solute and as a precipitate in restricting deformation in single and poly-crystals.
Stonehouse, Carradine and Beaver (38, p. 51) looked into the effects of purification, agglomeration and heat-treatment on the properties of beryllium single crystals. Their studies described the role of impurities in altering the mechanical behavior of beryllium single crystals at a purity level between that of the commercial grades of beryllium and the high purity materials. They also studied the alloying of zone-refined crystals with aluminum and iron. They achieved an agglomeration of impurities, by passing a floating zone through a beryllium rod in both directions (zone leveling), with retention of a relatively high metallic impurity content. The specimens prepared in this manner exhibited significantly high basal glide strains despite their impurity content. These zone-leveled crystals were oriented for both basal glide and prismatic glide and were tested in tension. The reversibility of this agglomeration effect is also illustrated.

Kaufman and Aronin (38, p. 87) described the effects of purification and realloying on the mechanical properties of zone-refined beryllium single crystals. Their single-crystal studies showed zone refining of beryllium produced the greatest enhancement of ductility of any other purification method. Material purified by zone refining showed its most significant improvement in the form of greatly increased basal glide capacity and reduced restrictions on prism glide. The major emphasis of their
study was a search for new modes of deformation which might alleviate the extreme plastic anisotropy of beryllium. Their procedure involved compressing zone-refined single-crystal specimens along the hexagonal axis to inhibit the activation of the known modes of deformation, while at the same time hopefully allowing activation of new modes with a slip direction out of the basal plane. No significant new modes of deformation were observed within the temperature range of 25° to 225° C, and the purity range represented by the resistance ratio range $R_{298}/R_{4.2} = 2.5$ to 1,300. A study of the effects of realloying zone-refined crystals demonstrated that iron added to zone-refined beryllium to the level of about 1,000 ppm increased the critical resolved shear stress for basal slip to 2,000 psi (the value characteristic of commercial purity metal) while retaining the high-glide capacity observed in high-purity, zone-refined material. They also briefly evaluated alloys containing binary and ternary additions, mainly, Be-Fe-Si and Be-Fe-Al-Si in an attempt to better understand the role of precipitation reactions as possible causes of embrittlement.

Fenn, Crooks, Coons and Underwood (38, p. 103) reported a study on the properties and behavior of beryllium-aluminum alloys. Their alloys contained 24 to 43 percent aluminum and were developed primarily for aerospace use. These alloys are claimed to possess ductility. Mechanical properties, physical properties and shop and service characteristics
are described for sheet and extrusion alloys developed during the course of this study. Structural efficiency comparisons showed magnesium and aluminum alloys to be about twice as heavy and titanium about three times as heavy as an equivalent load carrying Be-Al structure. Their data also suggested beryllium-aluminum alloys should be capable of achieving 75 percent of the weight savings possible with beryllium.

Scott and Lindsay (38, p. 145) reported their findings on some electron microscope observations of precipitation in beryllium. They applied thin-foil transmission electron microscopy techniques to the study of precipitates in commercial-purity beryllium. They investigated the effect of heat-treatment on the structures and these results were compared with the mechanical properties of the metal in these thermal conditions. They also discussed some observations on precipitation in dilute Be-Fe alloys.

Jacobson and Hammond (38, p. 179) examined and reported on the beryllium-rich end of five binary systems. Their study took the form of a re-examination of the beryllium-rich end of the binary systems of beryllium with aluminum, chromium, silver, copper and iron in order to more accurately determine the limits of solid solubility and the boundaries of the compound areas. Materials used in the study were zone-refined beryllium and high-purity alloying elements. Their investigation also included observations of the nature, structure, and appearance of second-phase
particles which are commonly found in beryllium microstructures. The five elements of their study are some which are commonly found as major impurities in beryllium, some which are being used as solid-solution alloying elements, and some which are used in ductile matrix alloys.

Another paper on the deformation aspects of beryllium was reported in the Philadelphia conference by Beasley and Moore (38, p. 227) who studied slip in beryllium single crystals compressed along the c-axis near 200° C. They claimed confirmation of the occurrence of wavy pyramidal slip in beryllium single crystals compressed parallel to the c-axis and its possible relationship to the ductile-brittle transition in polycrystals for specimens of 99.85 weight-percent beryllium zone refined twice and 99.95 weight-percent beryllium zone refined six times and tested from 148° to 350° C. They employed a hypothetical model and demonstrated that the critical resolved shear stress for (1125) slip observed in specimens compressed at 180° C could not be attributed to: (1) (1125) slip with Burger's vector in the basal plane; (2) cross-slip with (10\overline{1}0) <1120>; and (3) cross-slip on (10\overline{1}0) and (0001) planes in <1\overline{1}20> directions. The fact that large differences in the applied load which were required to initiate pyramidal slip suggested the occurrence of pyramidal slip is purity-dependent. They confirmed pyramidal slip in compression tests above 180° C and they suggested the critical resolved shear stress was purity dependent. They also mentioned the possibility of the operation
of pyramidal slip influencing the ductile-brittle transition in polycrystalline metal.

A second paper by Jacobson (38, p. 259) discussed factors affecting the ductile-brittle transition in beryllium. He investigated the factors controlling the ductile-brittle behavior of two grades of commercial-purity beryllium. Tensile testing between 23° and 500° C was performed on randomly oriented samples and three grain sizes of each material were studied with comparisons made between specimens tested in the aged and unaged condition. Mechanical properties of both materials were very similar after this ageing heat treatment and no advantage could be claimed for the higher purity electrolytically produced Pechiney beryllium. Ageing did reduce the amount of impurities in solid solution and did contribute to improved ductility in certain temperature ranges. Generally, the transition temperature was lower the smaller the grain size, the slower the strain rate, and the purer the material. They failed however to describe the ductile-brittle transition in terms of the dislocation pile-up theories for body-centered cubic metals. They proposed a theory of the ductile-brittle transition based on the thermally activated cross slip of screw dislocations from the basal plane onto pyramidal or prismatic planes. This ductile-brittle transition theory involves an increase in the probability that cross-slip will occur and it also takes into account the effects of stacking fault energy on
the observed deformation behavior of beryllium. They also mentioned other thermally activated processes which could control slip such as the Peierls mechanism or the dislocation intersection mechanism.

Tint and Herman (38, p. 293) have calculated the stresses required to move dislocations on the basal and prism planes of beryllium. Their treatment involved calculation of the temperature dependence of the frictional stress of a dislocation in beryllium on the basis of the predictions of the Kuhlmann-Wilsdorf "dislocation uncertainty" model. This calculation required the mean square displacement of an atom from its equilibrium position and this quantity was determined from the lattice vibration spectrum. The resulting calculated values of the frictional stress were then compared to the experimental critical resolved shear stress for both prism and basal slip. In this account, no consideration is made for any strain rate sensitive contribution to the flow stress. Furthermore, the values of the critical resolved shear stress represent the onset of gross plastic flow. Their results show that above 150° C the calculated values agree quite well with those experimentally determined. At the lower temperatures, the calculated frictional stress curve predicts a flow stress lower than observed. Reasons for the difference in this case are that at the lower temperatures the motion of screw dislocations is impeded by their
being pinned by portions cross slipping onto the basal plane and dissociating (20). They indicate the experimental values for the critical resolved shear stress fall between the values calculated for a dissociated and undissociated dislocation. These results suggested dislocations on the basal plane in beryllium behave as partially dissociated dislocations. It would then appear that the greater resistance to plastic flow exhibited by the prism plane at room temperature arose out of the undissociated dislocations moving on that plane and the pinning of cross-slipped screws.

Damiano and Herman (38, p. 335) conducted a general study of dislocations in deformed single crystals of beryllium. Their high purity beryllium single crystals were deformed in tension for basal and for prism slip. Based on the observations of dislocations in foils cut from the bulk crystals and from slip lines observed on the surface, the work-hardening mechanisms operating at various stages were deduced. As is customary in work-hardening experiments, the work-hardening graphs of stress versus strain are divided into three distinct stages. In stage I they observed long edge pairs and edge dipoles in foils cut from crystals deformed for basal slip. This suggested screw dislocations have high mobility on the basal plane in stage I. Also, the crystals exhibited very little hardening. The presence of numerous edge boundaries in stage II was associated with the onset of a rapid rate of work hardening just prior to failure. No
stage III was observed for basal slip. However, the three distinct stages of hardening were observed in crystals deformed for prism slip. Stage I showed the predominance of screw dislocation intersections with the grown-in networks producing jogs in the screw dislocations which acted to impede the further motion of the screw dislocations. In stage II complex interactions produced complicated tangled masses of dislocations. In stage III the beginning of duplex slip produced stable low angle boundaries as a result of dislocation interactions along intersections of glide planes. The stress-strain curves revealed a macroscopic yield stress for prism slip the order of 15 times that for basal slip. The work-hardening rate for prism slip was observed to be greater than that for basal slip. The examination of dislocation networks in the "as-grown" crystals revealed only Burger's vectors of the 1/3 <1120> type and those which were observed were found in the basal plane. Straight edge dislocations and elongated edge dipoles were observed in stage I in crystals deformed for basal slip. Bundles of edge dislocations were observed at high strains for basal slip in stage II. Foils deformed in stage I for prism slip revealed a predominance of screw dislocations. Additional slip-line studies revealed the presence of short prism slip line lengths as emerging edge dislocations. Many small dislocation loops were also observed in these foils. Finally, they associated the onset of duplex prism slip in stage III with a further increase in the work-hardening
rate. Foils cut from these crystals exhibited sub-boundaries not observed in crystals deformed in stages I and II. The conclusions of Damiano and Herman were as follows: They associated stage I hardening for both prism and basal slip with the intersection of glide dislocations with the grown-in networks. They support this noting since the Burger's vectors of the grown-in networks lie in the basal plane, intersections of the prism screw dislocations with the networks can produce jogs in the gliding prism screw dislocations but not in the gliding basal screw dislocations. The difference then explains the more rapid rate of work hardening in stage I for prism slip than for basal slip. Stage II hardening is associated with the formation of edge dislocation boundaries for basal slip. Complex tangles of dislocations are associated with stage II hardening for prism slip. Stage III hardening for prism slip is associated with the onset of duplex prism slip where stable boundaries were observed. They contend these boundaries arose from the interaction of dislocations on intersecting prism planes. No stage III hardening was observed for basal slip as their crystal failed in stage II.

Banfield and Li (38, p. 539) investigated the microstrain characteristics of beryllium. The microscopic yield stress (the stress to produce a permanent strain of $2 \times 10^{-6}$ in/in), the strain-hardening rate in the microstrain region and the friction stress (the stress to just move the first dislocations) of polycrystalline beryllium were determined and studied
as a function of dislocation substructure. The variations in dislocation density and distribution were brought about by controlled annealing and pre-straining treatments and then evaluated using optical and transmission electron microscopy. They found by annealing at elevated temperatures it was possible to produce considerable changes in the density and distribution of dislocations within a grain, without causing any change in grain size. However, the annealing resulted in a decrease in both the microscopic yield stress and the strain-hardening rate, which could then be correlated with the observed reduction in dislocation density. There was an approximately linear relation between stress and the square root of strain in the early stages of the microstrain region of beryllium for both material with a high density of tangled dislocations within a grain and material with only a few isolated dislocations within a grain. They found the actual microstrained region of beryllium to consist of two distinct stages. Stage A contained only a few basal dislocations available for slip and, here, heterogeneous plastic flow occurred. Stage B showed dislocation movement in many more grains as a result of prismatic glide and cross-slip. The results indicated the friction stress of beryllium contained a significant contribution from dislocation configurations. Their consideration of the operative deformation modes suggested the dislocation term is most likely to result from the elastic interaction of dislocation stress fields. They stated that
the maximum value of friction stress achieved by prestrain was possibly related to the initiation of prismatic glide.

The most recent beryllium symposium was the International Conference on the Metallurgy of Beryllium held at Grenoble, France, May 17 - 20, 1965. The conference was organized by the Department of Metallurgy of the French Atomic Energy Commission and the Grenoble Center of Nuclear Studies under the patronage of the French Society of Metallurgy (3).

The introductory lecture at the Grenoble Conference was given by D. McLean and his talk concerned the plastic behavior of beryllium and some other metals (3, p. 3). Numerous conclusions were stated concerning the extent of present knowledge of the deformation behavior of beryllium and these concepts must be kept in mind when dealing with any study involving the plasticity of beryllium. The transition range to low temperature brittleness is confined to a relatively narrow temperature range in beryllium compared to the other brittle hexagonal metals magnesium and zinc, and is due in beryllium to the great difficulty of causing (c+a).slip. The prevalent concept is that this is a Peierls force effect, so that a satisfactory theory of the Peierls force would hopefully throw some light on this most important property of beryllium. Because of beryllium's plastic anisotropy, texture has a very considerable influence on low temperature ductility because it controls the local stresses. It is generally accepted that the finest grain
size is desirable for best ductility. McLean stated alloying may sometimes improve the ductility as is the case with lithium in magnesium or rhenium in tungsten. The plastic behavior of beryllium becomes progressively more isotropic on raising the temperature and its ductility improves except that commercial material often suffers from a "ductility minimum" similar to that which has been overcome in other metals.

Scott and Lindsay (3, p. 141) conducted detailed observations on precipitation in beryllium using the electron microscope. Their results supported the view that a precipitation reaction occurred in commercial-purity beryllium and many features of the thermal treatment effects on the mechanical properties of the metal could be satisfactorily explained on this basis. The precipitates observed in beryllium annealed at 575° C (ductile), were considered to correspond to an overaged condition, while quenching from relatively high temperature (800° C) resulted in a lower high-temperature ductility due to solute atoms, or possibly very fine non-resolvable precipitates, interacting with dislocations. However, before the exact nature of this impurity-dislocation interaction could be explained, the significant element or elements had to be identified and their phase relationship with beryllium determined. Their quantitative estimates of the impurity concentration in precipitates indicated the content distributed as solute was likely to saturate all the dislocation lines. They considered non-metallic
impurity elements such as carbon might be involved and that further clues might be gained using, for example, pure metal from which carbon had been very carefully removed and also from studies on low-carbon alloys. They anticipated difficulties because of the possibility the solubility of non-metallic elements in beryllium could be so low that the limit of detection by chemical means would be above the solubility limit. In an alloy containing 1.2 weight-percent iron they found a precipitate $\text{Be}_{11}\text{Fe}$ in accord with the beryllium-iron equilibrium system. They were not able to correlate the matrix precipitation observed in the more dilute iron alloys with the binary beryllium-iron equilibrium diagram. Finally, they considered the possible occurrence of structural changes taking place during the tensile testing. The phenomena of strain-induced precipitation in the metals is well documented and their evidence indicated iron-rich centers might be preferentially nucleated in beryllium provided that suitable sites were available and if more general nucleation was impossible.

