THE ZIRCONIUM-SILVER SYSTEM

by

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THE ZIRCONIUM-SILVER SYSTEM

Introduction

Objectives. Before the full potentialities of a combination of two metals may be realized and an efficient commercial application made of the combination it is necessary to have a knowledge of the nature of the alloy system. This would include the physical and mechanical properties, methods of production and fabrication, and the equilibrium diagram for the system which describes the temperature and composition ranges for phases resulting from the combination. The nature of the study required to determine the equilibrium diagram is such that many of the characteristics of the alloys are brought to light, and in an alloy development program this feature is usually the first topic for investigation.

Aside from the commercial aspect of these studies, the information gained is added to the volume of experimental data that forms the groundwork for a clearer understanding of alloy systems in general.

Relatively little is known concerning the alloys of zirconium and silver and the major portion of the investigations have been confined to alloys of high silver content. This investigation was undertaken with the purpose of preparing alloys in the zirconium-rich portion of the system, determining the phase relationships present, and
presenting a tentative equilibrium diagram, that in combination with previous work, would provide a more complete understanding of the alloys of these two metals.

**Previous Work.** Difficulties have been encountered in successfully alloying silver and zirconium for several reasons. A large difference in melting points exists, pure silver melting at 960.5 °C and zirconium at 1860 °C. Coupled with this, silver has an appreciable vapor pressure even in the solid state and this increases rapidly as the temperature is increased above the melting point. This results in evaporation of silver before alloying can take place. Zirconium has a strong affinity for oxygen and nitrogen at elevated temperatures making it necessary to use vacuum techniques or protective, inert atmospheres, and in addition, the metal reacts with all known crucible materials producing serious contamination.

Investigations carried out on the alloys of silver and zirconium prior to 1940 were reviewed by Addicks (1, p.122). Marden and Rich (9, p.105) in 1921 prepared an alloy containing between 10 and 20 per cent silver and remarked that upon treatment with acids, the alloy yielded finely divided crystals. This might be interpreted as an intermetallic compound. deBoer (5, p.1256) was unable to prepare alloys and stated that zirconium does not dissolve in molten silver.
Sykes and Allibone (11, pp.179-189) were able to prepare alloys containing 0 to 30 per cent zirconium by heating a mixture of powdered zirconium and fine silver in vacuo in a high-frequency induction furnace. They found that alloying took place readily when the silver was molten, but the rate of solution was very slow when massive zirconium was used. The alloys were made in 10 to 30 gram charges placed in alumina crucibles and it was reported that a high percentage of the alloys were unsatisfactory owing to crucible contamination. The zirconium used contained 0.2 per cent hafnium and a small amount of oxygen but no figures were given for the oxygen content. Microscopic examination indicated that an intermetallic compound was formed, probably containing more than 30 per cent zirconium. The solid solubility of the compound in silver was very slight and not appreciably affected by temperature. The crystals of the compound were imbedded in a silver-rich matrix, but no eutectic structure was evident. The same authors also reported that uniform alloys could not be prepared by heating in a molybdenum furnace operated in cracked ammonia because the silver distilled before solution of the zirconium could take place.

Raub and Engel (10, pp.172-177) made an extensive study of the silver-rich portion of the system using thermoanalysis, x-ray, and microscopic examinations. The
results indicated very slight solubility of zirconium in silver, probably less than 0.1 per cent at the eutectic temperature. A eutectic reaction was observed at 2.5 per cent zirconium and 955 °C, just a few degrees below the melting point of pure silver. They also observed an intermetallic compound at higher zirconium concentrations and placed its composition at 45.8 per cent zirconium, corresponding to AgZr. This was determined by partial decomposition of the alloy by treatment with potassium nitrate. The silver present dissolved, leaving a residue consisting essentially of the compound. An extensive separation was also obtained by treatment in a potassium cyanide solution in an electrolytic cell. The residue was analyzed and varied from 46 to 50 per cent zirconium, which is close to the AgZr composition. Thermoanalysis indicated the melting point in this region was 1135 °C. The authors remarked that a reaction of zirconium with the crucible material continually occurred during melting and strong concentrations of this reaction product were present. An equilibrium diagram for the silver-rich portion of the system was proposed and is shown in figure 1.

During a preliminary survey of zirconium alloys the U.S. Bureau of Mines (2, pp.36-37) prepared several alloys with low silver content. These were melted in a graphite-resistor furnace and contained 0.10 to 0.20 per cent carbon, picked up from the carbon crucible. The cast structure of
Figure 1. Silver-zirconium equilibrium diagram (10, p174)
alloys to 7.74 per cent silver appeared to be single phase solid solution with a Widmanstätten pattern of acicular needles, typical of zirconium alloys quenched or rapidly cooled from the high-temperature solid solution region. Difficulty was encountered in producing uniform alloys by this method. No other direct information is available concerning the zirconium-silver alloys.

**Principles of Alloying.** With few exceptions, metals are soluble in each other when in the molten state. When this molten solution is cooled the resulting solid alloy may have vastly different properties and structure than the components making up the alloy. Considerable work has been done attempting to correlate the physical constants of the individual components with the structure resulting from a combination of the components in a binary alloy. This knowledge enables us to predict to a limited extent the type of structure or equilibrium diagram to be expected from a combination of given elements.

Several factors influencing the structure type have been proposed by Hume-Rothery (8, p.20) and are in general use. (4, pp.138-152)(3, pp.139-146).

The two metals may remain in solution when cooled from the molten state, resulting in a solid solution. Two types of solid solution are possible. In the substitutional type, solute atoms replace solvent atoms in the crystal lattice of the solvent; in the interstitial type,
solute atoms fit in spaces between the normal lattice sites of the solvent.

For the interstitial type to form, the solute atom must be small compared with that of the solvent. For this type of solution the atomic diameter of the solute is generally less than 59 per cent of that of the solvent atom.

If the atomic diameters of the solute and solvent atoms differ by more than 14 to 15 per cent, the tendency to form substitutional solid solutions is restricted, and for extensive solid solubility the diameter of the solute atom should be within 8 per cent of that of the solvent. When the atomic diameters are nearly equal the size factor is favorable for extended solubility, but this will be influenced by other factors.

Each metallic element forms in a specific type of lattice structure or crystal form, several elements having allotropic forms, and therefore, more than one crystal form, depending upon the temperature and pressure. Alloys of metals with the same crystal form are more apt to produce extended solubility than alloys of metals with different crystal forms. This is termed the structure factor or frequently the geometrical factor.

If other factors are equal, a metal of lower valency is more likely to dissolve one of higher valency than vice versa, termed the relative valency effect.
If a strongly electropositive element is alloyed with an electronegative element, the tendency is to form compounds, restricting the solubility range. As the difference in electrochemical position becomes greater, the tendency to form compounds is more pronounced and the compounds formed are more stable. To be favorable for extensive solution ranges the two elements must then have nearly the same periodic grouping, or position in Mendeleev's Periodic Table, both horizontally and vertically.

