THE MAGNESIUM-ZIRCONIUM ALLOYS

by

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INTRODUCTION

Objectives. Relatively little is known about the binary system of magnesium and zirconium mainly because of the difficulty encountered in preparing the alloys. The prime purpose of this thesis project was to study the problems of preparation of magnesium-zirconium and to prepare some of the alloys. It is the secondary purpose of this paper to assist in establishing the equilibrium diagram for the magnesium-zirconium system by suitable tests on any alloys produced.

The successful alloying of magnesium and zirconium is quite difficult for several reasons. Magnesium melts at 650 C and boils at 1100 C, while zirconium melts at 1860 C. Special precautions must be taken to keep the magnesium from boiling out of the alloy. Gravity segregation, brought on by the large disparity between the densities of the two metals, is a second major problem in alloying them. There is also the possibility of the metals' reactions being sluggish enough so that concentration segregation might occur. Finally, impurities both in raw materials and picked up during the alloying have been a source of trouble to previous investigators.

A study has been made of the various factors in the formation of the various types of alloys in an attempt to predict the constitution diagram for magnesium-zirconium. The literature on the general rules for alloying is mainly the work of Hume-Rothery.

Choice of Subject. A constitution diagram for the magnesium-zirconium alloys would be of immediate use in industry. Additions of zirconium to magnesium in amounts up to 3 per cent result in greatly improved corrosion resistance (3, p289), marked grain refinement (3, p135-138), and lowered iron content (3, p319). According to Beck, binary magnesium-zirconium alloys exhibited good corrosion resistance both to atmospheric and sea water attack, a resistance which nearly equals that of the binary magnesium-manganese alloys. Zirconium has a powerful grain refining effect on magnesium which makes possible a great increase in elongation which, in turn, can be converted into tensile strength by exploiting the capacity for work hardening. The refined grain structure in magnesium, due to small additions of zirconium, improves the extrusion properties of magnesium and its alloys. Iron is very detrimental to the corrosion resistance of magnesium, and to remove it zirconium is added to the melt where it combines with the iron to form $ZrFe_2$. The large particles

of iron-zirconium formed are separated from the melt by settling.

The magnesium-zirconium alloys of moderate zirconium content are used at present as master alloys. The Metal Hydrides Corporation advertises alloys of 40%, 50%, and 60% zirconium content. Then there is always the possibility that such investigation will discover some unusual property of these alloys that will give them commercial importance.

The only practical method for producing high-purity, ductile-zirconium, that has been developed so far, includes a reduction of zirconium tetra-chloride with magnesium (6, p1-10). To complete this reduction a 20 per cent excess of magnesium is necessary which subsequently mixes and probably alloys (to some unknown extent) with the zirconium. This extra magnesium is subsequently distilled out of the zirconium at 920 C under high vacuum leaving a zirconium sponge. Considerable difficulty is found in melting zirconium sponge that has too high a magnesium content; the material boils and sputters sporadically resulting in unsound zirconium ingots. It is felt that better understanding of the magnesium-zirconium system would be of use in correctly engineering these final steps in the zirconium process.

The magnesium-zirconium alloys, then, are already a problem for the metallurgist and he will not be able to efficiently solve the problems related to these alloys until the constitution diagram has been made.

Literature. H. S. Cooper (4, p225) was the first investigator to work on the magnesium-zirconium system. The following is Mr. Cooper's comment on the system in his paper, "The Preparation of Fused Zirconium."

> Zirconium has been alloyed with magnesium by the reduction of the oxide in vacuo, using a large excess of magnesium. Treatment with hydrochloric acid removes the magnesium without affecting the zirconium. If the zirconium is not too high the malleability of the magnesium is not affected by the latter.

The second investigation of the magnesium-zirconium alloys was made by Von Hans Nowotny, Egil Wormes, and Anton Mohrnheim (7, p41-42). These investigators covered the complete range of alloys. They melted their alloys under flux in a procelain crucible, stirring vigorously until solidification to avoid segregation. The zirconium that was available to these men was of rather poor quality containing 3 per cent impurities of iron, calcium, titanium and cerium; also, about 9 per cent of the zirconium was in the form of the unreduced oxide. Undoubtedly, this large amount of impurity had a major effect upon their results.

Von F. Sauerwald (8, p212-220) published a paper in "Zeitschrift Fur Anorganische Chemie" recently on his work with the magnesium-zirconium alloys. Sauerwald worked mainly with alloys having a zirconium content less than 5 per cent and constructed a partial constitution diagram for these alloys. The alloys were prepared in an iron crucible, supported in a sealed steel container, in an atmosphere of argon. A water-cooled steel cap on one end of the steel container was fitted with a ground joint and had access openings for a thermocouple, a stirring rod, and for argon. Zirconium powder was added to molten magnesium which was kept in continual agitation by an iron stirring rod. It was found necessary to keep the mix at 1000 C for reasonable diffusion speeds. A thin covering of NaCl + KCl over the melt was found to aid the melting. Figure 1-a is a replica of the partial constitution diagram constructed by Sauerwald from x-ray and thermal analysis data from his alloys.

According to some exploratory investigations by Siebel (3, p77)(1, p1228), a peritectic reaction takes place at a temperature close to the melting point of magnesium. The liquidus meets the peritectic temperature at 0.26% zirconium, and then rises very steeply with increase in zirconium until at temperatures of about 1000 C it curves toward the horizontal. Beck (3, p77), by

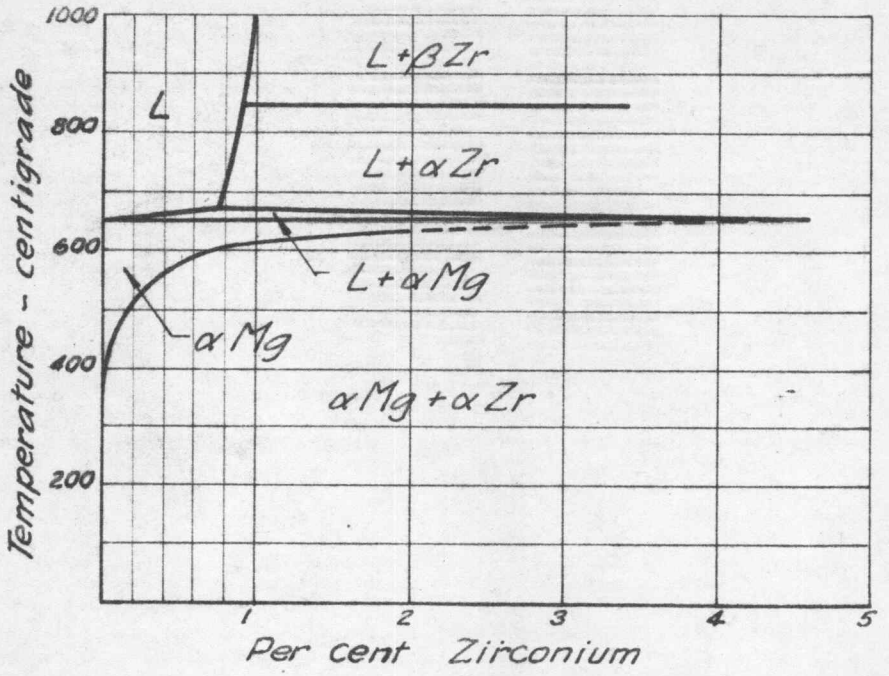

Figure 1-a Constitution Diagram for Magnesium-Zirconium, as given by Sauerwald (8, p. 216).