Ivanov, Gindin, Grinyuk, Lasareva et al. investigated the plastic behavior of zone-refined and prestrained beryllium single crystals (3, p. 239). This work considered the effect of zone refinement and of preliminary prestraining of 99.6 percent purity beryllium single crystals on the mechanical characteristics of specimens for two orientations under the conditions of compression in the temperature range $4.2^\circ - 300^\circ$ K. The
zone melting refinement was shown to lower critical shear stresses and to make basal, prismatic and pyramidal slip possible with a considerable plastic bend of the crystal lattice without cracks being formed. It was established that preliminary prestraining at 400° C, similarly to refinement, improved the plastic behavior of beryllium single crystals through the development of slip of all types. The magnitude of the effect depends on the stress level attained on prestraining. The increase of plasticity after prestraining is supposedly due to the diffusion rearrangement of point defects and the increase of homogeneity of the single crystal plastic strain. The redistribution of point defects relieves local overstresses and increases structure uniformity.

Tristen (3, p. 249) presented a short report on the effect of purity on tensile deformation in single crystals. His single crystals were 99.975 percent pure and were obtained from vacuum-cast Pechiney metal purified by six zone passes in argon and then recontaminated with carbon. The (0001) slip stress of the crystal increased from 400 psi to 1,770 psi at 200° C when contamination was effected. Experiments were attempted to investigate the effect of oxygen and nitrogen but no parallel increases in (0001) slip stress were noted. These high levels of (0001) slip stress are found in material of 99.90 percent purity and this fact is indicative of the relative importance of carbon as an impurity element. The action of carbon
in restricting deformation in single and polycrystalline material was discussed in terms of solutionized and precipitated states. A possible method of reducing the carbon content of beryllium was proposed and the effect of subsequently adding small amounts of an hcp material was discussed. It was argued the marked sensitivity of the critical resolved shear stress for slip to carbon contamination was due to carbon solute in the octahedral interstitial sites which gives rise to an asymmetrical strain field. Removal of this strain field would allow increased lattice bending, delay kink band formation and slip band plane cracking. He claimed these changes should be reflected in an increased strain to fracture. He claimed that true ductility at 20° C could be obtained by making the cleavage stress higher than the slip stress of (10\bar{1}X) with direction other than <hk o>. This might be done by removal of carbon and the addition of an hcp material.

Damiano, London, and Herman (3, p. 259) reported on the microstrain compression of a beryllium-4.37 percent copper alloy parallel to the c-axis. They described in detail microstrain c-axis compression tests performed on two beryllium-4.37 weight-percent copper crystals and also on a 12-zone pass unalloyed crystal. The test surfaces of their crystals were oriented to within three minutes of arc of the (0001) plane using specially constructed holding and lapping fixtures used in conjunction with a calibrated G. E. diffractometer. A non-basal pyramidal slip system
(11\bar{2}2) was actuated in the alloy crystal at a stress level of about 335,000 psi at 24° C along with simultaneous compressive twinning on (10\bar{1}1) planes. At 200° C the stress to initiate this pyramidal slip and twinning was reduced to about 198,000 psi. An unalloyed crystal tested at 24° C failed at about 330,000 psi with no trace of pyramidal slip. They reasoned when beryllium behaves in a brittle manner, it does so because cleavage rather than plastic flow is the more energetically favored phenomena. Brittle fracture could be ameliorated by the appearance of an additional slip system operating on a pyramidal plane in a slip direction which is not contained in the basal plane. The appearance of this type of slip mode would permit plastic flow to occur at the head of a basal crack and also permit polycrystalline beryllium to deform in a general and uniform way, that is, one in which no voids must form. The results contained in this report definitely indicated that alloying of beryllium with copper allows the desired new type of slip mode to be developed. Additionally favorable results are indicated by the new twinning mode also operative.

The first systematic and meaningful study on beryllium and beryllium alloys was conducted by A. R. Kaufmann, P. Gordon, and D. W. Lillie at the Massachusetts Institute of Technology in the late 1940's (32). Their effort was an attempt to find out whether or not beryllium could be made ductile. They investigated the effects of 35 alloying elements on the
the physical properties, microstructure, lattice parameter and electrical resistivity of beryllium. They reported only copper, palladium, cobalt, nickel and silver to have appreciable solid solubility in beryllium. The base beryllium metal used in their study would now be called only intermediate purity. A typical analysis of their beryllium would be aluminum, 800 ppm; calcium, 90 ppm; chromium, 130 ppm; copper, 50 ppm; iron, 850 ppm; magnesium, 50 ppm; manganese, 240 ppm; nickel, 140 ppm; silicon, 750 ppm and a minimum of 0.1 percent BeO. Furthermore, most of their large-scale melting of beryllium was carried out in beryllium oxide crucibles in a vacuum of about 100 to 500 microns using induction heating.

Kaufmann et al. identified most of the inclusions in beryllium as being due to aluminum, silicon, or carbon. Their conclusions were based on the microstructural appearance of dilute alloys of these elements. They found no conclusive metallographic evidence of iron in beryllium or in a 1-percent iron alloy. There was no indication of an oxide network as claimed by Sloman (53) and no clear-cut evidence of any oxide inclusions. Interestingly, they pointed out that latent metal to which large amounts of oxygen were added still showed no definite oxide phase, although some peculiarities were observed in the microstructure. They did not take this as evidence that oxygen is soluble in beryllium, but rather that the oxide does not remain dispersed in the metal. Beryllium to which nitrogen was added in the
molten state exhibited needle-like inclusions, but these were never observed in the original beryllium. They concluded there was no evidence in the microstructure of the "pure" metal to indicate that a precipitated impurity was causing the brittleness.

Based on claims in the literature (12), the above authors attempted to reduce the oxygen content of beryllium below 0.10-percent by small additions of a deoxidizer. They prepared alloys intended to contain one percent of titanium, zirconium, magnesium, calcium, aluminum, cerium, sulphur, and selenium. Results showed no appreciable amounts of sulphur, selenium, or magnesium remained in the beryllium. The titanium and zirconium appeared as a second phase in a eutectic structure. The calcium was observed as a second phase of cubic shape, evidently an intermetallic compound which occurred as a primary constituent. The cerium alloy also exhibited a second phase. Briefly, the results of these studies indicated that none of these alloys showed a greater ductility than pure beryllium and hence either they did not deoxidize the beryllium or whatever deoxidation did occur was ineffectual.

Kaufmann, Gordon, and Lillie next reasoned since the above mentioned alloys showed no enhanced ductility, they would look for elements having an extensive solid solubility in beryllium in the hope that such solid solutions would have better physical properties than the pure metal. The
alloying elements already mentioned, namely, aluminum, silicon, carbon, oxygen, nitrogen, titanium, zirconium, magnesium, cerium, calcium, sulphur and selenium - appear to have a negligible solid solubility in beryllium. It must be kept in mind the relative purity of the base metal beryllium these investigators were using. Photomicrographs and lattice parameter measurements on quenched alloys were given to support these conclusions. They state iron may have a solubility of the order of 1/2 atomic percent and this would have accounted for the difficulty in identifying a second phase due to iron in the one weight-percent alloy.

Table III shows the elements which were added to beryllium in searching for solid solutions. The table is reproduced from the work of Kaufmann, Gordon, and Lillie (32). If a micro-examination of the alloys listed in Table III revealed a large amount of second phase in the form of a eutectic or binary constituent, the solid solubility was taken to be small. Only copper, nickel, cobalt, silver and palladium showed appreciable solid solubility. Copper is reported to display the largest solid solubility, somewhere about 7 atomic-percent at 1,100° C.

It is interesting that the solid solubilities reported in this work agree fairly well with those predicted as being most probable by applying the Hume-Rothery rule which says atoms whose diameters differ by more than 15 percent will not form extensive solid solutions. However, there are some
TABLE III. - Microstructure of binary beryllium alloys as melted (32)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>10</td>
<td>Two-phase — 50% primary Be dendrites, 50% eutectic of Be in compound.</td>
</tr>
<tr>
<td>Cerium</td>
<td>1</td>
<td>Two-phase — fine precipitate.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>5</td>
<td>Largely one-phase — some compound at grain boundaries.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>10</td>
<td>Largely one-phase — compound at grain boundaries.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>15</td>
<td>Two-phase alloy — eutectic in form of stringers.</td>
</tr>
<tr>
<td>Columbium</td>
<td>10</td>
<td>Two-phase — compound at grain boundaries.</td>
</tr>
<tr>
<td>Copper</td>
<td>15</td>
<td>One-phase.</td>
</tr>
<tr>
<td>Germanium</td>
<td>10</td>
<td>Two-phase — light colored compound at grain boundaries and within grains.</td>
</tr>
<tr>
<td>Iron</td>
<td>6</td>
<td>Two-phase — partial network.</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1</td>
<td>Two-phase — eutectic network.</td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>One-phase.</td>
</tr>
<tr>
<td>Palladium</td>
<td>5</td>
<td>One-phase.</td>
</tr>
<tr>
<td>Palladium</td>
<td>10</td>
<td>Largely one-phase — very small amount of compound showing.</td>
</tr>
<tr>
<td>Silicon</td>
<td>1</td>
<td>Two-phase — inclusions in form of stringers.</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1</td>
<td>Two-phase — inclusions in form of stringers.</td>
</tr>
<tr>
<td>Tantalum</td>
<td>1</td>
<td>Two-phase — eutectic network.</td>
</tr>
<tr>
<td>Thorium</td>
<td>10</td>
<td>Two-phase — 5 to 10% angular compound in long stringers.</td>
</tr>
<tr>
<td>Titanium</td>
<td>1</td>
<td>Two-phase — eutectic network.</td>
</tr>
<tr>
<td>Tungsten</td>
<td>1</td>
<td>Two-phase — eutectic network.</td>
</tr>
<tr>
<td>Zirconium</td>
<td>1</td>
<td>Two-phase — precipitate of spheroids strung in lines at 120-degree angles.</td>
</tr>
<tr>
<td>Zirconium</td>
<td>5</td>
<td>Two-phase — 30 to 40% angular compound.</td>
</tr>
<tr>
<td>Calcium</td>
<td>1</td>
<td>Two-phase — angular compound.</td>
</tr>
<tr>
<td>Uranium</td>
<td>5</td>
<td>Two-phase — compound in cubic shapes.</td>
</tr>
<tr>
<td>Manganese</td>
<td>10</td>
<td>Two-phase — 10 to 15% compound.</td>
</tr>
<tr>
<td>Platinum</td>
<td>20</td>
<td>Two-phase — 20% compound as a eutectic network.</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>10</td>
<td>Two-phase — about 20% eutectic, fine precipitate in primary Be.</td>
</tr>
<tr>
<td>Osmium</td>
<td>10</td>
<td>Two-phase — 20 to 30% eutectic.</td>
</tr>
<tr>
<td>Rhodium</td>
<td>10</td>
<td>Two-phase — eutectic network.</td>
</tr>
<tr>
<td>Chromium</td>
<td>10</td>
<td>Two-phase — 30 to 40% eutectic network.</td>
</tr>
</tbody>
</table>

(Continued)
TABLE III. - Microstructure of binary beryllium alloys as melted (32)
(Continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>10</td>
<td>Largely one-phase — small amount of white compound in form of globules.</td>
</tr>
<tr>
<td>Bismuth</td>
<td>10</td>
<td>Immiscible in liquid state — only about 0.5% Bi in the Be.</td>
</tr>
<tr>
<td>Tin</td>
<td>10</td>
<td>Immiscible in liquid state.</td>
</tr>
<tr>
<td>Zinc</td>
<td>10</td>
<td>Zinc distilled off — only 0.6% Zn in the Be.</td>
</tr>
</tbody>
</table>
exceptions. Silver and palladium lie well beyond the 15-percent limit and there are many other elements closer to the limit which form no solid solution. A 10 weight-percent nickel and 15 and 32 weight-percent copper alloys in the work of Kaufmann et al., were fairly successfully cast and extruded.

The best values of the beryllium lattice constants reported by Kaufmann et al. are \( a_0 = 2.2854 \, \text{Å}, \quad c_0 = 3.5829 \, \text{Å}, \quad c_0/a_0 = 1.5677 \). They reported on the effect of the addition of titanium, silicon, aluminum, zirconium or oxygen on the lattice parameters is very small, noticeable only in the fourth decimal place, and then only after a solution heat treatment at 1,000° C. All of their samples, including the unalloyed beryllium, give substantially the same value, and they concluded either the amount of desired impurities was insufficient to change the lattice parameter within the precision of the measurement or else the desired impurities (most probably oxygen) caused the same change in parameter in all the samples.

Kaufmann et al. also carried out tensile tests at room temperature to evaluate the relative ductility of beryllium and the beryllium alloys of their study. In general, their work showed alloying and thermal treatments led to little improvement in ductility, but a small amount of ductility could be achieved in extruded metal in the extrusion direction. It is interesting to note in their study that in beryllium, because it is a brittle metal, the damage done to the specimen surface as a result of even the most
careful machining exerts a large influence on the tensile properties observed. They state, somewhat surprisingly, that removal of the specimen surface has a large effect on the tensile properties, but only when the main body of the metal is in the recrystallized condition. The inherent properties of the recrystallized material are intermediate strength and relatively high ductility, but the damaged surface layer causes premature failure and does not allow these inherent properties to be realized. But, if the metal is in a severely cold-worked condition throughout, it is inherently strong and very brittle and the surface damage resulting from machining has no appreciable effect on its tensile properties.

Other data indicated annealing at $800^\circ$ C also eliminated the effects of surface damage. The effect would not be totally unexpected because the annealing would recrystallize the cold-worked beryllium metal.

Tensile tests on the alloys investigated in their study revealed no appreciable improvement in either the strength or ductility of beryllium for any of the alloy additions. Kaufmann, Gordon, and Lillie concluded the only alloys which showed sufficient promise in the areas of casting and extrusion were those of copper and nickel. They conclude on a negative basis that their work uncovered no explanation of the brittleness of beryllium and they felt extensive ductility could not be achieved by further removal of impurities. Their beryllium metal to which various possible
deoxidizing elements had been added and also their beryllium solid-solution alloys with especially copper-nickel, and cobalt, showed no significant or meaningful improvement in ductility.