When the valency electron concentration is used as the basis for alloy composition rather than weight percent of solute element, significant effects are noted. The solubility limits of different systems are roughly the same when this basis is used, approaching a maximum value of 1.4. For the solubility of a di-valent element in a mono-valent element this rule predicts a maximum solubility of 40 atomic percent and such is the case in the copper-zinc system, for example. It is also noted that over a wide range of alloy systems, the intermetallic compounds formed often occur at specific valency electron concentrations and in most cases the crystal structure of compounds with the same electron concentration are the same. These are often called electron compounds.

For two elements that are very similar and all the factors are favorable for extended solubility, the alloys form a continuous series of solid solutions. Such is the
case with the systems of silver-gold, silver-palladium, and zirconium-titanium. When one or more of the factors are not favorable, restricted solubility is found, as in the case of silver-copper, where the other factors are favorable for extended solubility but the atomic diameters differ by more than 8 per cent.

When applying these generalizations it is very helpful to consider known alloy systems with analogous situations. Zirconium and titanium are very similar elements and the alloy system of an element with zirconium will in most cases be similar to the alloy system of that element with titanium.

**TABLE I**

**PHYSICAL CONSTANTS OF ZIRCONIUM AND SILVER**

<table>
<thead>
<tr>
<th></th>
<th>Zirconium</th>
<th>Silver</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>40</td>
<td>47</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>91.22</td>
<td>107.88</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>6.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Melting point C</td>
<td>1860 ± 10</td>
<td>960.5</td>
</tr>
<tr>
<td>Group in periodic table</td>
<td>4-a</td>
<td>1-b</td>
</tr>
<tr>
<td>Period in table</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Crystal structure (above 862°C)</td>
<td>HCP</td>
<td>FCC</td>
</tr>
<tr>
<td>Lattice dimensions, Å</td>
<td>α = 3.223</td>
<td>4.078</td>
</tr>
<tr>
<td></td>
<td>c = 5.123</td>
<td></td>
</tr>
<tr>
<td></td>
<td>α = 3.61</td>
<td></td>
</tr>
<tr>
<td>Closest atomic approach, Å</td>
<td>α = 3.19-3.166</td>
<td>2.88*</td>
</tr>
<tr>
<td></td>
<td>Q = 3.122*</td>
<td></td>
</tr>
</tbody>
</table>

* Computed from unit cell dimensions.

At room temperature zirconium and silver have different crystal structures and the atomic diameter of
silver differs from that of zirconium by approximately 10 per cent. Zirconium is in group 4-b of the periodic table, in the balance between electropositive and electronegative, while silver is strongly electropositive. These factors would indicate that limited solubility of silver in zirconium is to be expected and that compound formation is probable. Above 862 C zirconium has a body centered cubic structure, somewhat more compatible with the face centered cubic silver, and a more favorable size factor. These factors, in addition to the general tendency for an increase in solubility with increasing temperature would indicate greater solubility in the high temperature zirconium phase.

Few known alloy systems are available for comparison of the zirconium-rich portion. Preliminary investigation of the zirconium-copper alloys (2, p.20) indicates very little solubility of copper in the low temperature zirconium phase, with a eutectoid reaction in the vicinity of 2 per cent copper. An intermediate phase is formed at higher copper content and the work of Raub and Engel (10, p.173) indicates that this is an intermetallic compound with a composition in the vicinity of 33 atomic per cent copper.

The alloy systems of silver with several elements near zirconium in the periodic table have been
investigated but these elements differ from zirconium considerably in characteristics and crystal structure and not enough similarity is present to justify predictions from these systems.

The copper-zirconium and gold-zirconium systems have been investigated to quite high zirconium content (10, p.173). The copper and gold rich portions of these systems are similar as would be expected. An intermetallic compound is formed in each at the compositions Au$_3$Zr and Cu$_3$Zr. It is interesting to note that these correspond to a valency electron concentration of 1.75, one of the specific ratios for intermediate phases observed by Hume-Rothery. From the similarity of copper, gold and silver, an intermetallic compound would be expected in the silver-zirconium system at the same concentration rather than the AgZr reported by Raub and Engel.

Summarizing, for the zirconium-rich portion of the diagram, limited solubility of silver is to be expected with possibly more at temperatures above 862 C. Intermetallic compound formation is probable, and from comparison with the zirconium-copper alloys, in the vicinity of 33 atomic per cent silver. By comparison with the gold-zirconium and copper-zirconium systems, the compound Ag$_3$Zr is to be expected, although previous investigators did not find evidence of this.
EQUIPMENT AND PROCEDURE

Materials. The alloys produced in this work were prepared from 10 mesh, high-grade zirconium sponge and silver pellets. Montana Assay Office silver was used and, although not determined, the purity of this grade is expected to be at least 99.9 per cent. For the preparation of powder compacts, 200 mesh troy silver was used. The zirconium sponge was prepared at the Bureau of Mines laboratories, Albany, Oregon, by the magnesium reduction process and purified by a high temperature vacuum treatment in which additional magnesium chloride is removed. The batches used were chosen for low iron and nitrogen contents. The analyses of these batches are shown in Table II.

TABLE II
ANALYSES OF ZIRCONIUM SPONGE

<table>
<thead>
<tr>
<th>Chemical</th>
<th>YX-862-A</th>
<th>YX-1178-A</th>
<th>YX-702-A</th>
<th>D9-26</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All quantities in parts per million.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
<td>400</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>N</td>
<td>40</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Spectrographic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>&gt;500</td>
<td>&gt;300</td>
<td>&gt;200</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<tr>
<td>Cu</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Pb</td>
<td>50</td>
<td>100</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;500</td>
<td>&lt;300</td>
<td>&lt;200</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Cr</td>
<td>50</td>
<td>2</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
<td>300</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>2</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;60</td>
<td>&lt;20</td>
<td>&lt;60</td>
<td>&lt;60</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.5</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>
In addition to the above impurities the zirconium produced by this method contains an average of 0.08 percent oxygen. This material is of much greater purity than that used in previous investigations of the system.

**Alloying Techniques.** For the study of a binary alloy system the first requisite is to have materials of the highest practicable purity. Of equal importance is the necessity for obtaining alloys of the materials which retain that purity and are homogeneous throughout. The preparation of such alloys from zirconium and silver proved to be the most difficult part of this work. Several methods of alloying were tried, including two arc-melting techniques, melting in a high-frequency induction furnace, and the sintering of compacted powders.