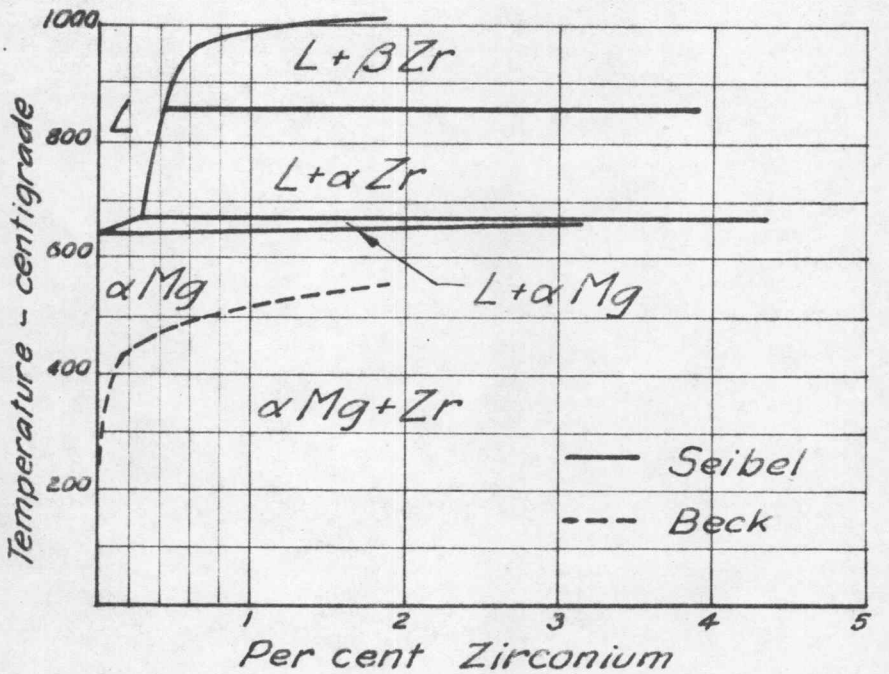

Figure 1-b Constitution Diagram for Magnesium-Zirconium, drawn by the author, from data by Seibel and Beck (3, p. 77).

measurements of electrical conductivity determined a solid solubility which at 500 C is equal to or greater than 0.8% zirconium in magnesium and at 400 C is less than 0.1% zirconium. Figure 1-b was drawn by the author from the data given by Seibel and Beck to be compared with the work of Sauerwald.

Prediction of Alloy Constitution. (2, p196-217) (5, p142-191) At present much thought is being given to find a master plan whereby the metallurgist may predict with some degree of accuracy the various properties of some embryonic alloy; or conversely, to use this master plan to prescribe an alloy from a given set of properties. There has been found a number of factors-of-alloying, mainly through the work of Hume-Rothery, that will in some cases allow predictions to be made. Some of the rules which govern the extent of solid solution ranges and the probability and placement of other homogeneity ranges in an unknown alloy are known.

The four factors which seem to have the greatest effect upon the characteristic of a particular alloy are listed below.

1. Atomic Size. The relative atomic size (closest atomic approach or atomic radius) of the parent metals seems to act as a compatibility factor between the

metals. For medium solubility ranges the atomic dimensions must be within 15 per cent and for large solubility ranges the atomic dimensions are usually within 8 per cent of each other.

2. Crystal-structure Bonding. The metals may be divided into four groups according to their preference for crystal-bonding structure. Harrington has published a rearranged periodic table to show the gradual gradation of chemical nature from the True Metals to the Non-Metals. Harrington designates the different groups as follows: "A"-group, Salts of Electrons; "T"-group, Transition Metals; "P"-group, Pseudo Metals; and "H"-group, Hybrid Metals. The above nomenclature will be used for the rest of this discussion.

The "A"-group and "T"-group metals are called the True Metals as they exhibit a metallic linkage in their structure. The "A"-group metals (mostly alkali metals) have their structure determined equally by the valency electrons and the atomic ions. They could be thought of as being positive ions immersed in a gas of negative electrons, which explains their name, "Salts of Electrons."

On the basis of chemical properties, the "T"-group metals are characterized by bonding in which the valency electrons dominate. The bond between atoms is then spatially undirected and may operate between any given

atom and an indefinite number of neighbors. Most of the "A"-group and the "T"-group metals form either base-centered-cubic, face-centered-cubic, or hexagonal-close-packed structures.

The Transition Metals shade gradually into the "P"-group, Pseudo Metals. The Pseudo Metals act more like True Metals than Non-Metals but tend toward homopolar binding. They share their valency electrons with their neighbors according to Hume-Rothery's "8-N" Rule. The "8-N" Rule states that in materials that have homopolar binding each electron will have eight minus the element's positive valence nearest neighbors. The Pseudo Metals generally have complex crystal structures.

The "H"-group, Hybrid Metals, behave about equally like metals and non-metals. Hybrid Metals tend toward homopolar crystal bonding and are characterized by complex crystal lattice structures.

3. Periodic Grouping. The periodic grouping refers to the position of the element in Mendeleev's Periodic Table. The left or right position in the table is of importance as well as the vertical position and the valency. The closeness in the periodic table is called the "electro-chemical factor." Extreme differences in periodic grouping give rise to intermetallic compounds at the normal valencies. These intermetallic compounds occur

at particular "valence" electron to atom ratios.

4. Type of Lattice. Each metal forms in some specific type of lattice structure (a few metals have allotropic forms and have several lattice structures) and to be considered similar two metals must have the same kind of lattice. This is called the geometrical factor.

The four factors just outlined are combined into some general rules which may be used to predict the extent of solubility ranges and the presence of intermetallic compounds. In most cases, the rules have to be used by first finding a set of similar known alloys and, in any case, all of the known alloy systems of each participating metal should be carefully studied for analogous situations.