A reasonable amount of information on the constitution of beryllium-rich alloys is available (61, p. 556). There are fairly reliable phase diagrams and detailed observations for the systems involving aluminum (32, 41, 52), silicon (37), silver (63), gold (62, 11), iron (56), copper (35), nickel (32, 34), and uranium (32, 10), with superficial data on zirconium (32, 26), tungsten (32), molybdenum (32), tantalum (32), cerium (32), calcium (32, 46), germanium (32), titanium (32), tin (32, 24), bismuth (32), boron (32), carbon (32), cobalt (32, 59), niobium (32), palladium (32), thorium (32), manganese (32), platinum (32), ruthenium (32), osmium (32), rhodium (32), magnesium (45), and zinc (32). The most outstanding conclusion from these data is that beryllium does not form extensive solid solutions with any element yet studied. The meaning of the word extensive in this context is not totally clear. What may be extensive solid solutions for beryllium systems may only be limited solid solutions in some of the more common systems because of the small atomic weight of beryllium.

An extensive discussion of the solid solution alloying possibilities for beryllium has been given by Raynor (48), using some of the principles developed by Hume-Rothery. Raynor took into account the following factors:
1. The relative atomic and ionic size of beryllium and the other elements. Atoms whose "diameters" differ by more than about 15 percent from that of the solvent are not supposed to enter into solid solution. However, if the "ion" of either kind of atom is small compared with its atomic "diameter," there is a greater chance for solid solution, even if the 15-percent limit is exceeded.

2. The number of valance electrons of beryllium and other elements. Atoms having more valance electrons than in solvent are supposed to dissolve to a greater extent than those having fewer valance electrons than the solvent, other factors being equal.

3. The relative position of beryllium and possible alloying elements in the electrochemical series. Beryllium is strongly electro-positive, and hence intermetallic compounds are to be expected with electronegative elements. Such compound formation is supposed to decrease the solid solubility.

Since the beryllium atom is unusually small, the 15-percent size difference rule appears to preclude solid solution formation with almost all the elements except those in the first transition series. Raynor points out that the alkaline metals would not be expected to form compounds with beryllium, since they are electro-positive; nor would they form solid solutions because of their large size. Lithium, the smallest in size,
might have a limited solubility. However, since all the alkalis develop high vapor pressure below the melting point of beryllium, any attempts at alloying would be difficult. The same arguments should apply to the alkaline earth metals. Efforts to alloy beryllium with magnesium at pressures up to 100 atmospheres have been unsuccessful (14, p. 279).

The solubility of aluminum in beryllium (32) is well below 0.1 weight-percent and there are no compounds. This indicates aluminum obeys the Raynor rules. However, the same alloying behavior is true of silicon (32, 37), and this is considered to be inexplicable by Raynor. He considers silicon to be electro-negative and therefore feels compounds should form with beryllium. On the basis of atomic size, there should be solid solution since compounds do not form. There is neither solubility of silicon in beryllium nor are compounds formed.

Based on experimental results, Raynor is able to conclude that copper, gold and the various transition elements should all have a comparable solid solubility. Kaufmann, Gordon, and Lillie (32) reported maximum solubilities of roughly 7 atomic percent copper, 1 atomic percent nickel, 1 atomic percent cobalt and 3 atomic percent palladium. Teitel and Cohen (56) found less than 0.4 atomic percent of iron in solid solution. Sidhu and Henry (11) found about 2 atomic percent gold to be soluble, but reportedly this latter work needs further checking. Cursory examinations
by Kaufmann, et al. (32) revealed the solid solubilities for the transition elements niobium, tantalum, thorium, titanium, zirconium, tungsten, uranium, manganese, ruthenium, osmium, rhodium, and chromium were very small, while platinum showed some solubility. The fact that the three metals namely copper, silver, and gold have the highest solid solubilities in spite of an unfavorable "size" factor indicates clearly it is the electronic band structure associated with d shells which is important for this question.

Very little is known about alloying with zinc, cadmium, and mercury. It may be that these three elements do not form solid solutions.

Beryllium forms one stable compound with uranium which is reported to have the formula UBe$_{13}$. Compounds of the same crystal structure as UBe$_{13}$ form with zirconium, titanium, and thorium (4).

Raynor (48) points out that in metallic beryllium the outer electronic energy band is essentially full and overlaps the next higher band in a direction perpendicular to the c axis. The condition is supposed to distort the crystal lattice in the c direction and cause the c/a ratio (1.568) to be less than the theoretical value for close packing (1.633). If the deformed lattice of beryllium is responsible for its brittleness it is conceivable a solid solution which increased the c/a ratio might have enhanced ductility. Mono-valent alloying elements such as copper, silver, and gold should decrease the number of electrons in the outer band and increase c/a.
Transition elements should do the same thing since the unfilled d band could accept electrons.

Solid solution alloys of beryllium with copper, nickel, and cobalt have been made and extruded by Kaufmann et al. (32). Without exception these alloys were less ductile at room temperature than "pure" beryllium. It is fairly well established that iron also has an embrittling effect. The minor increase of c/a ratio caused by these alloying elements did not increase ductility. An excellent treatment of the alloying behavior of beryllium is given in Chapter 9 of the work by Darwin and Buddery (14). The alloying behavior of beryllium is discussed in this reference as it pertains to the different groups of chemical elements respectively. Figure 6, originally formulated by Parthe (14, p. 270), indicates beryllium forms stable intermetallic compounds with a large number of metals. Parthe, in a study of the various metallic compounds, reported compounds with arsenic and, more surprising, with potassium. He excluded any reference to the solubility of beryllium with gallium or indium, and at least one compound as now known to exist between beryllium and niobium. These corrections have been made in Figure 6.

The following discussion of the various beryllium alloy systems studied by the authors indicated is a summarization of the compilation given in Chapter 9 of the reference by Darwin and Buddery (14).
FIGURE 6. The compounds of beryllium. (L = rare earth elements; Ac = actinide metals)
Williams and Jones, investigating the sintering of mixed elemental powders, found when beryllium was physically mixed with uranium, thorium, iron, copper, zirconium, titanium or vanadium powders, considerable growth or expansion in the form of a volume increase occurred when pressed compacts of the mixed powders were sintered. No expansion occurred in the compacts made from mixtures of beryllium with aluminum, magnesium, or silicon, and, with the exception of magnesium, where it has been shown that it is very difficult to obtain compound formation, the former group all give compounds while the latter do not. Where growth occurred the composition-growth curves showed a maximum in most cases corresponding to the composition of a compound. Williams and Jones concluded that the volume expansions were due to diffusional porosity during sintering.

There is very little information on the alloying properties of beryllium with the alkali metals. Claussen and Skehan (12) poured beryllium into liquid lithium and lost all the lithium by evaporation. Parthe showed a compound with potassium (14, p. 271). As has been shown previously and as pointed out by Raynor (48), the size factors of the alkali metals with the exception of lithium are so unfavorable that no alloying is likely, and indeed, he doubted even liquid miscibility. He thought the solubility in lithium was likely to be very limited; compound formation also seemed unlikely on electrochemical grounds.
A large number of workers have investigated the beryllium-copper system. The most significant contributions have been made by Raynor (48), Kaufmann, Gordon, and Lillie (32), Losana and Venturello (35), Borchers and Oesterheld (41 and 14, p. 272). It is meaningful to recall at this point that Kaufmann, Gordon and Lillie fabricated alloys of beryllium, containing 15 and 32 weight-percent copper; all the test pieces showed inferior properties to unalloyed beryllium.

The beryllium-silver system has been completely investigated by Oesterheld (41), Sloman (14, p. 276), and Winkler (63). At the present time there is disagreement as to the solubility of silver in beryllium. The results of Klein, Perelman and Beaver are somewhat lower than those of Winkler (63) and Kaufmann et al. (32). Von Batchelder and Raeuchle pointed out on the basis of possibilities suggested by Oesterheld (41) that Winkler's diagram needs modification at the beryllium-rich end. Most investigators felt that further work on this system would seem justified if silver can be regarded as an alloy to give a ductile second phase (14, p. 276).

The only diagram of the beryllium-gold system has been given by Winkler (63). Owen and Roberts reported the solubility of beryllium in gold as "a few tenths of one atom percent" (14, p. 277) whereas Winkler said that it was less than 0.9 atom percent.

Raynor (48) pointed out the big difference in size factor between the
alkali earth metals and beryllium would effectively prohibit solid solution. Successful attempts at making a magnesium and beryllium alloy have been reported by Baker and Williams and Williams and Jones (14, p. 278). Alloys of calcium with beryllium have also been reported (32, 46 and 14, p. 279).

Beaver (61) has reported two items of unpublished American work on Group III elements which indicated compound formation with boron: One worker reported a compound which might have been \( \text{Be}_4\text{B} \) or \( \text{Be}_3\text{B} \), while another mixed the elements in the right proportion for \( \text{Be}_3\text{B}_2 \) and obtained an exothermic reaction on heating, finding, on X-ray diffraction, three phases were present, one of which was beryllium. Two isotropic phases appeared under the microscope and no melting took place when the compacted powder was heated to 1,500° C. A more thorough investigation of the system has been carried out by Markovskii and co-workers who reported three compounds: (1) \( \text{Be}_2\text{B} \) which had a copper-red appearance, (2) \( \text{BeB}_2 \) which was a dark gray material, and (3) \( \text{BeB}_6 \) which was described as a brick-red crumbly powder, sometimes with a violet tinge (14, p. 280). Pearson (44) reported a beryllium-boron compound, and due to the uncertainty of its composition, listed its formula as \( \text{Be}_{4-5}\text{B} \).

Phillips has reviewed the beryllium-aluminum system and the presently accepted phase diagram of this system is due to him. Sawyer and
Kjellgren conclude the solubility of aluminum in beryllium is less than 1.27 weight percent; it is certainly nothing like the 8 percent quoted by Oesterheld (41). Losana put the solubility at about 5 percent. Kaufmann, Gordon, and Lillie indicated the solubility of aluminum in beryllium is low, possibly less than 1.27 percent (32). Pearson (44) maintains that there are no compounds in the binary aluminum-beryllium system. Darwin and Buddery (14), in Table 9.2, stated no improvement in room temperature elongation was found for several beryllium-aluminum alloys; however, these alloys showed improved malleability in rolling or extrusion, lower pressures being needed than with commercially pure material (14, p. 283).

The system beryllium-lanthanum was studied by Baenziger, Nielsen, and Duwell (14, p. 284) and Baenziger and Rundle (4) as well as Kaufmann et. al. (32) have investigated the beryllium-cerium system. Only compound formation is reported in these systems.

Rough and Bauer have summarized the available information on the beryllium-thorium system. These same two investigators have thoroughly reviewed the beryllium-uranium system and their work, along with that of Buzzard (10) accounts for the bulk of the work on this system.

Runnalls has done work on the beryllium-neptunium system and he indicates some small range of solubility. The only phase diagram available for the beryllium-plutonium system is due to Konodeevsky, who reported
that the eutectic composition was almost pure plutonium. Coffinberry and Ellinger have reported on the structure of the compound PuBe$_{15}$.

Kelman and co-workers and Elliott and Cramer studied the solubility of beryllium in liquid gallium. Elliott and Cramer also investigated the solubility of beryllium in liquid indium. In both these systems, this solubility was found to be very small (14, p. 289).

Among the Group IV elements, there is little information on the beryllium-carbon system, with the exception of the work on the carbide Be$_2$C. Judging from the work of Beaver (61) and from the photographs in a paper by Greenspan it would seem that the solubility of carbon in beryllium is certainly less than 0.3 percent. The phase diagram of the beryllium-silicon system by Masing and Dahl (37) contained a simple eutectic system. The two metals are shown as being completely insoluble in each other, facts which were partially confirmed by Kaufmann, Gordon and Lillie (32), who found a 1-percent silicon alloy showed two phases with inclusions in the form of stringers. Sloman (53) also deduced from microscopic examination that the solubility of silicon in beryllium is low. The low solubility of silicon in beryllium in the absence of intermetallic compounds suggested to Klein, Perelman, and Beaver the use of silicon to form a ductile second-phase alloy. Their results do not appear at all attractive (14, p. 293).
Kaufmann, Gordon and Lillie (32) reported that a 10-percent germanium alloy in beryllium appeared two phased. Kaufmann and co-workers also reported tin and beryllium are immiscible even in the liquid state. The most significant work on the beryllium-tin equilibrium phase diagram has been done by Elliott and Cramer and the presently accepted diagram is due to them (14, p. 294).

Claussen and Skehan (12) stated that additions of small amounts of titanium improved the malleability of beryllium, and they put the eutectic at between 1/2 and 2-percent titanium. Kaufmann and his colleagues (32) reported that a 1-percent alloy showed a eutectic network but, they were unable to confirm the improved malleability reported by the earlier workers; their measurements of the lattice parameters of a 0.73-percent titanium alloy indicated that there might be some slight solid solubility. Titanium and beryllium form several intermetallic compounds. One phase diagram for the beryllium-titanium system has been reported by McQuillan and McQuillan. They pointed out however that there diagram must be regarded as hypothetical and that there is no experimental foundation for the phase boundaries shown (14, p. 296).

Along with their observation that additions of small amounts of titanium to beryllium made it more malleable, Claussen and Skehan (12) reported the same results for additions of small amounts of zirconium. Kaufmann, Gordon and Lillie (32) again were unable to confirm this, however, and their experiments showed that both 1-percent and 5-percent alloys of zirconium in beryl-
lium were two-phased, indicating that the solubility of zirconium in beryllium is small. The first phase diagram produced by Hausner and Kalish (26) confirmed this. Hayes, in a review of the alloys of zirconium, produced an equilibrium phase diagram. However, apart from the zirconium-rich end, the whole diagram is rather uncertain (14, p. 298).

The behavior of beryllium with the Group V elements shows very little in the area of promising alloy behavior. Much of the work done deals with the various compounds formed in the individual systems. Various investigators (14, p. 298-300) suggest that the respective solubilities, in beryllium, of nitrogen, phosphorous, arsenic, antimony and bismuth are low. Raynor (48) thought it possible, on theoretical grounds, that there might be some solubility of vanadium in beryllium. The only attempted investigation of this system was reported by Rostoker and Yamamoto, who suggested that the solubility of beryllium in vanadium is less than 0.8 percent. Nothing in the beryllium literature could be found on an experimental determination of the solubility of vanadium in beryllium.

Kaufmann, Gordon and Lillie (32) found the solubility of niobium in beryllium was small. In the beryllium-tantalum system Kaufmann et. al. confirmed experimentally the prediction of Raynor (48) that the solubility of tantalum in beryllium would be low.
In the elements of Group VI the solubility of oxygen in beryllium has received the widest attention. The solubility of oxygen in beryllium, although certainly small, is not definitely known. One of the difficulties in this area lies in the determination of the oxygen levels by chemical analysis. In recent years the technique of neutron diffraction has tended to alleviate this problem. The effect of oxygen on the mechanical properties of beryllium has been extensively investigated. The effect on ductility is quite complex, depending on temperature, strain rate, and distribution of the oxide. Work of this nature is of particular industrial interest since metal fabricated from powder always contains appreciable amounts of oxide. Various investigations on the behavior of beryllium with sulphur, selenium, tellurium, and palladium have been concerned mainly with the compounds formed in the respective systems.