As previously mentioned, care must be taken at elevated temperatures to avoid oxygen contamination of the zirconium so any method of alloy preparation must involve vacuum technique or protective atmospheres. An arc-melting furnace operated in helium that is employed by the physical metallurgy section of the Bureau of Mines for alloy preparation was used to prepare the major portion of the alloys. Details of this furnace are shown in figure 2.

The furnace assembly is made of copper and is jacketed for water cooling to prevent melting. The base of the chamber is provided with four depressions that serve
Figure 2. Arc melting furnace

Figure 3. Burrell high temperature furnace
as molds for the alloy and one central depression holding a zirconium-titanium alloy that is used as a getter. A tungsten tip held in the end of a copper tube is used for the arc. This also is water cooled. The tip assembly enters the furnace through a vacuum tight ball joint that allows positioning of the arc within the furnace. Two sight holes with vacuum sealed windows permit a view of the furnace interior. The furnace chamber is evacuated by a Kinney vacuum pump to a pressure of 3 to 10 microns for the first pump-down and then backfilled twice with helium and left with an inert helium atmosphere for melting. Since the helium used is not completely free of oxygen, the arc is struck first on the zirconium-titanium alloy to effectively getter the system. Power for the arc is supplied by a D.C. generator and in operation 250 to 350 amps at 20 to 25 volts are employed.

The materials were weighed for correct alloy proportion, thoroughly mixed and compacted in a 3/4 inch diameter die to 20 tons per sq in. A charge of 25 to 50 grams may be used but in this work all the alloys were made in 50 gram lots. Four of these compacts are placed in the furnace chamber and melted by the moving the arc to each in succession. A layer approximately 1/8 inch thick in contact with the copper base remains chilled while the upper portion of the compact forms a molten pool that is stirred and mixed by moving the arc. It is
necessary to turn the compact and melt the bottom portion but this may be done without opening the furnace. The resulting alloy is in the form of a rounded button, illustrated in figure 4.

A layer type segregation occurred with these alloys that could not be eliminated by mechanical working and homogenization treatments. Also in alloys up to 20 percent silver over half the original silver content was lost by evaporation. With higher silver content the segregation was not as serious and more of the original silver content was retained. Machining the segregated alloys, compacting and remelting improved this condition in some cases. Turning the alloy three times in the furnace and melting also reduced the segregation. A cross section of the cast alloy was examined metallographically, with only those appearing homogeneous used for study of the system.

Another type of arc melting was tried in which the alloy mixture is added in small portions as melting continues. A water chilled copper mold approximately two inches in diameter forms the bottom of the furnace chamber. Ingots of one pound are produced. 100 grams of the alloy mixture is used as a starter for the arc. When this is molten, additional material is fed into the furnace chamber. Only the top portion remains molten and the material being fed in is in the correct alloy
Figure 4. Zirconium-silver alloys
proportion so that a homogeneous mass is built up. Since the chamber must be evacuated and backfilled with helium, means must be provided for feeding the additional material into the sealed chamber to the arc. This is accomplished by connecting another chamber to the furnace and evacuating the entire unit. A plate in this chamber holds a series of small buckets in which portions of the alloy mixture are placed. The buckets may be rotated by an external connection to the chamber. As they turn past a hole in the plate, their contents are dumped into a sloping trough that is vibrated, shaking the mixture into the furnace chamber.

Only one alloy was prepared by this method but it was homogeneous and a smaller portion of the silver was lost by evaporation. The furnace is in continuous use at the Bureau of Mines or more alloys would have been prepared in this way, for it appears to be the most economical of material and segregation is largely eliminated. In addition, the one pound ingot, when rolled to sheet, provides enough material for determination of physical properties as well as alloy studies.

Before the above method of alloying was attempted, two alloys were prepared in a high frequency induction furnace in an attempt to produce a uniform melt. The charge for this furnace is placed in a carbon crucible. The molten alloy is in contact with the carbon so that
carbon pick-up is inevitable. The furnace consists of a two inch diameter quartz tube with the bottom portion filled with 100 mesh graphite powder to act both as insulation and load for the induction coil. A graphite crucible holder is embedded in the powdered graphite and a graphite tube fitted into this for the crucible. The unit is provided with a vacuum head and is evacuated with a VMF-10 Distillation Products oil diffusion pump backed by a Cenco Hypervac mechanical pump. The melting, however, was done in helium rather than vacuum to avoid excessive loss of silver. Power for heating is obtained from induced eddy currents, initiated by a 3 KW Ajax spark-gap generator operated at approximately 50 kilocycles. The eddy currents heating the mass provide a whirling action that insures mixing of the alloy.

The furnace and crucible were degassed at approximately 1600 C under a pressure in the order of 1 micron prior to loading the alloy mixture to remove any vapors absorbed in the graphite. The alloy charge of 25 grams was made of 100 mesh zirconium and silver powders, compacted in a 3/4 inch die. The first of these alloys, 7.5 nominal per cent silver, was heated considerably above the melting temperature by mistake. A film formed over the top and melting was not observed until a higher temperature was reached. This alloy was molten
for approximately three minutes and when analyzed, yielded 5.7 per cent silver and 0.45 per cent carbon. The second alloy, 5.0 nominal per cent silver, was heated to just above the melting point and the power cut, so that it was molten for a shorter time. This alloy yielded 5.7 per cent silver also, and 0.10 per cent carbon. The shorter time in the liquid state prevented additional carbon pick-up and evaporation of silver. Both alloys were completely homogeneous when examined metallographically, the carbon present forming zirconium carbide, that was uniformly dispersed throughout the structure. Uniform alloys could be prepared in this manner if the addition of small amounts of carbon is not objectionable.

Hausner and Kalish (6, p.40)(7, p.625) describe a method for zirconium alloy preparation using powder metallurgy techniques and zirconium hydride powder. Zirconium sponge is extremely pyrophoric and cannot be ground to fine powder without burning. The fine particles present in zirconium sponge are generally of high iron content and are undesirable for alloy work, so it is difficult to obtain high purity zirconium powder. One method of producing fine powder is to heat good quality sponge in a hydrogen atmosphere, forming the brittle compound, zirconium hydride. This is easily ground to fine powder without burning. The hydrogen may be removed by vacuum
For producing alloys by sintering powder compacts it appeared advantageous to use the hydride directly, eliminating the distillation step and the possibility of contamination during that treatment. During sintering the hydrogen would be removed, providing a reducing atmosphere that lowers the vapor pressure of silver. In addition the dissociation of the hydride would provide added mobility to speed up diffusion.