For extensive solid-solubility ranges all four of the alloying factors must be favorable. The relative valency governs extent of solubility; a metal of lower valency tends to dissolve a metal of higher valency more readily than vice versa. Removal of valence electrons from a structure is more serious than the addition of a limited number of electrons above the fundamental "valence" electron-atom ratio for the structure. The more electro-negative the solute element and the more electro-positive the solvent, the greater is the tendency to restrict a solid-solution. The maximum solubility generally

corresponds to some specific "valence" electron-atom ratio for the structure. In binary systems, with other things equal, the solubility range for the high-melting metal is greater than for the low-melting metal.

The number and constitution of intermetallic compounds is mainly predicted through analogy with known alloys. However, the higher the electro-chemical factor the better the possibility that there will be an intermetallic compound, and the better the chance that it will be at the normal valencies of the elements. Most intermetallic compounds are not at the normal valencies of the elements. Increasing valency of the solute results in the beta phase occurring at a lower atomic percentage of the solute element. As with the solid-solution ranges, the intermetallic compounds tend to form at specific "valence" electron-atom ratios.

It is only possible to make rather vague generalizations in predicting the form of the magnesium-zirconium constitution diagram by means of the rules just outlined. The reason that more exact prediction cannot be made lies in the fact that there are very few metals metallurgically similar to either magnesium or zirconium, so, few analogies can be made to existing constitution diagrams.

Titanium is very similar to zirconium and a comparison of the four alloying factors of magnesium,

zirconium, and titanium are given in Table I. The only difference between zirconium and titanium, as shown in the table, is a somewhat smaller atomic size for titanium. Also attesting to the similarity between zirconium and titanium are the large solid solubility ranges in the alloys of these two metals. A comparison of the constitution diagrams for zirconium-aluminum and titanium-aluminum (1, p1167-1168), zirconium-copper and titanium-copper (1, p1205-1207), and zirconium-iron and titanium-iron (1, p1219-1221) will immediately show the similarity in alloying characteristics of zirconium and titanium. It is interesting to note that in all three of the cases just mentioned the solubility of titanium in the other element is larger than the solubility of zirconium in the other element. Thus, in these three cases, the rule that the more electro-positive the solvent and the more electro-negative the solute the greater is the tendency to restrict the solid solution, has been obeyed.

Kroll states that titanium and magnesium, as far as has been investigated, have been shown to be nearly immiscible at all temperatures. Then the foregoing discussion would show that the solubility ranges of magnesium and zirconium should also be very restricted. According to the general factors for alloying the similarity between the metals magnesium and zirconium (also titanium and

TABLE I

A COMPARISON OF THE ALLOYING FACTORS OF MAGNESIUM, ZIRCONIUM, AND TITANIUM

	Magnesium	Zirconium	Titanium
Type of Lattice	HCP	HCP	HCP
Lattice Constant "a" in Å	3.2022	3.223	2.953
"c" in Å	5.1991	5.123	4.729
Closest Atomic Approach in Å	3.19	3.166	2.915
Variation from Atomic Dimensions of Mg	0%	0.6%	8.9%
Position in Periodic Table	2L	4L	4L
Crystal Bonding Structure	A	T	T
Melting Point	651 C	1860 C	1800 C
Specific Heat 0-100 C cal/gm	0.250	0.068	0.1125

magnesium) would indicate large solubility ranges. The difference in position in the periodic table would indicate a smaller solubility range for zirconium but the higher melting point of zirconium might neutralize the valence effect.

Since magnesium and zirconium have a difference in valence of two, there could quite possibly be an intermetallic compound formed. Little can be done toward predicting a composition for a probable compound because of the lack of analogous alloy systems.

From a study of the magnesium alloys and the zirconium alloys, it is noticed that the solubility ranges are generally small for both metals. A combination of the various factors discussed would lead to the prediction of a constitution diagram, quite similar to the aluminum-zirconium diagram (1, p1168) with very small solubility, both in liquid and solid phases, and the possibility of an intermetallic compound.

PROCEDURE AND EQUIPMENT

Alloying Techniques. The alloying technique of Nowotny, Wormes, and Mohrnheim was not followed as it was believed that excessive amounts of impurity would be introduced when using a porcelain crucible at the necessary temperatures. The work of Sauerwald was not discovered until near the end of this investigation and, unfortunately, there was not enough time to construct as elaborate an apparatus as he used.

Alloying was attempted in three different ways: By fusing zirconium hydride powder and magnesium-shaving compacts; by melting compacts of zirconium and magnesium shavings in sealed steel bombs; and by enriching low-zirconium alloys by distillation of magnesium. A diffusion study was also made by soaking a piece of magnesium in a sealed zirconium container at 1000 C for twelve hours. Detailed descriptions of the three alloying procedures and of the diffusion study follow in the succeeding paragraphs.

1. Zirconium Hydride. All of this investigation was carried on at temperatures less than 1100 C (magnesium boils at 1100 C), which was necessitated by the fact that available equipment was adaptable to atmospheric and lower pressures only. From the literature (7, p41), the diffusion rate of zirconium into magnesium was known to be

moderately slow. Fine particles of zirconium in the melt would be very desirable from the standpoint of speeding the dissolving of the zirconium into the magnesium. Powdered zirconium is pyrophoric (1, p53) and, therefore, difficult to handle; so zirconium-hydride powder was chosen as a convenient means of handling fine particles of zirconium. Zirconium-hydride is brittle and easily powdered and the powder is not pyrophoric. Heating to 900 C, at atmospheric pressure, will drive substantially all of the hydrogen out of zirconium hydride and upon cooling below 700 C the hydrogen will be reabsorbed by the zirconium.

Several compacts were made with varying mixtures of zirconium-hydride powder and fine magnesium shavings. These compacts were formed in a hydraulic press at a pressure of 26 tons per square inch, and were one inch in diameter and about one inch long. Figure 2 is a photograph of one of the compacts.

The compacts were heated in the electric vacuum furnace shown in Figure 6. Three heating and pressure cycles were tried with only moderate success in all cases. The three cycles follow:

a)
1 hr at 300 C	in	vacuum
1 hr at 400 C	in	vacuum
3 hr at 900 C	in	helium
furnace cool	in	helium

b) heat to 900 C in helium
vacuum pump on for 30 seconds
soak for 18 hr at 900 C in helium

c) 18 hr at 1000 C in helium
furnace cool in helium

The vacuum program in the first two cycles was an effort to remove the hydrogen, released from the zirconium hydride during heating, so that it would not be reabsorbed upon cooling. During the vacuum part of the program a good part of the magnesium was distilled and so removed from the melt with the hydrogen. The alloys made with cycles "a" and "b" could not be considered satisfactory for they were not completely fused due to their final low magnesium content. Cycle "c", without a vacuum program, produced the best alloy. From the results obtained from cycle "c" it is believed that the vacuum step is unnecessary for alloys of compositions up to about 75 per cent zirconium. It may be that, during cooling, the magnesium shields the zirconium and thus prevents it from reabsorbing the hydrogen.