Hindle and Slattery (30, p. 651) reported a metallographic survey of some dilute beryllium alloys. Their work consisted of a study of the constitution of alloys at the beryllium-rich end of the following systems: beryllium-calcium, beryllium-aluminum, beryllium-silicon, beryllium-titanium, beryllium-chromium, beryllium-tin, beryllium-zirconium, and beryllium-iron. They used standard metallographic and X-ray methods, supplemented where necessary by electron-microprobe analysis. Alloys were examined as solidified, and no attempt was made to study the variation of solid solubility with temperature. They did report in all cases solid solubility appeared to
be extremely limited, and a second phase was visible in microsections containing as little as 0.1 weight percent of the alloying element. In the alloys with aluminum, silicon, and tin, the second phase consisted of the alloying element, and in the remainder, intermetallic constituents were identified, having formulas $\text{Be}_{13}\text{Ca}$, $\text{Be}_{12}\text{Ti}$, $\text{Be}_{12}\text{Cr}$, $\text{Be}_{13}\text{Zr}$, and $\text{Be}_{12}\text{Fe}$. As far as the routine metallographic work in the beryllium systems is concerned, their paper contained many practical and helpful suggestions which were employed often throughout the course of the present investigation.

Kaufmann, Gordon and Lillie (32) examined the structure of a 10-percent chromium alloy and found that it had 30 - 40 percent eutectic network. This suggested the solubility of chromium in beryllium was low, as predicted by Raynor (48). A recent investigation by Yans, Donaldson and Kaufmann has also suggested that the solubility is low, since chromium additions had little effect on the c-lattice parameter. Kaufmann, Gordon and Lillie (32) reported the microstructure of a 1-weight percent molybdenum in beryllium alloy was two-phased with a eutectic network. The equilibrium diagrams reported by most investigators cover only the molybdenum-rich end of the system.

Kaufmann, et. al. (32) reported low solubility of tungsten in beryllium.

Very little is known about the solubility of the halides of Group VII in beryllium and there is also little indication of their effect on mechanical properties, but it seems likely their presence results in a loss of ductility and an
increase in strength. Kaufmann, Gordon and Lillie (32) stated the solubility of manganese in beryllium is small. Work on the beryllium-rhenium system has been confined to compounds formed in that system (14, p. 307).

Some of the more interesting alloying behavior of beryllium occurs with the transition elements of Group VIII. A considerable number of workers have investigated the solubility of iron in beryllium. Sloman (53) noticed that annealing an alloy containing 0.01 - 0.05 percent iron caused the disappearance of a compound previously visible at the grain boundaries, while Kaufmann et. al. (32) showed that a 6-percent iron alloy was two-phased. Teitel and Cohen (62) have reported the solid solubility was less than 0.4 atom percent (2.4 weight percent) iron. A more recent investigation by Gelles, Ogilvie and Kaufmann disclosed the maximum solubility of iron in beryllium was 0.92 atom percent (5.46 weight percent) at 1,225° C, the eutectic temperature. The solubility fell rapidly at lower temperatures, reaching about 0.45 atom percent at 1,000° C and 0.18 atom percent at 850° C (14, p. 307). A modified equilibrium phase diagram by Teitel and Cohen (62) is the one presently accepted. Kaufmann et. al. (32) reported the solubility of cobalt in beryllium was 10 - 15 percent at 1,050° C and less than 5 percent at lower temperatures. The only fully complete equilibrium phase diagram is due to Venturello and Burdese (59).
The beryllium-nickel system appears to offer fairly extensive solid solubility. Losana and Goria (34) found the solubility of nickel in beryllium was between 10 and 15 percent at 1,230° C. Kaufmann et. al. (32) investigated metallographically the structure of a 10-percent nickel alloy in the as-cast state and found it to be single-phased. They also investigated quenched alloys and found the solubility to be 8 - 10 percent at 1,050° C. More recent work by Gelles, Ogilvie and Kaufmann has put the solubility as 4.93 atom percent (25.2 weight percent) at 1,065° C, i.e. the eutectoid temperature. Equilibrium phase diagrams for this system have been prepared by Jahn and also Gelles et. al. At present there is insufficient information to modify the diagram at the beryllium end (14, p. 312).

Most of the work on the behavior of beryllium with ruthenium, rhodium, osmium and iridium has been confined to the various compounds formed in these systems.

Kaufmann, Gordon and Lillie (32) reported a 10-percent palladium alloy in the beryllium-palladium system was largely single-phase but with a very small amount of compound showing. They found and reported the solubility of palladium in beryllium at various temperatures. One of the presently accepted equilibrium phase diagrams on the beryllium-palladium system is due to Winkler (63); unfortunately, his work is concentrated on the palladium-rich end of the system.
Kaufmann et al. (32) reported a 20-percent platinum alloy showed a eutectic network and concluded the solubility of beryllium in platinum is low. Klein, Perelman and Beaver failed to vacuum cast a 3-percent platinum alloy, since soaking at temperatures as high as 1,600°C did not dissolve the platinum. Measurements of the lattice parameters of vacuum-hot pressed powder mixtures suggested that no platinum was in solution.

The various compounds formed in all the individual beryllium binary systems have not been treated in this section. The reason for this is the mechanical properties of these intermetallic compounds are generally unfavorable. Ductility and elongations in these intermetallic compounds usually suffer at the expense of somewhat higher strengths.

In summary, concerning work directed toward producing beryllium in solid solution alloys, a variety of metals have been added to beryllium in an attempt to improve the mechanical properties, with particular emphasis on the ductility. Work has been directed toward deoxidation, grain refinement, and alteration of the crystal structure.

Powerful deoxidants, including zirconium, titanium, aluminum, magnesium, cerium, lanthanum, and calcium have been added to beryllium melts. Beryllium oxide is a very stable oxide, and the deoxidation characteristics of the foregoing elements, if any, did not impart any significant increases in ductility. Early workers claimed zirconium and titanium had a beneficial
effect and these additions imparted improved malleability. Unsuccessful attempts have also been made to produce beryllium-lithium alloys.

As-cast beryllium mainly exhibits coarse grains which are associated with very small elongations. Attempts have been made to formulate an alloy with a small equiaxed grain size, or alternatively to inoculate a melt such that nuclei would be provided for the solidifying crystals. In this respect, small additions of germanium, zirconium, and lanthanum appeared to have a grain refining effect on cast beryllium, but the extent of grain refinement is small and the grain configuration remains columnar. The inoculation of melts with titanium nitride and tungsten carbide powders has not succeeded in refining the cast structure.

Beryllium has a hexagonal close-packed lattice of low axial ratio, and other elements are found to have limited solubility in it. Those additions showing greatest solubility include copper, nickel, and silver. Sheet prepared from cast and extruded alloys containing up to 0.4 percent copper is reported to have increased tensile strength at equivalent ductilities. The addition of copper to beryllium results in a slight increase of the c/a axial ratio of the beryllium lattice, but the theoretical value for close packing is not obtained (14, p. 273). Again, the alloying behavior of beryllium with the other elements has been summarized in Table II and Figure 6.
MATERIALS

Some of the factors considered in selecting alloying elements to be added to beryllium were as follows: melting point, crystal structure, density and atomic size. On this basis, the elements selected were titanium, boron and manganese. These elements were added to the electrolytic flake beryllium starting material in compositions of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 atomic percentages.

The beryllium starting material was in the form of electrolytic flake. Details of the production of this electrolytic or electrorefined beryllium have been given elsewhere (65, 64, 66). The method consists essentially of electrorefining beryllium in a KCl-LiCl-BeCl₂ bath. Thin, plate-like crystals of beryllium metal are produced by electrolyzing technical-grade beryllium metal beads (about 94-percent purity) as the soluble anode. This fused-salt electrorefining of beryllium is carried out in electrolytes composed of a LiCl-KCl eutectic mixture containing varying amounts of BeCl₂. In this way high purity metal can be produced from low grade or scrap metals. Results claim a 99 percent or better reduction of oxygen and magnesium and a substantial reduction of other minor metallic impurities. Oxygen can be reduced from an average value of 3.0 percent in the anode feed to approximately 0.05 percent in the refined metal, and magnesium reduced from 2.6 percent to as low as <0.0003 percent. Aluminum, nickel, chromium and cobalt are reduced
so as to be almost undetectable by spectrochemical analysis; iron and silicon are also substantially reduced; and a lesser degree of reduction is indicated for manganese, copper and calcium. The analysis of the electrolytic flake beryllium metal used in this study is given in Table IV. If an analysis of the beryllium used in this study is compared to a typical analysis of beryllium produced by this electrorefining process, the two analytical reports show approximately the same amounts of silver, iron, manganese, nickel, silicon, tin, boron, cobalt, lead, titanium, vanadium, zinc and zirconium. The beryllium of the present work, however, contains slightly less nitrogen, chlorine, aluminum, calcium, copper, magnesium, and chromium than the typical metal, whereas the starting material beryllium used to form the different alloys in this research contained somewhat more carbon, oxygen, and hydrogen than an amount of beryllium metal randomly produced by this procedure.

The analyses for the three alloying elements are given in Table V. The titanium used was in the form of small chips which were produced electrolytically. Before arc melting the major impurities present in this electrolytic titanium were copper, manganese, molybdenum and silicon. As can be seen from Table V all these impurity contents are below the 200 ppm level. The manganese used in this study carried the trade name Matthey manganese. It was produced by Johnson, Matthey, and Company, Ltd. of London, England and distributed in the United States by the United Mineral
and Chemical Corporation. This manganese was also produced by a form of electrodeposition. The boron employed in this study was made available by the United Mineral and Chemical Corporation in the form of 99.8 percent pure boron granules. The major impurities in the manganese were magnesium and oxygen, while the boron contained iron, carbon and oxygen as its major impurities.
### TABLE IV. - Beryllium starting material analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>800</td>
</tr>
<tr>
<td>Carbon</td>
<td>700</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>20</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>50</td>
</tr>
<tr>
<td>Chlorine</td>
<td>800</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Iron</td>
<td>25</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1</td>
</tr>
<tr>
<td>Manganese</td>
<td>57</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Tin</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Silicon</td>
<td>47</td>
</tr>
<tr>
<td>Boron</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Barium</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Titanium</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Tungsten</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;400</td>
</tr>
<tr>
<td>Zirconium</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>

1/ Starting material for alloy study was Boulder City Electrolytic Flake Beryllium.
### TABLE V. - Alloying element analyses

<table>
<thead>
<tr>
<th>Analysis element</th>
<th>Electrolytic titanium</th>
<th>Matthey manganese 1/</th>
<th>Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>17</td>
<td>108</td>
<td>100</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>29</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Oxygen</td>
<td>211</td>
<td>577</td>
<td>100</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;50</td>
<td>--- 2/</td>
<td>50</td>
</tr>
<tr>
<td>Boron</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;50</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Cadmium</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cobalt</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt;130</td>
<td>---</td>
<td>200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>30</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Manganese</td>
<td>200</td>
<td>---</td>
<td>10</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>100</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;35</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;200</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Silicon</td>
<td>100</td>
<td>---</td>
<td>10</td>
</tr>
<tr>
<td>Tin</td>
<td>&lt;180</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Titanium</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Vanadium</td>
<td>50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Tungsten</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Zinc</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

1/ In the manganese analysis, elements reported as not detected are generally considered to be below a limit of 50 ppm.

2/ --- Not detected.
APPARATUS AND EXPERIMENTAL PROCEDURES

A. Weighing and Compacting

The beryllium starting material and the three alloying elements (titanium, manganese and boron) have been discussed with their respective analyses in the Materials section of this paper. These data are included in Table IV and Table V. The alloys to be studied were to contain 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 atomic percentages of these three elements in beryllium. Depending on first the individual alloying element and second the actual composition of the alloy to be made, either 20-gram, 25-gram, or 30-gram samples were produced. A relatively simple computer program was worked out for converting these atomic percentages to the respective weight percentages and, using the results of this program, the beryllium content and the alloy content for each individual alloy were weighed out to the nearest milligram on a conventional Gram-O-Matic balance.

At the outset of this work it was felt that some of the starting material beryllium or even perhaps some of the alloying element would be lost during arc melting. However, since the author could find no relevant data concerning possible molten metal loss in these systems, it was decided to weigh each alloy to the exactly calculated content. This procedure in effect assumes no loss of metal during arc melting when this is not actually the case. The exact theoretical content for each individual alloy was weighed and each alloy was thoroughly mechanically mixed in a separate large glass jar. The alloys were
then placed in a conventional 1-3/4-inch-diameter steel die and compacted on a standard hydraulic press at 40,000 psi. During compacting each specimen was kept at the 40,000 psi level for a period of from 1 to 2 minutes or until no further decrease was noted on the pressure dial of the press. Each specimen was carefully removed from the die and they were then ready for arc-melting.

B. Nonconsumable Arc Melting

Samples were removed from the hydraulic compacting press and each alloy specimen was placed in one of the six depressions on the water-cooled copper hearth plate of the nonconsumable arc melting button furnace shown in Figure 7. The actual arc melting procedure was as follows: Valve A of Figure 7 was opened and the entire system evacuated by means of a mechanical roughing pump to approximately 5 microns or less. Valve A was then closed and the entire system remained under reduced pressure for a period of time. The purpose here was to determine some sort of quantitative measure of the system leak rate using the thermocouple gauge. When the system leak rate was determined to be 2 microns per minute or less, it was considered suitable to proceed with the arc melting. Depending on the prior internal condition of the furnace, the times required to attain the stated 5 microns or less pressure were a minimum of 30 minutes and a maximum of 12 hours.
FIGURE 7. Non consumable arc melting button furnace
Valve B was opened after the acceptable leak rate had been assured, and helium gas introduced to a pressure of 10 inches of mercury as read on the pressure gauge. Valve A is still closed during the introduction of the helium gas. Generally, during the initial evacuation with Valve A open, Valve B was also open to permit pumping of any air which might have remained in the line leading to the helium tank. Of course, during this preliminary evacuation the valve on the helium tank would have to be closed.

When the internal pressure in the furnace had reached 10 inches of mercury or approximately one-third of an atmosphere, Valve B was again closed and Valve A opened to the roughing pump. The pressure inside the furnace was reduced again to 5 microns or less. This procedure of flushing the furnace was carried out three times in order to insure complete expelling of all air that could possibly remain in the furnace. Helium was chosen as the flushing gas for the furnace over argon because it was felt the major impurity in helium, namely methane, would be less harmful to the alloys during melting than oxygen which is likely to be the main impurity in argon.