Several alloys were prepared by this method, first forming the hydride and grinding it to pass a 200 mesh screen. This was then mixed with 200 mesh silver powder. The powders were weighed for alloy proportion, thoroughly mixed, and compacted in a 3/4 inch die to 45 tons per sq in pressure. 25 grams of alloy mixture formed a compact 3/4 inches in diameter that was approximately 3/4 inches high. With less than 7 per cent silver the mixture was difficult to form into good compacts at this pressure, for spalling occurred along the edges. With more of the ductile silver powder to act as a lubricant good compacts were obtained. Sintering was done in a Burrell tube furnace, equipped with a vacuum head, Distillation Products oil diffusion pump and a Cenco Megavac mechanical pump. The compacts were placed in a molybdenum boat to prevent contact with the porcelain tube and the system evacuated. It was felt that the compacts might break open if the hydrogen
was removed rapidly so the temperature was raised gradually in the 300 to 700 C range, keeping the pressure below 200 microns, as indicated by a Hastings thermocouple vacuum gage. Sintering was continued for 8 hours at 900 C, below the melting point of silver, and the temperature was then raised to 1000 C for an additional 12 hours. During this period pressure in the order of 1 micron was maintained. The thermocouple gage had been checked previously against an ionization gage for calibration and indicated 1 micron but the hydrogen atmosphere would possibly change its response.

Microscopic examination of these alloys indicated that all the primary silver had diffused into the zirconium but some porosity was evident. The compacts originally 3/4 inches by 3/4 inches had been reduced to 0.65 inches diameter and 0.65 to 0.70 inches in length, with a slight hour glass shape. Two of these were sheathed in iron cylinders and hot rolled to 0.100 inch sheet without breaking up, so the ductility was not seriously impaired.

There is considerable chance for contamination in this method, both in preparing the hydride and in the long sintering process. Also the removal of all the hydrogen is not assured. In addition, investigation would be required to determine the optimum compacting pressures, sintering times and temperatures. Since the
quality of the alloys produced does not warrant this in-
vestigation, the method was discarded in favor of arc
melting.

**Fabrication.** To promote homogeneity, the alloys up
to 7 per cent silver were given a mechanical working
treatment. This was carried out by sealing the alloy
within an iron sheath for hot rolling at 850 °C. The iron
serves as protection against oxidation at the rolling
temperature and does not bond to the alloy, so is easily
removed after rolling. The upper limit of rolling tem-
perature is set by the zirconium-iron eutectic reaction
at 934 °C. The alloys were checked for a low melting con-
stituent or eutectic reaction by heating to 1000 °C before
rolling was attempted to avoid the possibility of melting
during rolling.

No difficulty was experienced during this treatment
and the alloys were reduced to 0.120 inch sheet. The 50
gram arc melted button produced a sheet of this thickness
approximately 4 inches long. Half of one of these sheets
is illustrated in figure 4. No attempt was made to fabri-
cate higher percentage silver alloys, but the increasing
proportion of the brittle intermediate phase above 15 per
cent silver would probably limit the workability of those
alloys. Alloys in the silver-rich portion of the system
are very ductile and no difficulty was encountered in roll-
ing alloys containing up to 10 per cent zirconium.
Chemical Analyses. The analyses reported in this work were determined by the Technical Services Branch, Bureau of Mines. Two to three gram samples were taken of lathe turnings for each alloy. The silver determination was made by dissolving a weighed portion of sample in hydrofluoric acid. Sulfuric acid is added to this solution and the hydrofluoric acid boiled off, leaving a sulfate residue. The residue is again taken into solution with nitric acid and hydrochloric acid added. The silver chloride formed here is insoluble in nitric acid and thus precipitated. This is weighed and the weight percentage of silver computed. The zirconium content in all cases was taken by difference.

Metallographic Studies. Specimens of the alloys were examined as cast, after rolling, and after various heat treatments. These were mounted in bakelite molds and prepared for examination by successively grinding on a 120 grit belt sander, No. 2, No. 1 and No. 0 metallographic emery paper. Further grinding was done on rotary wheels, the first canvas with a 600 grit alundum and water mixture, the second billiard cloth with a 280 grit silicon carbide and water suspension. The final grinding was done on velvet with a soap solution and Linde Air Products powdered alumina.

All the specimens were etched with chemical reagents
and viewed on a Bausch and Lomb Metallograph. The etchants that were found to be satisfactory are listed in Table III.

**TABLE III**

**ZIRCONIUM-SILVER ETCHING REAGENTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 parts hydrofluoric acid 10 parts glycerin</td>
</tr>
<tr>
<td>2</td>
<td>2 parts hydrofluoric acid 8 parts glycerin 1 part nitric acid</td>
</tr>
<tr>
<td>3</td>
<td>1 part hydrofluoric acid 5 parts glycerin 10 parts water</td>
</tr>
<tr>
<td>4</td>
<td>Aqueous solution, 0.2 per cent each Chromic acid Concentrated sulfuric acid</td>
</tr>
</tbody>
</table>

Cast alloys of 15 to 50 per cent silver which stain badly are best etched with No. 1, applied 5 to 10 seconds with a cotton swab. No. 2 was used for low percentage silver alloys in the annealed condition. Alloys quenched from the high temperature solution field are very resistant to chemical attack and 1 to 2 minutes etching time with No. 3 is required. Etchant No. 4 was employed for silver-rich alloys, applied 10 to 20 seconds with a cotton swab.

**Heat Treatment.** The phases present in the alloy system at different temperature levels and varying compositions may be determined by microscopic examination of heat treated specimens. The specimens must be protected during
heating to prevent oxygen and nitrogen contamination.
In this case, heating in helium is preferred, rather than vacuum, to minimize evaporation of silver from the surface.

This was accomplished by sealing the specimens in quartz tubes in a partial pressure of helium. The specimens were placed in a tube sealed at one end, and the tube connected to a vacuum pump. The tube was then evacuated and backfilled with helium three times, and clamped off with a partial vacuum. The section of the tube containing the specimens was sealed off by heating with an oxygen-hydrogen torch, the partial vacuum causing the tube to collapse where heated.

Treatments up to 1000°C were done in electric tube furnaces with nichrome resistance windings. Higher temperature treatments were done in the Burrell high temperature furnace with silicon carbide heating elements shown in figure 3. Temperature control was provided so that soaking periods at constant temperature could be carried out. The temperature at the edge of the quartz tube containing the specimens was checked with a chromel-alumel thermocouple.

Water quenching was accomplished by rapidly pulling the tube from the furnace and breaking it in a container of cold water. The specimens from rolled sheet, approximately 1/4 inch square and 0.120 inches thick, were
sufficiently small so that a drastic quench was obtained throughout the section.

The specimens to be treated were cut to size and flat surfaces ground so that a minimum of grinding was required after treatment. Before sealing in the quartz tube they were washed in acetone and thoroughly dried to insure clean surfaces.

Homogenization treatments, consisting of soaking 60 to 70 hours at 950 to 1000 °C, were done on cast specimens for x-ray analysis in a tube furnace that was evacuated and backfilled with helium. The specimens were packed in a molybdenum boat with a getter of zirconium lathe turnings for further protection.