2. Steel Bombs. Magnesium and iron are believed to be immiscible at all temperatures, which allows the melting of magnesium in iron crucibles without appreciable contamination. The diffusion of zirconium in iron is slow up to temperatures in the vicinity of 900 C. Because of the foregoing facts, it was felt that fusing briquets of

zirconium and magnesium shavings in sealed steel containers would be a good way to make magnesium-zirconium alloys. As shown in Figure 3, steel containers were made of one-inch pipe nipples with a one-inch pipe cap welded on each end.

The steel bombs were heated in an electric muffle furnace. As each bomb was removed from the furnace it was shaken vigorously and then quenched in water. A list of the heating cycles used for the steel bombs follows:

a) 12 hr at 700 F

b) 60 hr at 800 F

c) 60 hr at 800 F
48 hr at 900 F

Even though the steel bombs scaled badly at the higher temperatures, the alloy inside was found to have been adequately protected.

3. Distillation. Zirconium is dissolved in magnesium to the extent of about 1 per cent quite easily. It is possible to effectively enrich this low zirconium alloy by distilling away some of the magnesium. It was felt that, in alloys formed in this way, the zirconium should be in a perfect condition for alloying with the magnesium. The zirconium would surely be in an extremely finely divided state as it came out of solution with the magnesium.

Figure 2. Compact of Zirconium-Hydride Powder and Magnesium Shavings in Iron Crucible.

Figure 3. Steel Bomb, used for making Magnesium-Zirconium Alloy, with Finished Ingot of Magnesium-Zirconium.

The United States Bureau of Mines at Albany, Oregon, attempted to make a magnesium-zirconium alloy of composition 50% Mg - 50% Zr in their reduction plant. A cross-section of the result of this melt is shown in Figure 4. Pieces out of the 1.7% zirconium side of the upper ingot were used as "starting" alloys to be lowered in magnesium content by distillation.

The vapor pressures of magnesium at various temperatures as given by Leitgebel (3, p117) are given in Figure 5. It can be seen from Leitgebel's graph that magnesium could be either sublimed at pressures below about 3 mm of mercury, or boiled at higher pressures. In this investigation the temperature of the alloy was kept above the melting point of magnesium so as to assure mixing of the melt. After a distillation program the alloys were subjected to a prolonged soaking at about 1000 C in helium at atmospheric pressure. This soaking period was to allow diffusion to take place and to assure a well-fused alloy.

Furnace temperatures of 650 C, 750 C, 850 C, and 900 C were tried for the distilling cycle with the higher temperatures being more satisfactory. The higher temperatures not only quickened the distilling process but caused the magnesium vapor to condense farther away from the crucible.

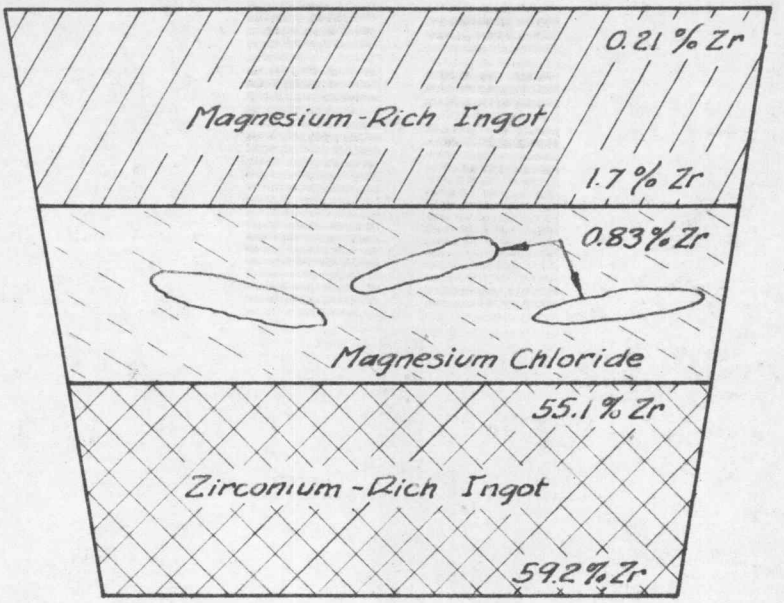

Figure 4 - Sketch of Magnesium-Zirconium Ingot produced by the Zirconium Reduction Plant, United States Bureau of Mines, Albany, Oregon.

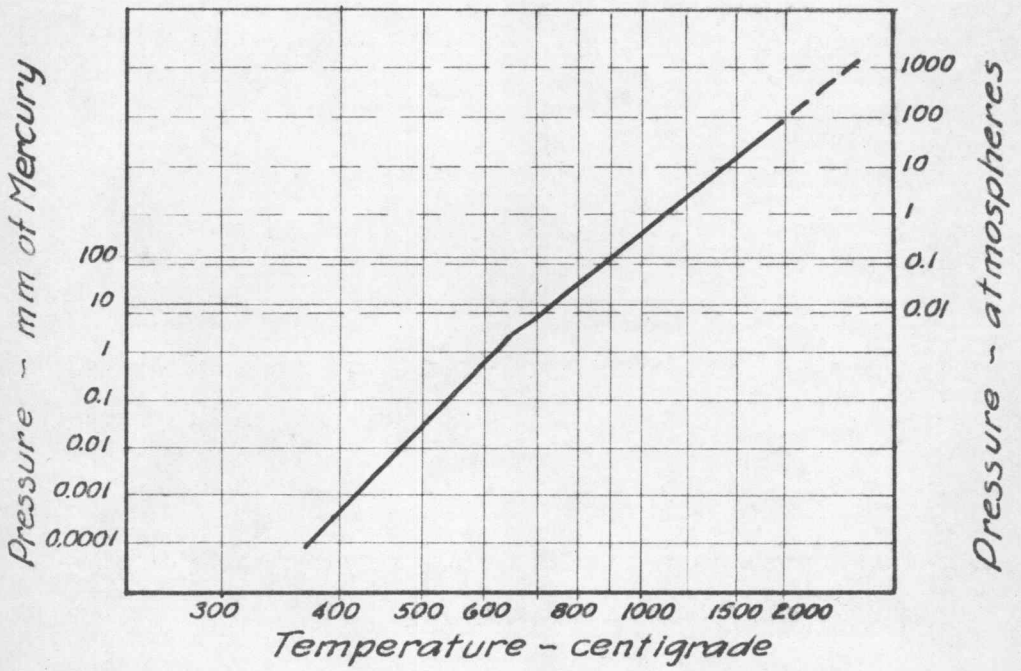

Figure 5 - Curve Showing Vapor Pressure of Magnesium as given by Leitgebel (3, p.117).