Valve A was again closed, Valve B opened and helium gas introduced into the furnace to a pressure 10 inches of mercury or approximately one-third of an atmosphere after the final flushing with helium. Valve B was then closed and the furnace was ready for melting. The cooling water to the copper hearth plate and to the electrode holder holding the thoriated tungsten electrode was
turned on, the flow adjusted to suitable levels, and allowed to run for some 5 minutes before melting. In practice this cooling water was turned on prior to or during the helium flushings.

The water-cooled copper hearth plate shown in Figure 7 contained six depressions around the periphery of the plate in which the compacted alloys were placed. There was also a depression in the center of the plate which held a 50-50 weight percent titanium–zirconium alloy which served as a getter button. The getter button was always melted first in order to remove any gaseous impurities from the furnace atmosphere. An arc was struck between the thoriated tungsten electrode and the titanium–zirconium getter button using a high frequency starter. The getter button was flipped over and melted again. The actual alloys were ready to be melted. Even though the furnace contained provisions for melting up to six alloys at one time, it was found optimal to melt only three alloys at any one given time because the impurities given off during the melting of beryllium were likely to contaminate the other samples. The compacted alloy samples were melted in the same manner as the titanium–zirconium getter button. A high frequency arc is struck between the thoriated tungsten electrode and the individual alloy sample and the sample is then melted. Currents required to melt the alloy samples ranged from 250 amperes to 400 amperes depending on the individual alloys. The beryllium–titanium and beryllium–manganese tended to require fewer amperes than the beryllium–boron alloy samples. The samples were flipped over between each melting a
total of three times. This provided two complete meltings on each side of the sample and was felt quite adequate for proper mixing of the alloying element in the parent metal.

Due to the toxicity associated with melting of beryllium, a special procedure had to be used for opening the furnace after melting was completed. This procedure is as follows: Valve B was opened and helium introduced into the furnace to bring the internal pressure to 1 or 2 inches of mercury below atmospheric pressure. Valve C was opened and the entire furnace atmosphere removed by means of a special beryllium filtration system designed especially for this purpose. As Valve C was opened and the gaseous products of melting were being removed, either Valve B was opened or the top of the furnace opened very slightly to allow an in-rush of helium or air to insure the complete removal of the furnace atmosphere resulting from melting. (After approximately 5 minutes,) the furnace was considered safe to open. Even with using this procedure, a respirator was usually worn while cleaning the furnace after melting.

The top of the furnace was removed and supported so as not to scratch or damage its inner surface which was in contact with a vacuum seal O-ring. The three alloy specimens which had been melted were removed from the furnace, washed in acetone when cool and placed in their respective sample containers. The entire inside of the furnace was vacuumed out to remove any solid particles which might have remained as a result of melting. All interior
surfaces of the furnace including the water-cooled copper hearth plate and the thoriated tungsten electrode along with the water-cooled electrode holder were thoroughly cleaned in acetone by swabbing with a damp cloth or paper towel which was later discarded. Three new samples are placed in the furnace on the copper hearth plate, the top is replaced on the furnace and the entire procedure is repeated again when the entire inside surface of the furnace is cleaned and dry.

Two papers presented during the 1961 Conference on the Metallurgy of Beryllium were directly concerned with a small segment of the present investigation, namely arc-melting beryllium. Kyffen and Craik (30, p. 677) and Eaton, Longstaff and Robinson (30, p. 687) provided in their respective works many suggestions which were of use during the preparation of the alloys for this study. Their works were concerned with consumable-electrode vacuum arc-melting of beryllium, whereas a non-consumable electrode technique was employed in the present study; but, their comments were nevertheless relative.

C. Machining and Sectioning

The alloy samples were in the familiar button shape after arc melting, that is, approximately 1-1/2 to 1-3/4 inches in diameter, and 1/4 to 1/2-inch high. The buttons were roughly circular. Each button was placed in the chuck of a conventional lathe and the two large flat surfaces on each side of the
button were machined smooth and parallel. Metal removal from the buttons during this machining procedure was of the order of 0.001 inches per pass. The turnings from the machining operation were saved and later served as samples for chemical analyses. Three different types of samples were then cut from these machined buttons. The largest of the three samples was the sample to be used for compression testing. This sample for compression was removed from the center of the machined button and its dimensions were approximately 1-inch long by 1-inch wide by 1/4-inch high. This compression specimen was cut using a standard cut-off wheel with a 1/16-inch or 1/32-inch-thick blade. Secondly, the pieces left over from the cutting out of the compression specimen were to serve as metallographic samples. Four such pieces were usually available. One or two of these samples intended for metallography was ground up to a particle size of ~230 mesh and, after suitable heat treatment, these powdered samples were ready for X-ray diffraction. And as mentioned previously the machine turnings served as samples for chemical and spectrographic analyses.

D. Metallographic Analyses

The pieces from the cutting of the compression specimens served as metallographic specimens. The largest surface of these metallographic specimens had already been cut on the cut-off wheel so it was not necessary to use any coarse grinding papers for the initial mechanical polish. Each alloy sample
was mounted in bakelite in such a way so as to permit examination of the large freshly cut surface. The samples were ground on 400-grit paper and 600-grit paper for approximately 5 minutes each. The next polishing steps were accomplished on cloth wheels using diamond paste of 18 micron, 6 micron, 1 micron, and 1/4 micron particle sizes respectively. A minimum of one-half hour polishing time was given on each individual diamond wheel. The samples were ready for microscopic examination after the 1/4 micron diamond wheel.

The optical microscopic examination was carried out on a Zeiss Universal Microscope equipped with reflected light optics and a xenon light source. It was unnecessary to etch any of the specimens prior to metallographic analysis. The internal structure, phases, grain boundaries, etc. could be clearly viewed using polarized light and all samples were examined in this manner. The Zeiss microscope used contained a cross nickel polarizing facility which made it ideal in this regard. The microscope also had provisions for photography of the metallography of each specimen.

E. X-ray Diffraction Analysis

Not all four pieces remaining from the compression specimen cutting were needed for metallography. One piece was taken for study by means of X-ray diffraction. Each sample was mechanically crushed into powder form so that the powder would pass through a -230 mesh sieve. The powdered
samples were taken and sealed in evacuated Vycor tubes which had been flushed two or three times with helium gas before sealing under vacuum. All powdered samples were heated to 500° C for 1/2 hour in order to relieve the stresses induced by the powdering process. It was felt this time and temperature would permit complete stress relief without allowing any significant recrystallization or grain growth.

One of the original intents of this research was to determine the effect of the selected alloying additions on the c/a ratio of beryllium. Consequently the powdered specimens were examined on a standard diffractometer. The particular model used in this research was a Basic Norelco Diffractometer operating at 45 kv, 35 Ma and using copper radiation. The scanning rate was kept constant at one-quarter degree per minute. The individual diffractometer patterns within each alloy system were compared with others of that same system. In other words, the seven diffractometer scans for the different alloys within the beryllium-titanium system were compared only among themselves. They were not compared to the other two alloy systems. The same was true for the respective diffractometer patterns for the beryllium-manganese system and the beryllium-boron system. The position and intensity of the individual diffraction peaks were the two main criteria used in these comparisons.
F. Chemical and Spectrographic Analyses

The machine turnings from the button facing operation provided enough material to give samples for both wet chemical and spectrographic analyses. The purpose of the wet chemical analysis was to determine the actual content of the alloying elements in their respective systems with beryllium. The beryllium-titanium system had each of the seven alloys analyzed for the percentages of titanium in the alloys; the beryllium-boron alloys were analyzed for the percentage of boron in each alloy; and, the beryllium-manganese system had each alloy analyzed for its manganese content.

A general qualitative spectrographic analysis was also performed on each alloy prepared by the arc melting procedure and major objective was to detect any gross impurities which might have been introduced into the samples as a result of arc melting. Possible causes of contamination during arc melting were copper from the copper hearth plate, tungsten from the thoriated tungsten electrode, titanium and/or zirconium from the getter button which was always melted first, or any other metallic impurities possibly remaining in the furnace as a result of improper cleaning.

All arc-melted samples in each beryllium alloy system were also analyzed for oxygen, nitrogen, and carbon. Possible oxygen and nitrogen contamination would undoubtedly arise because of incomplete flushing of the
furnace prior to melting or because of a somewhat greater leak rate than could be detected before or during melting. There were two main reasons for the carbon analysis. The first of these was methane, CH₄, a major impurity in the helium gas used for flushing out the furnace volume. Secondly, after each melting, the interior of the furnace was washed with large amounts of acetone. The cleaning of the interior was usually accomplished with a cloth saturated with acetone and simply wiped over the interior surfaces of the furnace. It was felt any acetone residue which might remain in the furnace after cleaning could possibly lead to contamination of the alloys in the following melt.

The starting materials were subjected to the same analyses prior to the compacting and melting processes used to produce the alloys in addition to X-ray diffraction, chemical, and spectrographic analyses of all samples after melting.

G. Compression Testing

Compression testing and the subsequent metallographic analysis of the samples was one of the major portions of this research and special care was taken with the compression test samples. The cubical-shaped compression specimens were cut from the arc-melted buttons and were electropolished in a 6-percent perchloric acid in methanol solution cooled to -76°C by means
of a dry-ice and acetone cooling bath. This produced a high surface luster on the samples. The voltages needed to polish the samples ranged between 50 and 80 volts depending on the sizes of the individual samples being polished. The samples were rinsed in absolute ethyl alcohol after electropolishing, dried, and examined metallographically using the same Zeiss instrument previously mentioned. The electrolytic polishing and metallographic examination were done prior to the actual compression testing; first, to prepare the specimen surfaces for the actual compression testing; and, secondly, to allow some sort of comparison between the metallographic results obtained using conventional polishing techniques and those obtained here using electropolishing methods. Each sample was ready to be tested in compression after this optical metallographic examination.

The compression test was done on a screw type Tinius Olsen Universal Testing Machine (range 0 - 30,000 lbs) at a strain rate of 0.025 inches per minute. The three alloy samples were deformed to a point just slightly beyond the onset of plastic flow, following proper alignment of the instrument. A pure beryllium sample for comparison purposes was deformed also, although somewhat more extensively.

Then, following this initial deformation, the three alloy samples containing nominally 0.5 atom percent titanium, 1.0 atom percent manganese, and 0.5 atom percent boron were examined metallographically with particular
emphasis being placed on slip and slip lines, twinning, and cracking. Cross slip and the shape of the twins present in the material were also studied. The results of this metallographic examination were recorded photographically and the three alloy samples were then repolished electrolytically using the same solution described above. This second electropolish permitted removal of some of the physical markings on the samples caused by the first stage of deformation in addition to preparing the specimen surfaces for the second stage of the deformation process. In effect this means the slip lines and cross-slip lines would be removed by this second electrolytic polish whereas cracks and twins present in the sample would not be removed by this second polishing.

Each sample was further deformed plastically to the 30,000 pound limit of the compression instrument. The samples, all remaining intact, were examined again microscopically and the results recorded.
EXPERIMENTAL RESULTS

X-ray Diffraction

All alloy samples in each respective alloy system were found to exceed the solubility limits of that particular system by using the methods of X-ray analysis discussed in the Experimental Procedures section. No alloy was found to be completely single-phased solid solution. Extra peaks on the individual diffractometer scans were present for each alloy studied and these peaks were attributed to the presence of a second phase in the system.

It was hoped that in the samples containing only 0.5 atom percent of the alloying element the alloy samples would be single-phase solid solutions with lattice parameters only somewhat different (larger or smaller) than pure beryllium. This was not the case. The alloying constituent atomic percentages were small in the case of many of the alloys; however, the small atomic weight and density of beryllium were equivalent to much higher corresponding weight percentages of alloy and hence the solubility limits were exceeded in all cases.

In the beryllium-boron system, the major second-phase constituent identified was Be$_{4-5}$B. The formula for this compound is written in this manner because of the uncertainty of its composition. Elliot (18, p. 109) reports the compound as Be$_5$B and as being the product of a liquid eutectic decomposition. The reported eutectic is observed at approximately 11 atom
percent B, somewhat higher than the composition of sample Be/0.5B (actual composition 0.37 atom percent or 0.44 weight percent B). Some eutectic or possibly peritectic structure was observed in the present study in the metallographic examination of specimens in the beryllium-boron system. For some unknown reason, a trace amount of manganese, found to be present as Be$_8$Mn, was located in sample Be/5.0B.

The major second-phase constituent identified in the beryllium-manganese system was Be$_8$Mn. The compositional formula of this compound is accepted as Be$_8$Mn by several other investigators (18, p. 165). Interesting analyses were reported from the X-ray (not chemical) data on sample Be/0.5Mn. The compound Be$_{4.5}$B was present as a minor constituent and if a judgment were based on only the individual boron and manganese contents, it might be assumed that during the course of this study, samples Be/5.0B and Be/0.5Mn were somehow switched. However, sample Be/0.5Mn was also found to have traces of Be$_8$Mn, the compound known to be present in the beryllium-manganese system. The reasons for this apparent mix-up is still uncertain. Initial impurity analyses of the alloying elements are also inconsistent with this anomaly. Sample Be/1.0Mn containing no detectable boron was chosen for mechanical testing for this reason.
The major second-phase constituent identified in the beryllium-titanium system was $\text{Be}_{12}\text{Ti}$. The compositional formula is also accepted by most recent investigators (18, p. 172). A few small but definite peaks were present in the diffractometer scans of the various alloys in this system and these peaks were unable to be indexed on the basis of known possible structures (carbides, oxides, or nitrides, etc.) and still other peaks were found in the higher titanium content alloys which could be indexed as $\text{Be}_{17}\text{Ti}_2$. The latter compound is known to exist in this system. No metallic impurity compounds were detected (using X-ray analysis) in any of the alloys in this particular system.

Two pure beryllium samples (+230 mesh and -230 mesh) were submitted (as a check on the suitability of the X-ray method for this type analysis) to the identical experimental treatment as the alloy samples and the lattice parameters for the two alloys were measured and calculated. The -230 mesh sample yielded a $c/a$ ratio of 1.5694 and the +230 mesh sample gave a $c/a$ ratio of 1.5691. These values are well within experimental error of the accepted $c/a$ ratio of 1.568. Thus, there exists little doubt on the credibility of the X-ray method employed.

**Metallography**

There appeared to be direct metallographic evidence of a eutectic or peritectic type reaction in the beryllium-boron system. Elliott (18, p. 109)
does report a eutectic reaction between beryllium liquid and the components pure beryllium and the compound \( \text{Be}_5\text{B} \). The difference between a peritectic and eutectic decomposition can often be quite difficult to determine metallographically. The only discerning factor appears generally to be a gradient in the composition of one or both of the components in a peritectic reaction, whereas, in a eutectic reaction this is not the case. The gradient in composition is often easier to detect metallographically in a peritectic reaction. The problem becomes increasingly difficult when the peritectic or eutectic portion is only a small fraction of the total amount of sample. Such would be the case if a phase boundary had just been crossed in going from a single phase to a two-phase region.