These treatments satisfactorily protected the alloys from oxidation. No appreciable loss of silver from the edges could be observed when the alloys were examined.

Thermoanalysis. Differential heating and cooling curves were employed to establish the temperature of the eutectoid reaction. A nickel neutral body and an alloy specimen were heated simultaneously with a differential thermocouple employed to measure the temperature difference between the specimen and the neutral body. Nickel is used for the neutral body for no phase transformations are exhibited until it reaches its melting point.

Upon heating, either no temperature difference or a
Figure 5. Thermoanalysis unit

Figure 6. Thermoanalysis specimens with stand
small constant difference is present between the nickel body and the specimen until a phase change occurs in the alloy specimen. Since heat is required to effect this transformation, the specimen temperature remains constant for a short period while the nickel continues to rise in temperature. This difference is indicated by the differential thermocouple until the phase change is completed and equilibrium again established between the nickel and the specimen. The temperatures at which changes occur are indicated by the specimen thermocouple. Upon cooling the reverse occurs, and heat is given up by the specimen during the phase change. A change in temperature difference is again observed until equilibrium is established.

The unit used for this work is illustrated in figure 5. The electric furnace used for heating the specimens may be raised or lowered over the porcelain tube that forms the heating chamber. The specimen and neutral body are supported in the tube by a quartz stand shown in figure 6. The thermocouple leads are taken out through the bottom plate of the chamber with vacuum tight compression joints. The chamber is connected to a Cenco Hyvac vacuum pump and in use was evacuated to a pressure of 1 micron, indicated by a Hastings thermocouple gage, before filling with helium.

Chromel-alumel thermocouple wire was used with the cold junction maintained at 0°C in an ice bottle. Copper
wire was used from the cold junction to the measuring instrument with each thermocouple wire wrapped around its copper lead and inserted in a glass tube containing a mercury pool. These tubes were kept in the ice bottle for constant cold junction temperature.

A Leeds and Northrup X-Y recorder, shown on the left of Figure 5, was used for plotting specimen temperature on the X axis and the temperature difference on the Y axis. As the thermocouple emf from the specimen is fed into the potentiometer circuit of the instrument, the balancing mechanism moves the recorder pen in the X direction. The differential emf is put through a converter and controls a motor that drives the chart in the Y direction. The internal resistors of the instrument are adjusted so that 1 inch on the X axis is equivalent to 1 millivolt emf, with a full scale deflection of 10 millivolts or approximately 250°C. One inch of Y deflection is equivalent to 0.1 millivolt or approximately 2.5°C. Since the full scale deflection of the X axis does not cover the temperature range to be investigated it is necessary to use an external potentiometer in the specimen temperature thermocouple circuit. This was connected in parallel with the thermocouple leads. When the temperature of the specimen produced 10 millivolts, and the recorder was at the end of its travel, 10 millivolts unbalance were set on this potentiometer, bringing the
recorder back to the zero position.

The furnace temperature was controlled by the Wheel-co Capacitrol rate controller shown in the center of figure 5. Various heating and cooling rates may be applied to the specimen by use of this controller that employs a clock driven cam to move the temperature set point at a uniform rate. The cams are cut individually for any desired heating, soaking, or cooling cycle and are interchangeable. A chromel alumel thermocouple located near the heating elements of the furnace is used for the sensing element. The controller is of the proportioning type so that practically point control is obtained with no cycling about the set point. Thermal capacity of the furnace further damps oscillation so that the specimens within the tube experience the uniform rate of heating or cooling necessary for use with the sensitive differential thermocouple.

The nickel neutral body used was a cylinder of "A" nickel, 0.25 inches in diameter and 0.475 inches long, weighing 3.151 grams. A hole 1/4 inch deep and large enough to hold the thermocouple bead snugly was drilled in one end. The specimens of cast material were machined to cylinders approximately the same size and also drilled for inserting the thermocouple bead. Specimens of rolled material were made of three plates tightly wired together to form a block of material approximately the same size as
Figure 7. North American Phillips x-ray unit
the nickel body, with the center plate drilled to hold the thermocouple bead.

The eutectoid composition was determined metallographically. Three separate alloys near this composition were investigated to determine the temperature of the reaction. No attempt was made to determine the temperature limits of the two phase regions on either side of the eutectoid by thermoanalysis, for the heat effect of the eutectoid reaction alone was very small.

X-ray Analysis. X-ray diffraction data were used to verify the phases observed by metallographic examination of the system and to determine the composition of the intermetallic compound in the zirconium-rich portion of the diagram. Diffraction patterns were obtained on the North American Phillips unit illustrated in figure 7.

With this unit a monochromatic x-ray beam is obtained by operating the x-ray tube at high enough potential to excite the characteristic spectra of the target material. A filter material is used to cut off all but the Kα radiation. A copper target and nickel filter were used for these alloys.

The specimen is held in a goniometer head and rotated at a constant rate, so that the angle the x-ray beam strikes the specimen is constantly increased. A Geiger-Mueller counter pickup is also attached to the
goniometer head, but rotates at twice the rate of the specimen. When an angle is reached where one set of crystal planes within the metal are oriented so that reinforcing reflection can occur, the intensity of that diffracted beam is measured by the counter pickup. That angle is precisely measured on the goniometer head. At separate angles, different crystal planes will exhibit this reflection at varying intensities, depending on the atomic population of the plane.

A chart is provided and the angular movement of the counter pickup is continually recorded. The radiation pulses picked up by the counter are electronically integrated to give the total intensity at that angle, which is also recorded. When an angle is reached where reflection occurs, the peak intensity is plotted, giving a record of diffraction angles versus intensity. From the chart the crystal planes belonging to one phase may be separated and the phases present identified.

Cast specimens that had been given a homogenization treatment were used for this analysis. After treatment they were mounted in bakelite and examined on the metallograph so that the results of the two methods could be correlated. It was impossible to powder this material so these mounted specimens were deeply etched to remove the effects of polishing and the flat surface used for the x-ray specimen.
RESULTS AND DISCUSSION

Alloys. The alloys used for investigation of the system were all prepared by arc melting in the 50 gram "button" furnace, with the exception of a 7 per cent alloy which was arc melted in the one pound ingot furnace. The compositions of the alloys used are shown in Table IV. Alloys other than those shown were prepared, but were discarded due to segregation. In cases where the analysis appeared doubtful additional samples were taken, as indicated by more than one analysis in Table IV.