The vacuum furnace, shown in Figure 6, was used for making these alloys. A stainless steel liner was used in the refractory tube of the furnace, for the tube would be ruined by contact with molten magnesium or magnesium vapor. The liner acted as the condenser for the magnesium vapor and so it was made in three pieces for easy cleaning. A carbon crucible was used to hold the melt. Figure 7 is a photograph of the steel liner, a carbon crucible, and an ingot from this process.

The magnesium condensed in the form of flat hexagonal plates and dendrites, needle-like dendrites, or three-dimensional crystals, depending on the furnace temperature, distilling pressure, and distilling time.

4. Diffusion Study. A piece of magnesium was sealed in a tube of zirconium, Figure 8, and the assembly soaked at 1000 C for 18 hours. It was hoped that the resulting specimen would have a cross-section showing the microstructures of the magnesium-zirconium alloys from pure zirconium to "α"-magnesium. This specimen was heated in the vacuum furnace under helium at atmospheric pressure.

Metallographic Studies. Specimens of all the alloys made were mounted in bakelite for metallographic examination. A Bausch and Lomb Research-metallograph was used in studying the microstructure of the specimens and in taking micrographs.

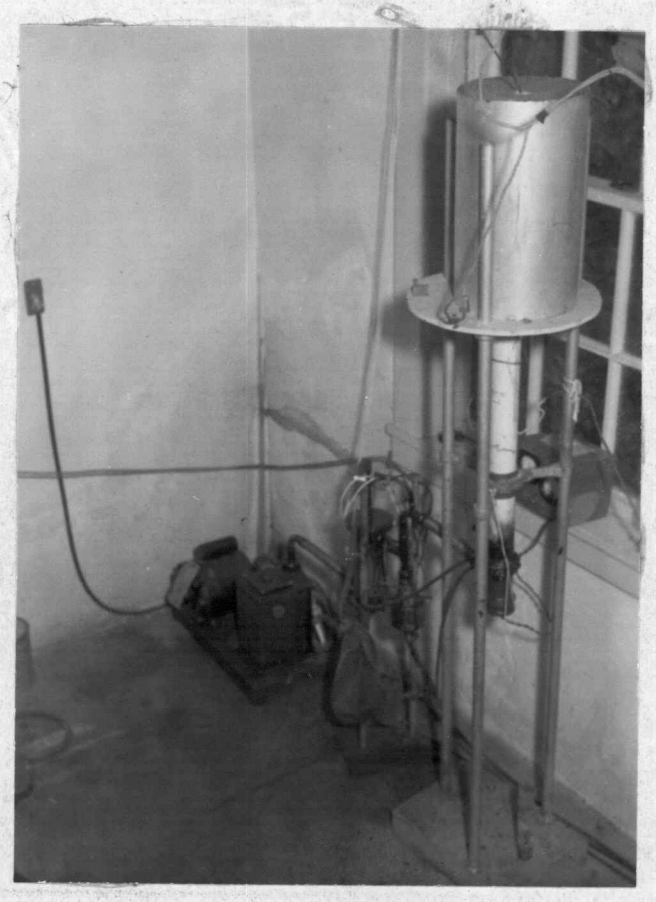

Figure 6. Electric Vacuum Furnace used for Alloying Magnesium with Zirconium.

Magnesium-zirconium alloys are very difficult to polish. Special technique is required to prevent the magnesium from being ground away much more rapidly than the zirconium and leaving an undesirable relief effect. The following polishing procedure resulted in flat surfaces on the alloy specimens.

#2	paper
#1	paper
#0	paper
#00	paper
#000	paper soaked with benzine cut with paraffin
Linde "A"	polishing powder on Gamal cloth

For the pure metals, magnesium and zirconium, the following polishing procedure gave good results.

#2	paper
#1	paper
#0	paper
#00	paper
280	Aloxite on canvass
600	Silicon-carbide on billiard cloth
Linde "A"	polishing powder on Gamal cloth

Electrolytic polishing worked very well on the pure magnesium, but was not successful with the mixed metals as the magnesium solid solution was attacked much more vigorously than the zirconium globules.

Pure magnesium and the magnesium solid solution alloys were etched to best advantage with 3 per cent Nital. Many other recommended etching solutions were

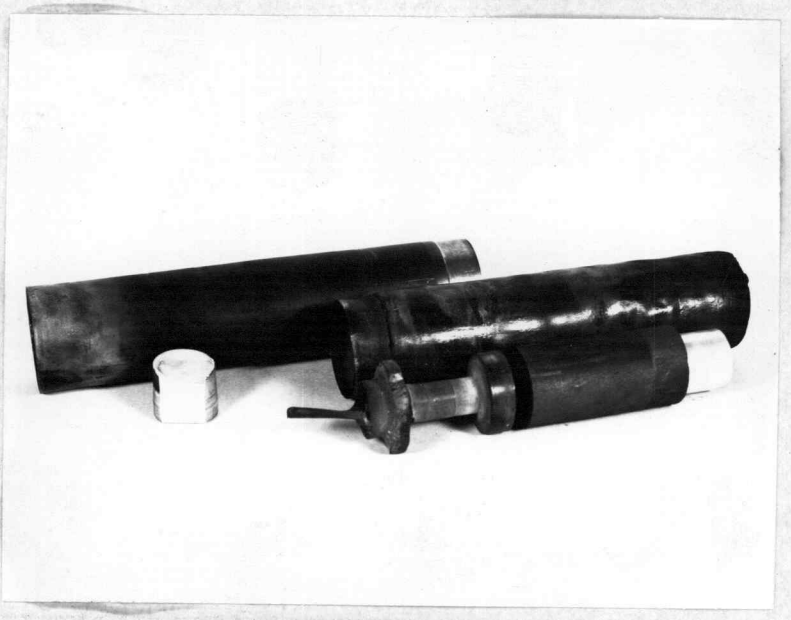

Figure 7. Steel Liner-Condenser, used for Distilling Magnesium from Magnesium-Zirconium Alloy, shown with Specimen Holder, Carbon Crucible, and Finished Magnesium-Zirconium Ingot.

Figure 8. Cutaway View of Magnesium-Zirconium Diffusion Specimen with Carbon Crucible.

tried but none were superior to Nital. The zirconium-rich portion of the alloys can be etched, without affecting the magnesium, with a 10 per cent solution of HF in alcohol. Additions of glycerin to the HF solution will selectively stain the specimen and so give greater contrast between grains.

Micro-hardness. Hardness measurements were made of the phases appearing in the microstructure of the alloys. A Tukon Tester equipped with a Knoop indenter was used for these measurements. The Knoop indenter gives a diamond-shaped impression, the diagonals of which have an approximate relation of 7 to 1. The long diagonal is a measure of the indentation hardness of a material. The Tukon Tester applies loads of from 0.025 Kg to 3.5 Kg and a load is chosen within these limits to keep the indentation, of the Knoop indenter, within a suitable length range.