Except for sample \( \text{Be/4.0B} \), all boron alloy samples were shown by standard methods of wet chemical analysis to be significantly lower than the nominal boron content.

X-ray analysis confirmed the metallographic evidence of a second phase in the beryllium-boron system with its composition reported as \( \text{Be}_{4.5}\text{B} \). The second phase is shown in the lighter regions of Figures 8-A and 8-B. The appearance of dendrites in these figures was characteristic of several metallographic samples within this particular alloy system. All samples were examined under polarized light.
FIGURE 8. Second phase $\text{Be}_4\text{B}$ in beryllium – boron alloy
Definite evidence is present for a eutectic reaction in the beryllium-manganese system. This fact is demonstrated in Figure 9. Figure 9 is a photomicrograph of sample Be/4.0Mn and is shown to be very nearly 100 percent eutectic composition. Electron microprobe analysis for the sample Be/4.0Mn showed a manganese content of approximately 22.0 weight percent. This figure for manganese content is an average value with the actual determinations ranging from 20.4 to 23.6 weight percent. These figures are only slightly higher than the nominal composition of 20.25 weight percent (4.0 atom percent) which this sample was made up to be. The electron microprobe analysis was conducted on the actual metallographic sample and thus the values cited above should be taken as nearer the true value than those obtained through wet chemical methods. Standard wet chemical analysis was done on another portion of the same sample from which the metallographic sample was cut and this procedure yielded a manganese content of 18.8 weight percent (3.66 atom percent). Samples higher and lower in manganese content than sample Be/4.0Mn showed corresponding amounts of this eutectic phase. In general, all the manganese alloy samples were shown chemically to be somewhat low in manganese content as compared to their nominal composition.

X-ray analysis had previously shown the second phase in the beryllium-manganese system to be present as Be₈Mn, with some authors maintaining another possible composition, Be₁₂Mn (18, p. 165). Figures 10-A, 10-B and
FIGURE 9. Eutectic phase in Be/4.0 Mn
10-C show the small dark particles of phase $\text{Be}_8\text{Mn}$ as they appear in the beryllium matrix. In some instances the second phase in this system, as in the beryllium-boron system, also appeared in the form of dendrites. This was most pronounced near the eutectic composition.

There did not appear to be any metallographic evidence of eutectic or peritectic reactions in the beryllium-titanium alloy system. The results are consistent with the higher reported values of yield stress and work hardening rate found in this work for the $\text{Be}/0.5\text{Ti}$ alloy. All beryllium-titanium alloys contained two phases as suggested in the X-ray analyses. The two phases were probably pure beryllium and the compound $\text{Be}_{12}\text{Ti}$. In the higher titanium alloys a mixture of compounds $\text{Be}_{12}\text{Ti}$ and $\text{Be}_{17}\text{Ti}_2$ was present. This is not inconsistent with the phase diagram presented in Elliot (18, p. 172).

The particles of second phase $\text{Be}_{12}\text{Ti}$, as they appear in the beryllium matrix, are given in Figure 11. They are shown as the small lighter areas in this figure. Dendrites were noticeably absent in this alloy system. In general, the titanium alloy samples after arc melting were shown chemically to be only slightly lower in titanium content compared to their nominal composition.

The alloys chosen for compression testing on the basis of the above considerations were $\text{Be}/0.5\text{B}$, $\text{Be}/1.0\text{Mn}$ and $\text{Be}/0.5\text{Ti}$. The respective compositions of these samples after arc melting are given
in Table VI along with their individual oxygen, nitrogen and carbon analyses. The individual boron, manganese and titanium contents given in Table VI were obtained using standard methods of wet chemical analysis. The carbon and nitrogen analyses reported were similarly obtained; however, the oxygen contents were determined by neutron activation analysis.

**TABLE VI. - Alloy compositions after arc-melting of samples used in compression testing experiments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal content (atomic percent)</th>
<th>Actual content (atomic percent)</th>
<th>Oxygen (ppm)</th>
<th>Nitrogen (ppm)</th>
<th>Carbon (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be/0.5B</td>
<td>0.5(Boron)</td>
<td>0.37(Boron)</td>
<td>2200</td>
<td>1090</td>
<td>291</td>
</tr>
<tr>
<td>Be/1.0Mn</td>
<td>1.0(Manganese)</td>
<td>0.99(Manganese)</td>
<td>600</td>
<td>987</td>
<td>223</td>
</tr>
<tr>
<td>Be/0.5Ti</td>
<td>0.5(Titanium)</td>
<td>0.48(Titanium)</td>
<td>400</td>
<td>4620</td>
<td>305</td>
</tr>
<tr>
<td>Pure Be</td>
<td>(Beryllium)</td>
<td>(Beryllium)</td>
<td>200</td>
<td>320</td>
<td>1100</td>
</tr>
</tbody>
</table>

**Mechanical Deformation**

Mechanical deformation in the form of compression testing was carried out for several reasons. First and perhaps most importantly, the representative sample from each alloy system (i.e., Be/0.5B, Be/1.0Mn and Be/0.5Ti) was deformed as nearly as possible to a predetermined equal amount. Photographs of these previously electropolished specimens had already been obtained in the annealed or as-
FIGURE 10. $\text{Be}_8\text{Mn}$ phase in Be/1.0 Mn
FIGURE 11. Be$_{12}$Ti phase in Be/0.5 Ti (200X)
melted condition and the objective was to follow the twinning behavior of these alloys as a function of increasing strain. The results are presented in another portion (Slip and Twinning) of this section. Secondly, from the load-elongation curves and the corresponding stress-strain curves for these polycrystalline specimens, the work hardening rates could be calculated and possibly yield some insight into the operative dislocation mechanisms on the basis of already postulated theories. Lastly, from these same curves, values of the yield strength for the different alloys could be calculated and compared with those of other metals and alloys. The stress value at the point of departure from linear elastic behavior was taken as the value of the yield strength. The results of these two latter objectives are presented in Table VII.

**TABLE VII.- Work hardening rates and yield strengths for beryllium alloys**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Work hardening rate, pounds/in²</th>
<th>Yield strength, pounds/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be/0.5B</td>
<td>1.07 x 10⁶</td>
<td>47,200</td>
</tr>
<tr>
<td>Be/1.0Mn</td>
<td>1.3 x 10⁶</td>
<td>56,500</td>
</tr>
<tr>
<td>Be/0.5Ti</td>
<td>1.52 x 10⁶</td>
<td>81,250</td>
</tr>
<tr>
<td>Pure Be</td>
<td>1.02 x 10⁶</td>
<td>19,750</td>
</tr>
</tbody>
</table>
The yield strengths of alloys Be/0.5B and Be/1.0Mn do not give a significant increase over the yield strengths of many of the common forms of commercial beryllium. It does appear, however, that the alloy Be/0.5Ti has a somewhat higher yield strength than the range of 40,000 psi to 60,000 psi normally quoted for various forms of beryllium (2, p. 1198).

The samples were all deformed up to the limit of the compression instrument (30,000 pounds). The total deformation sustained by each sample was as follows: pure beryllium — 11.65%, Be/0.5B — 4.52%, Be/1.0Mn — 2.05%, and Be/0.5Ti — 2.22%.

**Slip and Twinning**

Many sources indicate twinning is one of the prevalent deformation modes in both single crystal and polycrystalline beryllium (61, 14, 25, 32). One major objective of the present study was to determine whether or not the twinning deformation mode would also be present in the three alloy systems selected for study. The presence or absence of twinning should be important along with the degree to which the specific types of twins (shape, length, etc.) were altered.

Specific factors considered in the slip and twinning aspect of this study were as follows: The length and width of the twin bands (at comparable magnifications), straight or wavy character of the slip lines present, presence or absence of cross-slip, presence or absence of microcracks, the angles...
between the twin bands, general shape of twin bands, relative amounts of
twinning, whether or not the slip lines cross the twin bands and the inter-
action of the second-phase particles to the twin bands.

These various factors will be discussed first in relation to pure
beryllium and then the differences exhibited by the various alloy systems
will be brought out.

In pure beryllium, the twins are generally quite long, sometimes
extremely long, and they are also often quite wide with perhaps some con-
striction on the end of the twin band. Typical deformation twins in pure
beryllium are shown in Figures 12-A, 12-B and 12-C, the dark bands being
the twins. The slip lines in beryllium which, at small amounts of deformation,
are quite straight are indicative of slip in the basal plane, as shown by Lee
and Brick (61). These straight slip lines are also shown in Figure 13.

Large amounts of cross slip are evident at higher values of strain
as shown in Figures 14-A and 14-B. The angles between the twin bands are
generally large, obtuse angles. Many twins in pure beryllium, in addition to
being fairly wide are lenticular in shape, as in Figures 12-A and 12-C. Twin-
ning is quite profuse with slip lines, in some instances, crossing the twin
bands. Figures 15-A and 15-B depict the phenomena of slip lines crossing
the twin bands. It is significant that in no instance in a pure beryllium sample
was a twin seen to be constricted anywhere along its length. Some instances
FIGURE 12-A. Microstructure of deformed pure beryllium
FIGURE 12-B. Typical deformation twins in pure beryllium

FIGURE 12-C. Typical deformation twins in pure beryllium
FIGURE 13. Straight slip lines in pure beryllium
FIGURE 14. Cross slip in pure beryllium
FIGURE 15. Slip lines crossing twins in pure beryllium
of terminal (or initial) twin constriction were detected, but never along the main body of the twin band. Very few microcracks, as determined by polishing, restraining and repolishing, were evident in pure beryllium.

The length of the twins seems to be both long and short in the beryllium-boron system. But, generally, the longer twins are wide and the shorter twins are narrow. Representative typical twins in this alloy system are shown in Figures 16-A and 16-B. The large round particles in these photographs were believed to be the second phase Be$_{4-5}$B that was detected by X-ray diffraction. Slip lines were somewhat difficult to see, owing to the large amount of second phase present in the specimen. Cross-slip correspondingly was also difficult to detect and for the most part was non-existent. The most significant fact about the Be/0.5B alloy looked at in this system was the extremely large amount of microcracks present. The presence of these microcracks as microcracks and not as wavy slip lines was supported by the technique of polishing the sample electrolytically to remove all prior surface damage and then confirming this fact microscopically. The sample was again strained a predetermined amount. The sample was then examined again under the microscope, taking careful note of the amount of slip lines and twinning present. The sample was repolished electrolytically until all definite slip lines and twin bands were removed. The sample was further polished unsuccessfully to remove what had to now be classified
FIGURE 16. Typical deformation twins in Be/0.5 B
as microcracks, rather than wavy slip lines as reported by Kaufmann, Gordon and Lillie (32, p. 386). These microcracks are shown as the light wavy lines in Figure 17. Significantly, the angular intersections between the twins were the most acute of all the systems and many of the twins were curved twins. "Curved" here is used in the sense of having more curvature than lenticular twins. Twins with this rather pronounced curvature are given in Figure 18. And although some small areas are heavily twinned, much of the matrix is untwinned. In many cases the microcracks cross a twin band indicating they formed after the twin band had propagated.

The twin bands are generally shorter in the beryllium-manganese system than in all the other alloy systems, as shown in the photographs of Figures 19-A and 19-B. The twins are also generally narrower, with some being very narrow. Some extremely narrow twins are shown in Figure 20. They appear as the three dark shorter lines in the middle portion of the figure. Again because of the large amount of second phase, definite slip lines are present but they are quite hard to see. In some instances, the slip lines appear wavy. The amount of microcracks present in this system is roughly comparable to pure beryllium and to the beryllium-titanium system but definitely less than in the beryllium-boron system. It is surprising to note that many of the twin bands in this system intersect within a given sample at angles very close to right angles. The significance of this fact is
FIGURE 17. Microcracks in Be/0.5B
FIGURE 18. Curved twins in Be/0.5B
FIGURE 19. Representative deformation twins in Be/1.0 Mn
FIGURE 20. Very narrow twins in Be/1.0Mn
not yet clear, but is shown in Figure 21. The shape of the twins in this system is similar to those in the pure beryllium. Many are lenticular, constricted often on the ends but never along the body of the twin. And, although the actual twins themselves are the smallest of any of the alloy system, the relative amount of twinning is greater than in the other two alloy systems. Figure 22 depicts a relatively heavily twinned area. Generally speaking, for this system, the slip lines or microcracks do not cross the twin bands.

The twin length is actually only slightly shorter in the beryllium- titanium system than in the pure beryllium. There are however some extremely short twins associated with the scattered particles of second phase (Be$_{12}$Ti). The short twins are shown at high magnification either terminating or originating at second phase particles in Figure 23. And in general the twins in the titanium alloy samples are narrower than those found in pure beryllium. Some of the twins in this Be/0.5Ti specimen are very thin, as shown in Figure 24. Slip lines are definitely present, but much shorter in length than those in pure beryllium. Even with the short slip lines, it is still possible to discern a certain amount of cross-slip. Slip line interaction occurs mostly as the intersection of wavy slip lines rather than as the intersection of the largely straight slip lines in pure beryllium. Some of the more heavily deformed areas may be extensively cross-slipped, but detection of
FIGURE 21. Twin intersections in Be/1.0Mn
FIGURE 22. Extensive twinning in Be/1.0Mn
FIGURE 23. Short twins and second phase in Be/0.5 Ti
FIGURE 24. Narrow twins in Be/0.5 Ti
this is somewhat uncertain because of the extensive mechanical damage. Slip lines formed during the early stages of deformation are shown in Figure 25-A, while further deformation yields the wavy slip lines of Figure 25-B. The presence of microcracks in this system is also uncertain. It is quite possible the heavily deformed areas are a combination of microcracks and wavy slip lines denoting cross-slip. The angular intersections between twins were more acute than in pure beryllium, but not as acute as in the beryllium-boron system. Twin shapes were mostly very narrow, with some lenticular and constricted. It is in the shape of the twins that this system exhibits its unique and most interesting behavior. Many of the twins are internally constricted and this, along with other anomalies in the odd shape of the twins is presented in Figures 26-A, 26-B, 26-C and 26-D. The twins appeared somewhat longer in general in the beryllium-titanium system but with less profusion than in the other alloy systems. Twins with the slip lines crossing them are showing in Figure 27.
FIGURE 25. Slip lines in Be/0.5 Ti
FIGURE 26. Irregular twins in Be/0.5 Ti
FIGURE 27. Slip crossing twins in Be/0.5 Ti
DISCUSSION AND CONCLUSIONS

One of the major differences noted between pure beryllium and the beryllium-base alloys of this study was after plastic deformation much less cross-slip was found in the alloys than in the pure metal. It is possible this decrease in the relative amounts of cross-slip in the alloys is related to a corresponding decrease in the stacking fault energies of the alloys. It is known that beryllium has a fairly high stacking fault energy, of the order of 180 ergs/cm². This value of the stacking fault energy is of the same order as aluminum, (200 ergs/cm²) (28, p. 90), a metal in which extensive cross-slip occurs.