TABLE IV

COMPOSITION OF ZIRCONIUM-SILVER ALLOYS

<table>
<thead>
<tr>
<th>Alloy number</th>
<th>Per cent silver nominal</th>
<th>determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA 3000</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>WA 3001</td>
<td>2.0</td>
<td>0.4</td>
</tr>
<tr>
<td>WA 3002</td>
<td>3.0</td>
<td>0.7</td>
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<tr>
<td>WA 3003</td>
<td>4.0</td>
<td>2.1</td>
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<td>WA 3004</td>
<td>5.0</td>
<td>1.5</td>
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<tr>
<td>WA 3005</td>
<td>7.5</td>
<td>3.0</td>
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<tr>
<td>WA 3006</td>
<td>10.0</td>
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<td>WA 3481</td>
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<td>WA 3482</td>
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<tr>
<td>WA 3483</td>
<td>12.0</td>
<td>3.6</td>
</tr>
<tr>
<td>WA 3484</td>
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<td>WA 3485</td>
<td>15.0</td>
<td>6.0</td>
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<tr>
<td>WA 3486</td>
<td>20.0</td>
<td>13.9</td>
</tr>
<tr>
<td>WA 3487</td>
<td>30.0</td>
<td>26.3</td>
</tr>
<tr>
<td>SA 3191</td>
<td>40.0</td>
<td>33.9, 34.3</td>
</tr>
<tr>
<td>WA 3099</td>
<td>40.0</td>
<td>28.7, 28.6</td>
</tr>
<tr>
<td>WA 3100</td>
<td>50.0</td>
<td>45.8</td>
</tr>
<tr>
<td>WA 3101</td>
<td>90.0</td>
<td>--</td>
</tr>
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</table>
A considerable portion of the silver in alloys up to 15 per cent silver was lost during melting. Part of this was a result of remelting, done to improve the homogeneity, but the largest loss no doubt occurred during the first melting while the silver was in the uncombined state. With higher percentage silver the loss of silver was not as serious and most of the alloys were uniform. This was probably due to the lowering of the melting point in this region.

Arc melting in the one pound ingot furnace appears to be the most feasible means of preparing these alloys from the standpoint of both economy of silver and homogeneity. This is illustrated by comparison of alloy SA 3191 with two other alloys of 10 per cent nominal silver prepared in the "button" furnace. Of these, WA 3006 was turned only once in the furnace and WA 3085 turned three times for remelting.

The procedures used for the investigation have been described. Rather than present the results of these procedures separately, they will be discussed as they apply to a specific feature of the equilibrium diagram.

The designations given to various phases in the alloy system comply with the nomenclature in common use. The low temperature hexagonal form of zirconium is referred to as alpha, and the primary solid solution of
any alloying element with this form is termed the alpha solid solution. The high temperature cubic form has been designated beta, and the solid solution of any alloying element with this form is termed the beta solid solution. Other nomenclature used is self-explanatory.

Approximately 130 specimens were prepared for metallographic examination. Representative photomicrographs were selected from these to show the main features of the system.

The Alpha Field. For determination of the room temperature solubility of silver in zirconium, specimens of rolled sheet were heated for one hour at 900 C and slowly cooled to produce an equilibrium structure. Metallographic examination of these specimens indicated the presence of a second constituent in alloys with as low as 0.1 per cent silver. This increased in proportion as the silver content increased and became recognizable as a eutectoid structure. This progression is shown in figures 9, 10 and 11. The eutectoid is present as a dark-etching grain boundary constituent in the 0.50 per cent silver alloy.

Since the solubility is so limited, the impurities in the zirconium would be of the same order of magnitude, making metallographic determination of the solubility limit impossible. This is due chiefly to the iron impurity, which forms a eutectoid when in excess of 0.02 per
Figure 8. 0.44 per cent Ag
750 °C 4 hr water quench
X75 Etchant No 2

Figure 9. 0.50 per cent Ag
900 °C 1 hr furnace cool
X500 Etchant No 2

Figure 10. 2.1 per cent Ag
900 °C 1 hr furnace cool
X500 Etchant No 2

Figure 11. 3.6 per cent Ag
900 °C 1 hr furnace cool
X500 Etchant No 2
The iron content of the zirconium used for these alloys was from 0.03 to 0.06 per cent. As further proof of the negligible solubility of silver, data from the x-ray diffraction pattern of a 6.0 per cent silver alloy are shown in figure 29. This pattern contained all the reflections for the alpha zirconium phase plus extra reflections due to the intermediate phase. The lattice dimensions of the alpha phase were found to be the same as those for unalloyed zirconium. With other than negligible solubility, a change in lattice parameter of the solvent would be evidenced, so it was concluded that the solubility could not be determined any more accurately by these methods.

To check for an increase in solubility in the alpha phase at higher temperatures, specimens were heated to 750 C, held for 4 hours, and quenched in cold water. Examination of these specimens indicated that the eutectoid present had spherodized, as shown in figure 8 for a 0.44 per cent alloy, instead of the second phase going into solution. This would indicate that there is no appreciable increase in solubility at temperatures up to the eutectoid reaction.

The Eutectoid. A eutectoid reaction between alpha zirconium and the intermediate phase, Zr2Ag, was observed in alloys slowly cooled from above 850 C. The composition
of this reaction was determined by microscopic examination of heat treated alloys containing up to 7 per cent silver.

The amount of the eutectoid present increases with an increase in silver content until at 3.6 per cent silver, illustrated in figure 11, it occupies 50 to 60 per cent of the field. The excess alpha zirconium in this hypo-eutectoid alloy is the bright, non-etching phase. The eutectoid is very fine here, with the alternate plates not well resolved even at a magnification of 500 diameters. The structure of a 5.5 per cent silver alloy, slowly cooled from 900°C is shown in figure 12. This was included to show the spherodization or separation of the eutectoid that occurred in some treatments. It appears to have an excess of the intermediate phase in some areas, but the rounded particles of this phase occur in bright areas of the alpha phase, indicating a separation of the eutectoid into its two components. The structure of this alloy, heated for two hours at 1000°C and slowly cooled is shown in figure 14. Here it appears to be 100 per cent eutectoid. On the basis of several specimens of this alloy with different heat treatments the composition of the eutectoid reaction was placed at 5.5 per cent silver.

Hyper-eutectoid alloys are illustrated in figures 15, 16 and 17. None of the hyper-eutectoid alloys were completely free of the eutectoid separation but the excess of the dark etching intermediate phase is evident. The
Figure 12. 5.5 per cent Ag
900°C 1 hr furnace cool
X500 Etchant No 2

Figure 13. 3.6 per cent Ag
1000°C 2 hr furnace cool
X500 Etchant No 2

Figure 14. 5.5 per cent Ag
1000°C 2 hr furnace cool
X500 Etchant No 2

Figure 15. 7.0 per cent Ag
1000°C 2 hr furnace cool
X500 Etchant No 2
13.9 per cent alloy shown in figure 17 was held at 950 C for 50 hours to homogenize the structure for x-ray analysis. During the long soaking period the excess Zr₂Ag collected at the high temperature grain boundaries, outlining those grains in the structure of the slowly cooled specimen.