X-ray Diffraction. X-ray diffraction studies were made on three alloys of magnesium-zirconium using copper radiation and a nickel filter. A General Electric diffraction unit equipped with a Debye-Scherrer camera was used. Small wedges, of the alloy to be tested, were prepared and the x-ray beam was passed through the sharp edge of the wedge. The sides of the wedges were carefully prepared on No. 00 paper and finally etched to remove any

cold work.

Vacuum Furnace. A vacuum furnace has as essential parts a roughing pump, a drier, a diffusion pump, and a heating chamber. The roughing pump is essentially a mechanical air compressor with the vacuum system connected to the intake. The drier consists of trays of phosphorus-pentoxide over which the gases leaving the diffusion pump must pass. If water vapor is not absorbed a good vacuum is impossible. A diffusion pump works on the same principle as an aspirator. In an inner chamber of a diffusion pump a low-vapor pressure oil is boiled and the hot vapor ejected from the upper part downward toward the cool outer walls of an outer chamber. The oil condenses as it hits the cool outer wall and runs to the bottom of the pump to be reboiled. In traveling its circuit the oil aspirates the gas to be evacuated out of the high vacuum region. The roughing pump must lower the pressure to 100 microns of mercury, or less, at the diffusion pump for correct operation of the diffusion pump.

In this experiment an electric resistor furnace equipped with an aluminum oxide tube was used for heating the specimens. A Brown potentiometer connected to a platinum platinum-rhodium thermocouple was used to control the temperature in the furnace. A valve on the drier connected a rubber bag full of helium to the system so

that a helium atmosphere could be maintained in the furnace. Figure 6 is a photograph of the vacuum system used.

The passages in a high vacuum system should be as large and direct as possible and should be scrupulously clean and dry. Most cleaning fluids should not be used in vacuum systems. Small leaks in the system are usually plugged with wax applied melted with a small torch.

DISCUSSION OF ALLOYS PRODUCED

Metallographic Examination. Photomicrographs for pure magnesium (Dominion, high purity) and for ductile zirconium (99.5% zirconium, 0.1% carbon, 0.1% iron) are shown in Figure 9 and Figure 17, respectively. All polishing and etching treatments given to any sample were also given the pure metals for comparison purposes.

The area shown in Figure 9 of Dominion magnesium, was particularly chosen as it illustrates the microstructure of some of the impurities found in magnesium. By a comparison, with the microstructure of inclusions as given by Beck (3, p38-45), the two large inclusions in the light grain are probably calcium while the small black dots are iron. Also to be found in the magnesium, though not shown in Figure 9, are very small gray inclusions of manganese.

The photomicrograph of ductile zirconium, Figure 17, shows the typical grain structure of alpha zirconium plus randomly oriented plates of zirconium carbide (ZrC).

Metallographic examination of the low-zirconium alloys shows a solubility of zirconium in magnesium of about 2 per cent. Alloys containing 1.7% zirconium and 1.8% zirconium were made, and when etched with either 3 per cent Nital or a 10 per cent HF solution in alcohol,

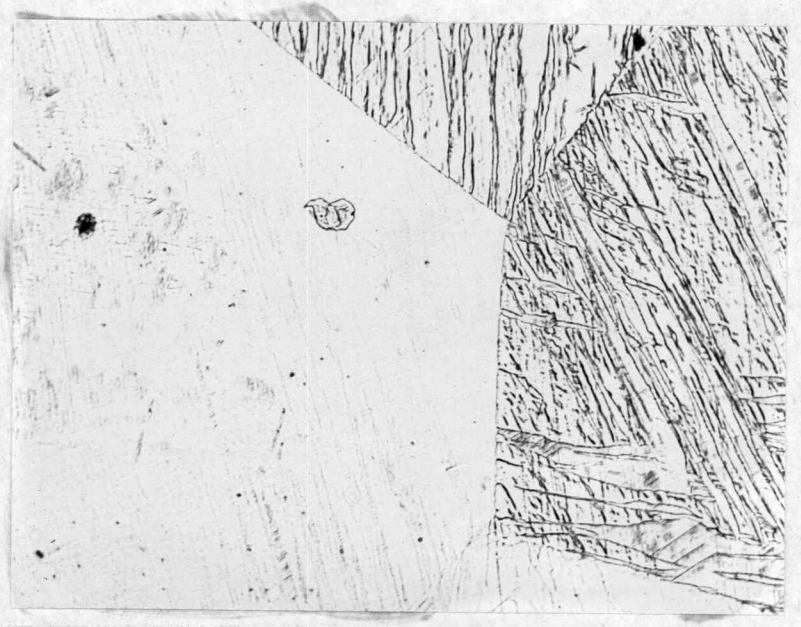

Figure 9. Dominion, High Purity, Magnesium
3% Nital Etch, 100x.

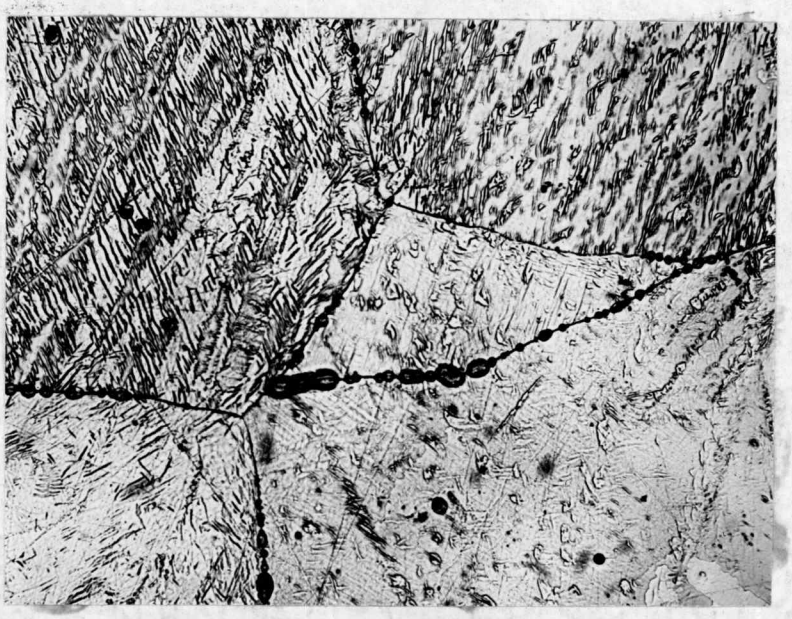

Figure 10. Magnesium-Zirconium Alloy Containing
1.9% Zirconium, 3% Nital Etch, 250x.

looked no different than the pure magnesium. Finer grain size did, however, accompany an increase in zirconium content. Figure 10 is a photomicrograph of a 1.9% zirconium alloy and a precipitation, presumably of zirconium, can be seen at the grain boundaries. The alloy shown in Figure 10 had been soaked at 650 C for 18 hours after which it was removed from the hot zone of the furnace to cool in helium.