An explanation of the manner in which high stacking fault energy metals cross slip has been given by Seeger (19, p. 243) and that reasoning can be applied to this problem of the beryllium alloy systems. Dissociation of unit dislocations into extended dislocations of a certain width depends upon the stacking fault energy. The dissociation is independent of the character (edge, screw or mixed) of the dislocation. The important fact to note is, unlike an unextended dislocation, the extended dislocation defines a specific plane and will be constrained to move in this plane, the plane of the stacking fault. The two parts of this extended dislocation called partial dislocations move as a unit maintaining the equilibrium width. Extended dislocations themselves cannot cross slip. However, it is possible to form a constriction
in the extended dislocation, particularly in extended screw dislocations, and then the smaller unit dislocation at this constriction will be free to move in other planes providing it still maintains its screw character. A definite amount of energy (called the stacking fault energy) is associated with the formation of this constriction which will form more readily in metals with a high stacking fault energy. It then follows that cross-slip will occur most readily in metals such as beryllium with a high stacking fault energy and it will be most difficult in metals with a low stacking fault energy. These concepts account readily for the profuse cross-slip in pure beryllium and if the alloying additions tended to lower the stacking fault energy of the beryllium, the alloys would be expected to and in fact do cross slip less.

The concept of the stacking fault energy of a metal changing with solute concentration is not unfamiliar. Most alloy systems investigated have shown a decrease in the stacking fault energy with increasing percentage of the alloying element. Howie and Swann (27) have shown the stacking fault energy of quenched alpha brasses decreasing continuously with increasing percent zinc. Bell, Okamoto and Thomas reported the stacking fault energy decreasing with increasing tin content in alpha copper-tin alloys (5). Chromium appears to lower the stacking fault energy as it is added in cobalt-nickel-chromium alloys (17) but the situation is considerably more complex for ternary alloys. The rule is not universal, however for in binary cobalt-
nickel alloys the stacking fault energy increases with increasing nickel content (17). Ruff and Ives (51) further support this trend reporting the stacking fault energy of silver-tin alloys to decrease smoothly with increasing tin content. Bell, Roser and Thomas (6) explain the noticed increase in stacking fault energies in copper-zinc alloys above 25 atomic percent zinc as being due to short range ordering since this increase was always accompanied by the appearance of many dislocation pairs (extended dislocations or super dislocations).

The magnitude of the changes in the stacking fault energy vary with the individual alloy system involved. Ruff and Ives (51) demonstrated in silver-tin alloys a nearly linear decrease from 23 ergs/cm² (the value for pure silver) to a value of 4.5 ergs/cm² for a silver alloy containing 7.84 atomic percent tin. Howie and Swann (27) reported for copper-zinc alloys the stacking fault energy decreased from 40 ergs/cm² (the value for pure copper) to approximately 6 ergs/cm² for an alloy containing 36.8 weight percent zinc. These same authors showed for copper-aluminum alloys a decrease to nearly 2 ergs/cm² for an alloy with 8 weight percent aluminum. Howie and Swann (27) presented further data which indicated for silver-zinc and silver-aluminum alloys decreases from 23-25 ergs/cm² (the approximate value for pure silver) to around 2.5 ergs/cm² and 1 erg/cm² for alloys having 20 weight percent zinc and 5 weight percent aluminum respectively.
Work on metals of higher stacking fault energies is less plentiful. Howie and Swann (27) stated the stacking fault energy of nickel-cobalt alloys decreased from 150 ergs/cm² (the value for pure nickel) to around 6 ergs/cm² for an alloy with 69.5 weight percent cobalt. The decrease in the probability of cross-slip for the beryllium alloys is not surprising if the percentage decrease for the beryllium alloys of the present work is of the same order of magnitude as for the nickel-cobalt alloys. This fact is especially meaningful as beryllium is known to possess a high stacking fault energy value (approximately 180 ergs/cm²). The results on the deformation characteristics of a material can be quite marked if the slope of the stacking fault energy versus composition curve is steep in the low solute concentration region.

The concept of the Peierls force (or Peierls-Nabarro force as it is sometimes called) should be mentioned as it relates to the deformation behavior of the beryllium alloys in this study. A dislocation at equilibrium will lie in a symmetrical position relative to its neighbors. As the dislocation is displaced from this equilibrium position, a force is experienced by the dislocation tending to oppose its motion. This force arises because of the non-symmetrical strain field experienced by the atoms in the slip plane. The force necessary to drive a dislocation through a lattice depends then on this unsymmetrical configuration produced by slip (or glide). Beryllium is known to exhibit slip on both basal and prism planes, and, for this reason, the Peierls
force here must be small. The dislocations on these planes are glissile and this observation further suggests a small Peierls force. But a small Peierls force is usually associated with a dissociated glissile dislocation whereas, in beryllium, the dislocations are known to be largely undissociated because of the high stacking fault energy. The dislocations do dissociate slightly, approximately 2 to 4 angstroms (20, p. 54), and this may account for the above discrepancy. The fact that dislocations cross slip from the basal plane to the prism plane may indicate a Peierls force increasing more rapidly with deformation on the basal plane than on the prism plane. When the basal plane value overtakes that of the prism plane, cross-slip can occur onto the prism plane. The fact that probably neither Peierls force value is very large is consistent when the stress levels involved are considered. A satisfactory theory relating the stacking fault energy to the Peierls force (with dislocation behavior as the common element) would be invaluable in examining this problem. Again, the unextended nature of the dislocations observed in beryllium suggests small Peierls forces on both basal and prism planes. The degree to which the stacking fault energy is lowered by the alloy additions will determine the amount of dislocation extension and hence, the expected increase in the Peierls force.

The segregation of solute atoms to the extended dislocations is not expected to any large degree for reasons similar to those mentioned above. The
dislocations are largely unextended and the width of the stacking fault is small. The heterogeneous distribution of solute atoms around a dislocation is a type of chemical interaction with the dislocation often referred to as Suzuki locking. This phenomenon is not to be expected in pure beryllium; and, its occurrence in the alloys must be strongly related to the degree to which the stacking fault energy is lowered by the alloying additions. A sufficient decrease in the stacking fault energy could extend the partial dislocations enough so that this effect would become significant.

Highly irregularly shaped twins associated with the beryllium-titanium alloys were observed during this investigation. The odd-shaped twins have been given previously in Figures 26-A, 26-B, 26-C and 26-D. It appears quite possible the shape of these twins is a result of some type of interaction between the twins themselves and particles or obstacles in the matrix. Inherent in this reasoning is the assumption that the twins are nucleated as normal twins and their disfigurement occurs during their motion.

Twin nucleation in hexagonal metals is known to require high stresses while subsequent twin growth occurs somewhat more easily (20). Etch pit and thin film observations have shown, in both metallic and non-metallic crystals, lattice defects are generated during repeated twin growth and contraction (49). Partridge (42) has suggested that lattice imperfections in the form of microtwins can be generated in the path of a moving twin boundary if
local lattice strains cause the twin boundary to become incoherent. Other types of lattice imperfections might result from prior surface oxidation. Partridge's work on magnesium showed small secondary twins associated with oxide particles; the present work observed these same type small secondary twins emanating from metallic Be$_{12}$Ti second phase particles as given in Figure 23. The traces of these secondary twins (i.e. microtwins) arise from the pinning of the moving twin boundary by the second phase particles. The pinning points produce incoherent boundary regions which subsequently become embedded in the growing twin as a constriction. It is an acceptable way for a twin encountering local lattice distortion to relieve the strain; namely, by producing a local displacement along its boundary. Another possibility is that the markings observed in the beryllium-titanium twins were due to small regions of the matrix that had not twinned with the rest of the band. The effect would be expected to be most prevalent with a large amount of strain.

Partridge and Roberts showed in a supporting investigation (43), that in zinc and magnesium local stresses (induced with a micro-hardness indenter) caused extremely incoherent twin boundary regions. And they further state after indentation large internal stresses remain and these residual stresses can be large enough to cause local bowing (curving) of subsequently formed twins. The results of Partridge (42) and Partridge and Roberts (43)
and the present work tie in with observations made by Katz and Greenspan (31) while studying the recrystallization of various grades of beryllium. They reported twins suffering rather severe constrictions resulting from some type of precipitate interaction after passing through a network of MBe_{13} type precipitate particles. M here stands for any metallic element. The constricted twins which Partridge observed in magnesium were (10\,\overline{1}1) twins and not (10\,\overline{1}2) twins found in beryllium. Magnesium is known to twin on both these planes. This fact, coupled with the twinning shear considerations brought out in a subsequent paragraph, could suggest twinning on planes different than \{10\,\overline{1}2\}. They point out this type of constriction inhibits the twinning mode of deformation and can thus be regarded as a strengthening mechanism. This explains the higher yield strength values obtained for the alloys in this present work.

Damiano et. al. (3, p. 259) have reported the existence of (10\,\overline{1}1) twins in a beryllium-4.37 weight percent copper crystal deformed in c-axis compression. The stress levels to attain this pyramidal twinning were quite high, of the order of 198,000 psi at 200° C. It is suggested that the beryllium-titanium alloys twin on a plane other than (10\,\overline{1}2), quite likely (10\,\overline{1}1), (11\overline{2}1) or (11\overline{2}2), at much lower stress levels than those observed for the beryllium-copper alloys. Whether this new and lower stress level (110,000 psi maximum) is sufficient to improve the ductility of polycrystalline beryllium alloys must be further verified experimentally.
The above explanation could account for the constrictions and kinks along the length of the twins in the beryllium-titanium specimens. What still remains to be explained is the extremely narrow nature of the twins in the system. Generally, the formation of a deformation twin can be divided into three stages: nucleation of a thin lamella, propagation of this lamella parallel to its long dimension and thickening parallel to its short dimension. The first two of these stages appear to have occurred normally. The stress required for nucleation is usually considerably more than that required for propagation; hence, once a twin nucleates in a uniformly stressed specimen it propagates at high speed. The high stress which was necessary for nucleation is further increased locally near the tip of the advancing lamella by the stress concentrating effect of the twin itself. Very little third stage widening type growth has taken place. Cooper and Washburn (13) report the stress required for widening of a twin in hcp zinc exceeded that for nucleation of additional twins. Thus, if any large amount of stress were present in the region of the twin and if this stress were dissipated at a kink or constriction in the twin boundary, the possibility of any further widening of the twin would be precluded. This appears to be the case with the present work. Since the shape of the twin depends on the twinning shear (small shears yield wide twins) the narrow twins in these alloys may be due to large shears. The large shears are known to occur on higher index planes, e.g. \{11\overline{2}1\} and
this suggests twinning on planes other than \(\{10\overline{1}2\}\) in the beryllium-titanium alloys.

Very few twin interactions (in the form of intersecting twins) are found in deformed pure beryllium, while intersecting twins are quite abundant in all the deformed alloy samples. Interactions occurred between the twins when their arrangement was such that one twin blocked the normal growth of the other. These twin interactions were the least abundant in the beryllium-titanium samples. This would suggest the method of relieving the strain energy in these specimens is different from the beryllium-boron and beryllium-manganese alloys.

It can be seen in cases where twin intersections do occur, as shown in Figures 16-A and 16-B and 19-A and 19-B, that if the twins meet along a common surface, their interactions result in the blocked twins being severely kinked in the vicinity of the surface of contact. Roberts and Partridge (50) have observed the same phenomena in \((\overline{1}012)\) and \((10\overline{1}2)\) twins in magnesium and they maintained the kinks producing in the twin bands near the point of intersection relaxed the stresses present by a rotation of the lattice. (This occurs when the axis of this rotation lies along the single direction common to both intersecting twin planes). None of the twin interactions observed by Thornton (58) in hcp copper-germanium as V-shaped traces or zig-zag cross twins were observed in the present experiments. The fact is not too surpris-
ing because the twins observed by Thornton were \(10\overline{1}1\) twins, which are not found in beryllium. He did observe some twin traces associated with local heavy basal slip lines and also some groups of parallel twin traces having no clear association with basal slip. The latter two categories bear definite resemblance to some of the deformation twins seen in the beryllium-titanium alloy shown in Figures 26-A, 26-B, 26-C, 26-D and 27. Thornton (57) has reported on some pyramidal \(10\overline{1}1\) twins in an hexagonal phase of copper-germanium which are markedly similar to the curved twins of this work shown in Figure 18.

Since the alloy samples were saturated solid solutions containing even inclusions of a second phase, it is to be expected the alloy samples would be considerably stronger than pure beryllium. This premise is supported by the results in Table VII. DeLuca and Byrne (15) have obtained the same results by adding alpha manganese to several other hcp metals not including beryllium.

Very little offset of the grain boundaries intersected by impinging twins was detected in all the samples (pure beryllium and alloyed) in this study. This is true even in light of the fact that numerous twins were observed close to the grain boundaries. These facts are in conflict with those reported for body-centered cubic niobium by Wasilewski (60), even though body-centered cubic metals generally have high stacking fault energies as does beryllium. There has been no reported offset of grain boundaries (in hexagonal metals)
resulting from twins intersecting the grain boundary. There is grain boundary movement in body-centered cubic metals, but apparently not in the hexagonal metals which have equally high stacking fault energies.

The question of whether or not slip precedes mechanical twinning should be raised in regard to the results of this work. Upon examining photographs of samples in which both slip and twinning are present it is immediately noticed that (as in Figures 12-C, 13, 18, 19-B and 26-B) there are adjacent areas on individual samples where one grain will contain both slip lines and deformation twins while a neighboring grain will contain only straight or curved slip lines. The fact some grains contain only slip lines indicates that for both the pure beryllium and for each of the alloy systems studied slip definitely precedes twinning. This finding has not been previously reported for beryllium. No grain was found to consist solely of twins without any slip markings. This observation is not evident in many of the photographs because before taking the photograph the sample was rotated to show maximum contrast between the twin and the matrix and in so doing the slip lines were obliterated. Whether or not slip occurs at a lower stress level than twinning is uncertain. Admittedly the above reasoning is deductive but it is known that in many cubic metals mechanical twinning does occur below a stress for gross slip (7) although it would seem unreasonable not to imagine some sort of intergranular or atomic level slip taking place before this time. These obser-
vations on beryllium and the alloys agree with the results of Bolling and Richman (7) who found evidence for slip prior to, as well as concurrent with, the gross propagation of a twin in body-centered cubic iron-25 atomic percent beryllium single crystals. The problem of deformation in polycrystals is much more complex in hcp metals where deformation must involve slip as well as twinning to cope with compatibility requirements, and, therefore, gross slip must also occur. This is precisely the reason for different states of deformation in different grains of the same samples in this work. Bolling and Richman suggest that for polycrystals the existence of an invariant twinning stress points out that local internal structure, rather than gross slip, is the determinant of twinning. This would certainly be the case if a second phase were present in the alloy. However, for a single phase alloy it seems this would not necessarily be true. An assumption that twin boundaries of near minimum energy should form on planes of comparable stacking fault energy would be required. If the stacking fault energy were too high the local internal structure might not be the determining factor for twinning. Temperature would also be an important variable here.