The temperature of this transformation was determined by thermoanalysis methods. The heat treatments had bracketed the temperature to between 750 and 900 C, so the 700 to 950 C range in particular was investigated. Heating and cooling rates of 4 C per minute were employed for the first run on each alloy with subsequent curves taken at other heating and cooling rates. In almost every case the transformation after the first cycle appeared to extend over a wider range of temperatures with a smaller heat effect. This is believed to be the result of the absorption of small amounts of oxygen picked up from heating in the helium atmosphere.

The results of several runs on three different alloys are shown in Table V. The reactions on heating and cooling for all the runs were averaged and this taken as the temperature of the eutectoid transformation. This was placed at 910 ± 5 C.
Figure 16. 6.0 per cent Ag
1000 °C 60 hr furnace cool
X500 Etchant No 2

Figure 17. 13.9 per cent Ag
950 °C 50 hr furnace cool
X500 Etchant No 2

Figure 18. 1.0 per cent Ag 900 °C 1 hr
water quench X150 Etchant No 2
TABLE V

THERMOANALYSIS DATA

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Eutectoid Reaction C</th>
<th>heating</th>
<th>cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA 3099 6.0 Ag</td>
<td>812</td>
<td>803</td>
<td></td>
</tr>
<tr>
<td></td>
<td>814</td>
<td>806</td>
<td></td>
</tr>
<tr>
<td></td>
<td>810</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>WA 3487 5.5 Ag</td>
<td>816</td>
<td></td>
<td>793</td>
</tr>
<tr>
<td>WA 3100 13.9 Ag</td>
<td>807</td>
<td></td>
<td>804</td>
</tr>
<tr>
<td></td>
<td>821</td>
<td></td>
<td>806</td>
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<tr>
<td></td>
<td>814</td>
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</table>

No attempt was made in this investigation to determine the upper temperature limits of the alpha plus beta field. As previously mentioned, small amounts of oxygen produce a temperature extension of this field; a few tenths of a per cent oxygen raising the alpha to beta transformation by as much as 50 C. Figure 18 shows the two-phase structure resulting in a 1.0 per cent silver alloy, rapidly cooled from 900 C. This alloy should be all beta at temperature but islands of the alpha phase are present with the acicular, transformed beta structure. The beta solid solution in zirconium alloys is not retained at room temperature by quenching. The transformation product is the Widmanstätten pattern of alpha needles illustrated, that give an indication that the structure was beta at temperature.

The upper limit of the alpha plus beta field was therefore placed by theoretical considerations only.
It is shown as a straight, dashed line, extending from the eutectoid point to 862°C, the alpha to beta transformation temperature of zirconium.

**The Beta Field.** The limit of solubility of silver in beta zirconium was determined by microscopic examination of alloys that had been subjected to solution and quenching treatments.

Specimens of hot rolled sheet containing up to 7 percent silver were quenched from temperatures of 900, 1000, 1100 and 1200°C. Specimens of cast material were used for higher percentage silver.

Typical structures resulting from these treatments are shown in figures 19 to 22. The second phase, Zr$_2$Ag, dissolved quite rapidly at these temperatures; one hour at 1000°C being sufficient to obtain complete solution for the 5.5 percent silver alloy. Two hour soaking periods were used for the majority of the treatments for longer times did not appear necessary.

The Widmanstätten pattern of alpha needles, typical of the quenched beta solid solution, is illustrated in figures 19 and 20 for 3.6 and 5.5 percent silver alloys. The cold water quench was sufficiently drastic, as evidenced by the uniformity of the structure at the grain boundaries of these alloys.

Complete solution was not obtained at 1000 or 1100°C for the 7 percent silver alloy, shown in figures 21 and
Figure 19. 3.6 per cent Ag
1000 °C 2 hr water quench
X150 Etchant No 3

Figure 20. 5.5 per cent Ag
1000 °C 2 hr water quench
X150 Etchant No 3

Figure 21. 7.0 per cent Ag
1000 °C 2 hr water quench
X150 Etchant No 3

Figure 22. 7.0 per cent Ag
1000 °C 2 hr water quench
X150 Etchant No 3
22. After two hours at 1100 C, particles of the Zr$_2$Ag remained in the grain boundaries of the beta solid solution. Comparison of figure 22 with the annealed structure of this alloy, shown in figure 15, illustrates the extent of solution obtained. No melting occurred in alloys up to 13.9 per cent silver at the 1200 C treatment. The 7 per cent alloy still had a few particles of undissolved Zr$_2$Ag in some areas at this temperature, but was single phase solid solution for the most part.

The placing of the solubility line for the beta solid solution field was hampered by the lack of alloys between 7 and 10 per cent silver. A straight line was extended from the eutectoid reaction through points indicated by the 1000, 1100 and 1200 C treatments of the 7 per cent alloy, for it is believed that this composition is very nearly the extent of solid solubility at 1200 C. This is supported by observations of alloys heated at 1250 C. Slight melting occurred on sharpened edges of the 7 per cent alloy at this temperature. If the solubility at 1250 C was much greater than the 7.5 per cent indicated on the tentative diagram, melting would not occur in this alloy until quite higher temperatures were reached. Although not a positive indication, this supports the other evidence, and the line is believed to be essentially correct.
No attempt was made to determine the solidus line for the beta field. It is shown as a dashed line extending from 1860°C, the melting point of zirconium, to the limit to solid solubility at the eutectic temperature.

The Eutectic. Examination of the cast structure of higher percentage silver alloys indicated the existence of a eutectic reaction between beta zirconium and the intermediate phase, $\text{Zr}_2\text{Ag}$. None of the alloys prepared consisted entirely of the eutectic structure, although the 13.9 per cent alloy appeared quite close. Several of the segregated alloys had areas of complete eutectic but were not uniform enough to sample for chemical analysis.

The cast structure of the 13.9 per cent silver alloy is shown in figure 23. This high magnification was necessary to show the structure of the eutectic. The excess constituent here is the intermediate phase $\text{Zr}_2\text{Ag}$, appearing in greater proportions than would be expected due to the small area covered at that magnification. Figure 24 illustrates the cast structure of a 26.3 per cent alloy. This alloy consists of islands of the intermediate phase in a eutectic matrix. At lower magnification the intermediate phase in these higher percentage silver alloys appears quite dendritic.

To determine the temperature of the eutectic reaction, specimens were prepared in the shape of wedges
to give a thin, sharp edge. These were heated at 1200, 1230 and 1250 °C for 15 minutes and examined after each treatment for evidence of melting. The specimens were sealed in quartz tubes as in previous heat treatments. The temperature at the edge of the tube was measured with a new chromel-alumel thermocouple to check the controller setting for each of the treatments.