At medium zirconium concentrations small globules of zirconium collect at the grain boundaries as shown in Figure 11 and Figure 12. The alloy photographed in Figure 11 and Figure 12 has a zirconium content of 20.8%. Using the polishing technique used for the pure metals, as outlined previously, these clusters of zirconium globules look very much like a eutectic structure. At low magnification the microstructure might be interpreted incorrectly, even though careful polishing, as outlined for mixed magnesium-zirconium structures, had been performed. Figure 11 shows these small zirconium globules at low magnification. Figure 12 shows the same area as Figure 11, but at three times the magnification; the individual zirconium globules are now very apparent.

Magnesium-zirconium alloys containing above 20 per cent zirconium take on a structure of zirconium globules in the magnesium solid solution. Figure 13 and Figure 14

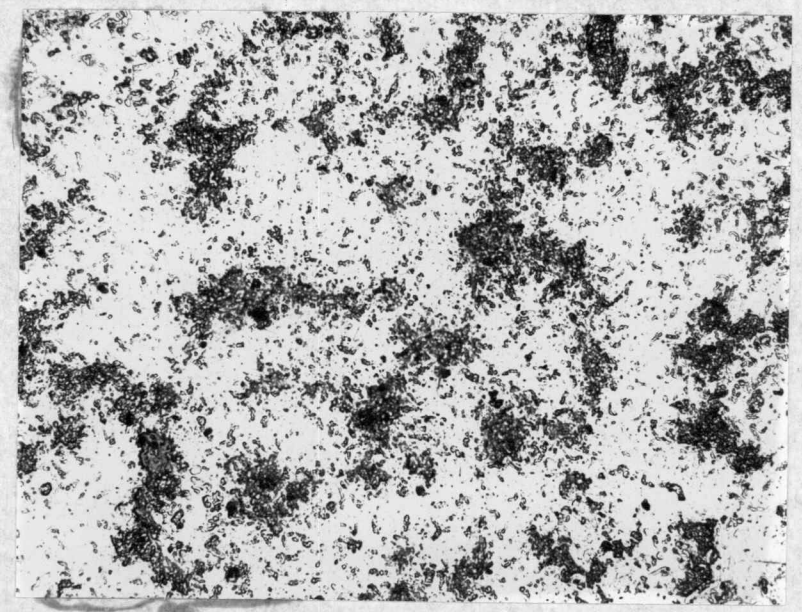

Figure 11. Magnesium-Zirconium Alloy Containing 20.8% Zirconium, Unetched, 250x.

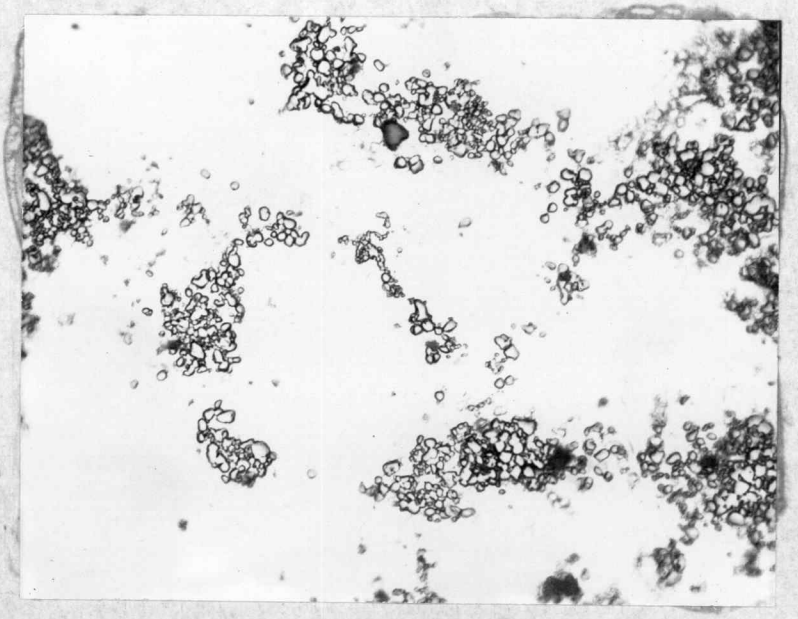

Figure 12. Magnesium-Zirconium Alloy Containing 20.8% Zirconium, Unetched, 750x.

show how zirconium shavings have been broken down into these globules. Figure 13 is a micrograph of an alloy containing 80 per cent zirconium, made with large shavings of zirconium; the shavings are just starting to disintegrate. Figure 14 is a micrograph of an alloy containing 50 per cent zirconium, made with small shavings of zirconium; the shavings have been completely changed to small globules. This radical change of physical shape of the zirconium shavings, without a eutectic structure being formed, indicates a peritectic reaction.

The alloys formed in the steel bombs at 700 C showed a marked deterioration of the zirconium shavings to nodules; indication of a peritectic temperature below 700 C.

Figure 15 and Figure 16 are photomicrographs of the diffusion specimen. An unetched picture of zirconium globules leaving the interface between the magnesium and zirconium is shown in Figure 15. The interface and part of the zirconium of the diffusion specimen, etched with a solution of HF in alcohol and glycerin, is shown in Figure 16. A transition zone may be seen in Figure 16 between the magnesium and the zirconium but this observer believes that with better polishing this transition zone would disappear.

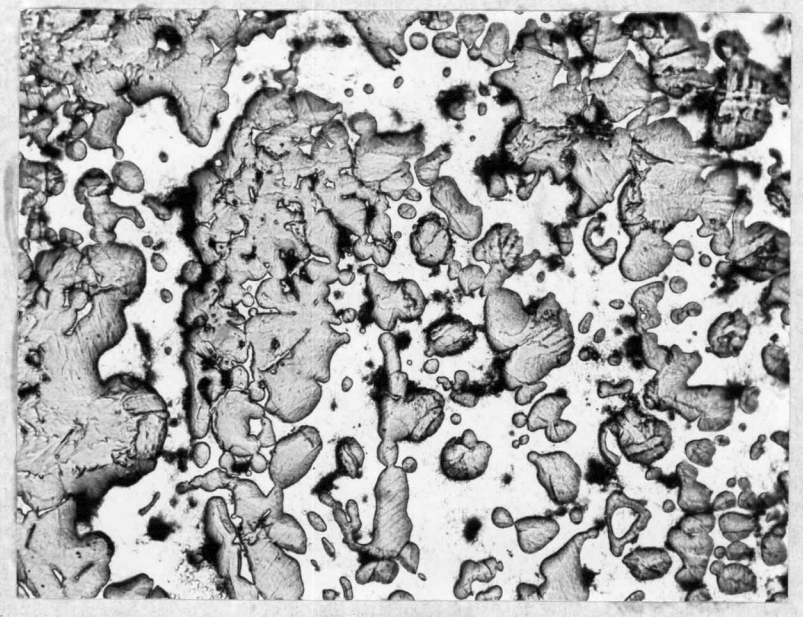

Figure 13. Large Shavings of Zirconium, in Magnesium, Disintegrating to Globular Structure, Unetched, 250x.