Worthington and Smith (67), report in polycrystalline three percent silicon iron at -196° C, slip occurs before twinning and, perhaps more importantly, that twinning arises as a result of slip. They attribute their finding to an appreciable difference between the stresses necessary for twinning
in fine and coarse grained material because the grain boundaries will act as barriers to the slip processes. They do not explain why slip causes a twin to form, instead of the stress concentration being relieved by slip in a neighboring grain. Orientation effects undoubtedly play a large role. It is interesting to note the predictions of Worthington and Smith (67) have for the most part been verified experimentally by Kossowsky (33) in beryllium binary alloys.

Altshuler and Christian (1) indicated pure iron twins are not nucleated, even in the work hardened state, until the stress reaches a value characteristic of deformation by slip. The characteristic stress value for single crystals is noticeably higher than for polycrystals and, Altshuler and Christian attribute this to twins being nucleated in grain boundary regions where stress concentrations give appreciable local flow, whereas in single crystals there is normally little dislocation motion below the yield stress. A possible interpretation of the results of this study and those of Altshuler and Christian is that twins are formed only when appreciable numbers of dislocations begin to move. Then, even in the work hardened state, the local stress reaches the macroscopic flow stress before twins can form. Once the local flow stress is reached, further deformation takes place by slip if the dislocation velocity is sufficiently low (this will be a function of many variables, i.e. prior dislocation density, strain rate, temperature, etc.), but above some critical
velocity twins will be nucleated. The heart of this matter is whether or not nucleation is the critical stage in the twinning process. If it is, the question then is one of the ready availability of suitable nuclei.

Due to the existence of inevitable stress concentrations it would not have been significant to measure the stress levels at which twins formed in the polycrystals used in this study.

The alloys in the beryllium-boron system, after plastic deformation, displayed large amounts of what must now be called microcracks and not wavy slip lines as first reported by Kaufmann, Gordon and Lillie (32, p. 386). The samples were electrolytically polished to remove all the gross surface damage introduced during cutting and mechanically polishing the specimen. Electropolishing was continued until microscopic examination indicated neither slip lines nor twins to be present on the surface. The same sample was then deformed (strained) a predetermined amount. Microscopic examination then denoted the locations and amounts of slip lines and twins present. This process was aided greatly by the rectangular parallelepiped shape of the test specimens. These specimens were polished again electrolytically until all the slip lines and twins were removed. The fact that the twin bands were also removed indicates that polishing took place more than just superficially on the surface. Further electropolishing was continued to hopefully remove the wavy slip lines mentioned by Kaufmann et. al. After a polishing time
sufficient to remove several hundred atomic layers (approximately fifteen minutes), the markings as shown in Figure 17 still remained. The author was then forced to conclude these markings to be microcracks and not wavy slip lines. Although the results of Kaufmann and co-workers are somewhat dated (1950), and much work has been done on beryllium and its alloys since that time, this fact apparently has never been reported. Perhaps some of the newer theories of cleavage, fracture and crack propagation (57, 67, 54, 55) could be applied to this presence of microcracks in beryllium alloys and in so doing shed further light on the ductility problem.

Numerous twins were observed close to the grain boundaries in all the samples deformed and examined in this study. Although grain boundary areas are known to be regions of high energy, it is difficult to reason deductively whether the twins emanated from the grain boundary or from some possible stress concentration within the grain itself. The apparent tendency for twin-induced microcrack formation is in good agreement with previous reports on molybdenum, tungsten and chromium (23). Gilbert et. al. (23) argue that fracture is initiated as grain boundary cracks rather than as cleavage cracks. They indicate these grain boundary cracks can be slip-induced (as in chromium), in which case propagation can then occur either intergranularly or transgranularly, or cracking can occur by the intersection of twins with grain boundaries (as in chromium, molybdenum and tungsten) where
in this instance the actual cracking is intercrystalline. Although the beryllium-boron alloy was strained plastically approximately four percent, no actual catastrophic failure or fracture occurred. The limit of the compression machine was attained before this could happen. The experiments were done in compression and it is doubtful whether the cracks present could have propagated to failure or not.

Judging from the results of Figure 17, it appears that although the microcracks may have nucleated at the grain boundaries, they do not propagate along the grain boundaries but rather directly into the grain. It is reasonable to deduce that seeking a minimum energy state the cracks would nucleate at the grain boundaries and move out into the grain where because of the anisotropy present the strain energy would be less. The same reasoning might be applied to twin nucleation and propagation and, if so, would explain why no grain boundary offset was observed. The nearly parallel microcracks seen in Figure 17 indicate that cracking was taking place along certain crystallographic planes — a hint that perhaps failure might occur through some form of cleavage rather than cracking. The cleavage though would have to be twin-induced rather than slip-induced because of the locally heavily twinned areas in the vicinity of the microcracks. Hull (29) has made observations of twin/twin intersections and twin/grain boundary intersections giving rise to cleavage cracking in body-centered cubic silicon-iron. He makes a
significant observation in that of the cleavage cracks nucleated at the inter-
sections of twins themselves and twins with grain boundaries, only those
intersections involving twins on a plane normal to the applied stress pro-
duced cracks. If the specimens in this study could have been strained to
failure, it would have been very informative to note if cracking was trans-
granular or intergranular and to observe the exact relation of the twins and
twin boundaries to the fracture cracks.

Wasilewski (60) reports that perhaps no real general cause-and-effect
relationship exists between twins and crack formation in metals. Without
actually intending to do so, he may have provided some starting points for
future research along these lines by reasoning that the tendency for micro-
crack formation appears to be related to the position of the element in the
periodic table, and hence, possibly to the stacking fault energy. Elements
with half-filled bands in the free atom can be expected to form symmetrical
bonds, and thus to possess high stacking fault energy because of the bond
distortion. The introduction of additional electrons such as by alloying could
promote extensive twinning, with a large increase in ductility, because as
Hull (29) points out, appreciable plastic deformation can occur by twinning.
SUMMARY

The objective of this work was to develop some relatively ductile form of beryllium by means of solid solution alloying rather than by the often attempted various purification methods. Reasoning if certain elements would have some solid solubility in beryllium, the c/a ratio of beryllium (1.567) could be significantly altered so that new or different slip systems could be initiated and they would tend to increase the ductility of beryllium. Using such criteria as atomic size, melting point, crystal structure and density, boron, manganese and titanium were selected for addition to beryllium.

The three elements were added to electrolytic flake beryllium in compositions of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 atomic percentages. All alloys were non-consuming arc melted, machined and sectioned. Specimens for wet chemical, spectrographic, X-ray diffraction and metallographic analysis as well as for mechanical (compression) testing were produced.

X-ray diffraction and metallographic analysis showed all alloy samples in each respective alloy system exceeded the solubility limits of that particular system. Second phases, namely Be_{4-5}B, Be_{8}Mn and Be_{12}Ti were evident and detectable in their own respective systems. Solid solution amounts were negligible and this fact made determination of significant changes in the c/a ratio impossible, even for the most dilute alloys. Evidence for a eutectic or peritectic reaction was found in the beryllium-boron alloys. The eutectic composition in the beryllium-manganese system was established at very
nearly 22.0 weight percent manganese. Diffractometer scans of some beryllium-titanium samples indicated small but definite peaks which were unable to be indexed on the basis of known oxide, carbide or nitride structures. Be<sub>17</sub>Ti<sub>2</sub> peaks were also detected in this system. Dendrites were prominent in both the boron and manganese specimens, but not present at all in the titanium samples.

Mechanical compression testing for the Be/0.5B, Be/1.0Mn and Be/0.5Ti samples gave yield strengths of 47,200 psi, 56,500 psi and 81,250 psi respectively. These same specimens yielded work hardening rates of 1.07 x 10<sup>6</sup> psi, 1.3 x 10<sup>6</sup> psi and 1.52 x 10<sup>6</sup> psi respectively. Only the values of the beryllium-titanium alloy appear significantly higher than the values for these same properties quoted for pure beryllium.

All the samples displayed interesting characteristics in their slip and twinning behavior. Twins in pure beryllium are long and wide and the slip lines are straight at small amounts of deformation. Much cross slip is evident at large strains. No twin constriction along the body of the twin is seen in pure beryllium.

Long wide or short narrow twins are found in the beryllium-boron samples. Cross-slip is almost negligible but large amounts of microcracks are found in these specimens, not wavy slip lines (as previously reported).
Generally, the shorter and narrower twins characterize the beryllium-manganese system. Slip lines, cross-slip and microcracks are detectable only in minor amounts. The size of the twins in these samples is the smallest observed in this study but the relative amount (in the form of actual area twinned) of twinning is the greatest of the three systems investigated.

The small twins in the beryllium-titanium system are seen to emanate from the particles of second phase, Be$_{12}$Ti. But these small twins constitute only a small percentage of the total twinning in this system. The majority of the twins are long and narrow and are seen to be constricted internally along the length of the twin. These constrictions have been ascribed to a strain relief process, possibly at a second phase particle, which further prevented the twin from growing parallel to its shorter dimension.

The almost total absence of cross-slip in the three alloy systems has been attributed to a lessening of the stacking fault energy as a result of increasing the solute concentration. This decrease in the probability for cross-slip makes any extensive deformation more difficult and explains the higher yield strengths and work hardening rates.

Evidence is presented which suggests slip occurs prior to the gross propagation of twins.

Considerations of the twinning shear and of the twin shapes in the beryllium-titanium specimens give evidence which suggests twinning in these alloys on planes other than {1012}, perhaps higher order {1121} and {1122} planes.
SUGGESTIONS FOR FUTURE WORK

The author is still convinced after completing this research project of the potential industrial and commercial feasibility of ductile beryllium alloys. The word "ductile" again must be understood here as being used in a limited context. Unalloyed beryllium can never be ductile in the same sense as copper, aluminum or mild steel. It and alloyed beryllium should be capable of improvements which render them at least fabricable into less intricate shapes and forms. The term "workable" might be more exact than use of the word "ductile" in this context.

There are many preliminary problems which must be solved before the fabrication state is reached. Single crystal and polycrystalline studies are the two major obvious divisions here. In the single crystal realm, beryllium of the highest purity possible should be used as the starting material. Some of the electron beam — melted twelve pass zone — refined beryllium presently available is a step in this direction. When material of this type is available, say with a total impurity level of 50 ppm or perhaps 100 ppm or less, then instead of testing this material outright to determine its mechanical properties, efforts should be directed toward ascertaining the role of certain impurities in this high purity single crystal material. Hydrogen, nitrogen, oxygen, carbon and silicon (and perhaps sulphur and chlorine) should receive major emphasis. Some sort of doping scheme would
have to be employed here to keep the impurity concentration isotropic, if this is possible.

The limits of solid solubility for the various metallic elements in high purity beryllium need to be more adequately established. Some elements copper, nickel, silver and palladium for instance, do dissolve fairly extensively in beryllium and their respective phase fields are known. But there are many other elements for which this information is lacking. The effects of these various elements on the c/a ratio of pure and alloyed beryllium is another problem area. Unfortunately, many of these elements are insoluble in beryllium to the point where present techniques of X-ray diffraction, metallography, electron microprobe analysis, etc. are not sufficiently sophisticated to yield this information. The influence of other elements in the band structure of beryllium and the relation between band structure and the stacking fault energy need to be determined. Adding or removing electrons by alloying could significantly affect the electronic bond symmetry (or distortion), in a metal or alloy. Once this information is obtained, a more adequate appraisal of the problem can be made. Then and only then can meaningful mechanical property data be collected and analyzed.

Polycrystalline material may be looked at after the single crystal data has been gathered. The approach here should be the same. Starting with the ultra high purity beryllium mentioned above, the role of grain boundaries
should be studied in the pure metal. The role of the five major nonmetallic impurity elements (hydrogen, nitrogen, oxygen, carbon and silicon) should be investigated as they relate directly to the grain boundary. Do they migrate to it or remain in solution, etc.? Then materials which were found from the single crystal studies to enter into solid solution could be alloyed with the high purity beryllium (without any other impurities present) for further testing.

The important aspect to use as a guideline is to be systematic and orderly and to have each subsequent step be governed and directed by the results of the preceding step in the investigation. These suggestions involve much exhaustive research work but this work needs to be done before the precise role and capabilities of pure and alloyed beryllium can be pinpointed.


45. Pereslegin, V. A. Alloys of magnesium with beryllium. Metal-
46. Raine, T. and J. A. Robinson. The corrosion of beryllium and
    alloys of beryllium with calcium in carbon dioxide. Journal of
47. Ranzetta, G. V. T. and V. D. Scott. An electronprobe microanalysis
    investigation into the effect of heat treatment on the metallographic
    structure of beryllium and some dilute beryllium alloys. Aldermaston
    ment. AWRE-O-14/63)
48. Raynor, G. V. Beryllium, beryllium alloys and theoretical prin-
    ciples affecting alloy formation with beryllium. Journal of the Royal
49. Reed-Hill, R. E., J. P. Hirth and H. C. Rogers. (eds.). Deform-
50. Roberts, E. and P. G. Partridge. The accommodation around(10\bar{1}2)
    \langle10\bar{1}1\rangle twins in magnesium. Acta Metallurgica 14:513-527. 1966.
51. Ruff, A. W., Jr. and L. K. Ives. Dislocation node determinations of
    the stacking fault energy in silver-tin alloys. Acta Metallurgica
52. Sawyer, C. B. Beryllium as a light metal compound. Metals and
53. Sloman, H. A. Researches on beryllium. Journal of the Institute of
54. Smith, E. The formation of a cleavage crack in a crystalline solid.
55. Smith, E. The formation of a cleavage crack in a crystalline solid.
56. Teitel, R. J. and M. Cohen. The beryllium-iron system. Transac-
    tions of the American Institute of Mining and Metallurgical Engineers