No melting could be detected in the 1230 °C treatment. The 13.9 per cent alloy did show slight melting in the 1250 °C treatment. Holding another specimen of this alloy for 1/2 hour at 1250 °C did not produce complete melting so it was felt that this temperature was very close to the eutectic horizontal. It is realized that this method is not an extremely accurate means of determining the melting point, especially if the alloy is not close to the eutectic composition. The temperature measurement is subject to some error for actual contact with the specimen is not obtained, although the quartz tube and specimen are probably very nearly the same temperature. The eutectic temperature was therefore placed at 1250 ± 10 °C.

Slightly more than 1/2 gram of the material that had melted and formed projections on the specimen heated at 1250 °C could be chipped off. Chemical analysis of this yielded 12.0 per cent silver. Pitted areas on the specimen where slight melting had occurred were examined
Figure 23. 13.9 per cent Ag
As cast x750
Etchant No 1

Figure 24. 26.3 per cent Ag
As cast x500
Etchant No 1

Figure 25. 26.3 per cent Ag
1000 C 60 hr furnace cool
x500 Etchant No 1

Figure 26. 34.3 per cent Ag
1000 C 70 hr furnace cool
x150 Etchant No 1
Figure 27. 45.8 per cent Ag
As cast X500
Etchant No 1

Figure 28. 90 per cent Ag
900 °C 2 hr furnace cool
X150 Etchant No 4
metallographically. This material appeared to be complete eutectic, so 12.0 per cent silver was taken as the eutectic composition.

The Intermediate Phase. The dark-etching second phase occurring at low silver contents continued to increase in proportion as the silver content of the alloys increased. It is illustrated in figures 24, 26 and 27 for alloys of 26.3, 34.3 and 45.8 per cent silver. Figure 25 illustrates the room temperature equilibrium structure of the 26.3 per cent specimen. The 60 hour homogenization treatment has destroyed the eutectic seen in the cast condition. The intermediate phase is the darkly stained material surrounding the areas of spheroidized eutectoid. It is a brittle phase, but is friable rather than hard. It is stained badly by all the etchants employed and even discolored in a few minutes by water.

The 34.3 per cent alloy shown in figure 26 is largely the intermediate phase but a two-phase structure is evident. This specimen had also been homogenized for x-ray analysis. The second constituent here is alpha zirconium. Considerable internal cracking occurred in this alloy in the cast state. These cracks were not healed in the homogenization treatment and are evident in figure 26.

The next alloy in this series, 45.8 per cent silver,
is shown as cast in figure 27. A mottled stain occurred on the columnar structure of the intermediate phase. In this alloy a new phase is evident, occurring as star-shaped dendrites randomly oriented throughout the structure.

The composition of the intermediate phase is evidently between 34.3 and 45.8 per cent silver. The only simple atomic ratio in this range is for $Zr_2Ag$, at 37.1 per cent. Since intermetallic compounds usually occur at these simple ratios, this was taken as the composition of the intermediate phase.

Figure 28 shows an intermetallic compound present in a 90 per cent silver alloy. This is possibly the same phase as the new phase appearing in the 45.8 per cent specimen. It is embedded in the silver matrix of the annealed alloy.

X-ray diffraction patterns were obtained for a series of these alloys. The results of this analysis are shown in figure 29. The crystal structure of the intermediate phase was not determined but several conclusions can be drawn from the data.

The complete pattern for alpha zirconium was obtained for the alloys of lower silver content with extra reflections due to the intermediate phase. The zirconium lattice was not altered by alloy additions of silver, indicating negligible solubility of silver in the room.
Figure 29. X-ray diffraction data
temperature zirconium form.

With increasing silver content the reflections of the zirconium phase become less intense while those of the intermediate phase become stronger, until at 34.3 per cent silver only the strongest of the zirconium lines remain as weak reflections.

The constant d spacings for the intermediate phase indicate that its lattice is not altered by composition changes. It is therefore a fixed composition with no solubility field.

The zirconium reflections are absent in the 45.8 per cent alloy indicating that the composition of the intermediate phase has been passed, as was observed for the metallographic specimens. New lines appear in the 45.8 per cent pattern that are also present in the pattern for 90 per cent silver. These are no doubt due to the intermetallic compound observed in the microstructure of the 90 per cent silver alloy. Only a few reflections for this phase were observed however. The strongest silver lines are evident also in the pattern for the 90 per cent silver alloy.

These data support the metallographic examination of the system and rule out the possibility for more than one intermetallic compound occurring in the zirconium-rich portion.
The melting point for the intermetallic compound was not determined, so the portion of this line above the eutectic temperature is shown as a dotted line.
Figure 30. Tentative zirconium-silver equilibrium diagram.
CONCLUSIONS

The Tentative Diagram. From the results described in the previous chapter a tentative equilibrium diagram for the zirconium-rich portion of the system is proposed. This is shown in figure 30.

The outstanding features of this system have been described previously and are only listed here.

1. Negligible solubility of silver in alpha zirconium was found with no appreciable increase up to the eutectoid temperature.

2. A eutectoid reaction at 5.5 per cent silver and 810 ± 5 C.

3. 5.5 per cent silver is soluble in beta zirconium at the eutectoid temperature, increasing to a maximum solid solubility of 7.5 per cent at the eutectic temperature.

4. The melting point of zirconium is depressed to 1250 ± 10 C with the addition of 12.0 per cent silver, where the liquid phase solidifies in a eutectic formation.

5. An intermetallic compound is formed with the composition 37.1 per cent silver, corresponding to Zr$_2$Ag.

The diagram proposed is believed to be essentially correct although a more detailed study would undoubtedly
refine the temperatures and compositions reported slightly.

Recommendations For Future Work. The feature of the system that has the least supporting evidence is the eutectic reaction, both in temperature and composition. More alloys need to be prepared in this region with melting point studies carried out. The composition of the eutectic was based on one analysis and it should be checked by several.

For a more complete study of the system it would be desirable to have several alloys in the range from 7 to 12 per cent silver. This would provide more detailed information on the hyper-eutectoid alloys.

The x-ray diffraction pattern for the intermediate phase \( \text{Zr}_2\text{Ag} \) was obtained but the crystal structure and lattice dimensions of this phase were not determined. With the other melting point studies, the melting point of this compound should be determined.

No attempt was made in this work to check the existence of the compound \( \text{ZrAg} \) reported by Raub and Engel that is shown in figure 1. Evidence of the existence of another intermetallic compound was found in the 45.8 and 90 per cent silver alloys. No eutectic structure was observed in the 45.8 per cent alloy, only a mixture of two compounds, which would possibly indicate that the new phase formed from a peritectic reaction. This area would need to be investigated also for a complete picture of the system.