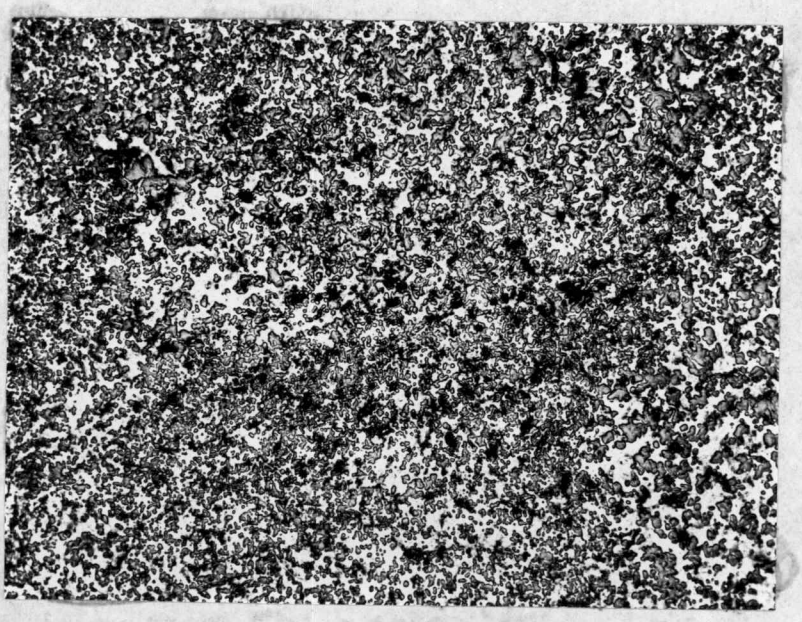

Figure 14. Complete Breakdown of Fine Zirconium Shavings, in Magnesium, to a Globular Structure Unetched, 250x.

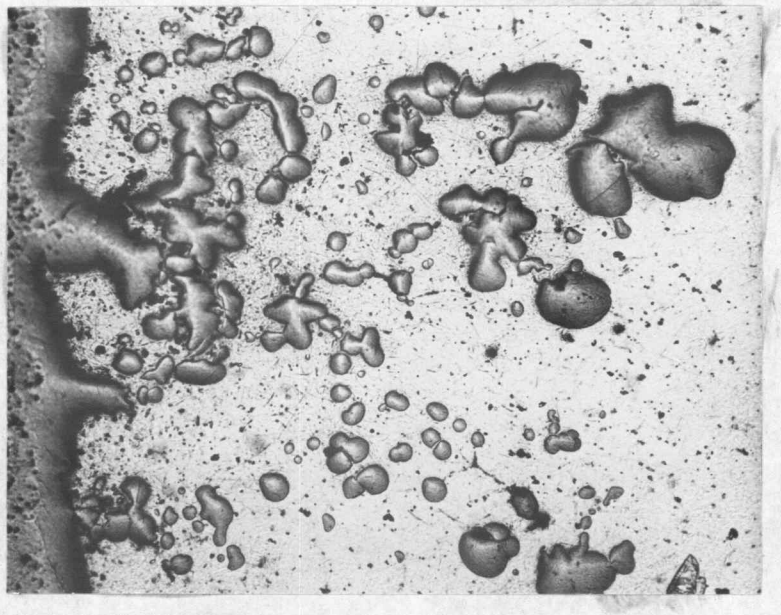

Figure 15. Globules of Zirconium Leaving the Interface between the Magnesium and Zirconium in a Diffusion Study Specimen, Unetched, 250x.

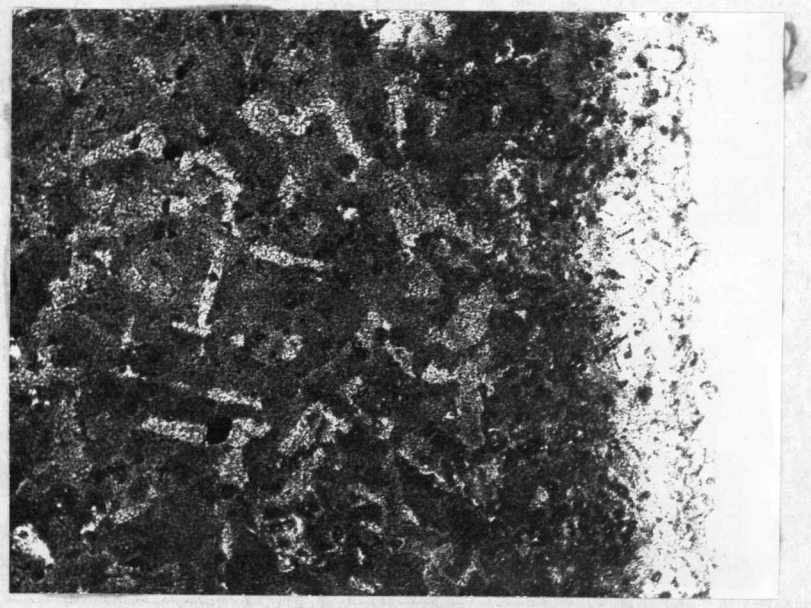

Figure 16. Transition Zone in Magnesium-Zirconium Diffusion Specimen, Alpha Grain Structure Shown in Zirconium, 10% HF - 60% Alcohol - 30% Glycerin Etch, 100x.

Metallographic examination of the magnesium-zirconium alloys showed many different structures most of which proved false. Extremely careful polishing and etching procedure is necessary to assure correct micro-structures. Various mixtures of the solid solution of magnesium with zirconium globules were the only true microstructures found in the magnesium-zirconium alloy system.

Micro-hardness. Micro-hardness tests were made on many of the alloys and the hardness measurements confirmed the results from the metallographic study. The hardness of the zirconium globules was found to be very close to that of pure zirconium (Knoop 220). An alloy of 2 per cent zirconium in magnesium showed an average hardness of Knoop 37, which was slightly higher than that for pure magnesium (Knoop 25). The light constituent surrounding the zirconium globules invariably had a Knoop hardness near 50. Since the hardness measurements were all made on single grains the hardness varied with the angular orientation of the long axis of the indenter. In the Dominion magnesium the hardness was found to vary between Knoop 17.6 and Knoop 31.9. The elastic recovery of indentations made with the Knoop indenter varied markedly also being greatest with the indenter in the direction of highest hardness.

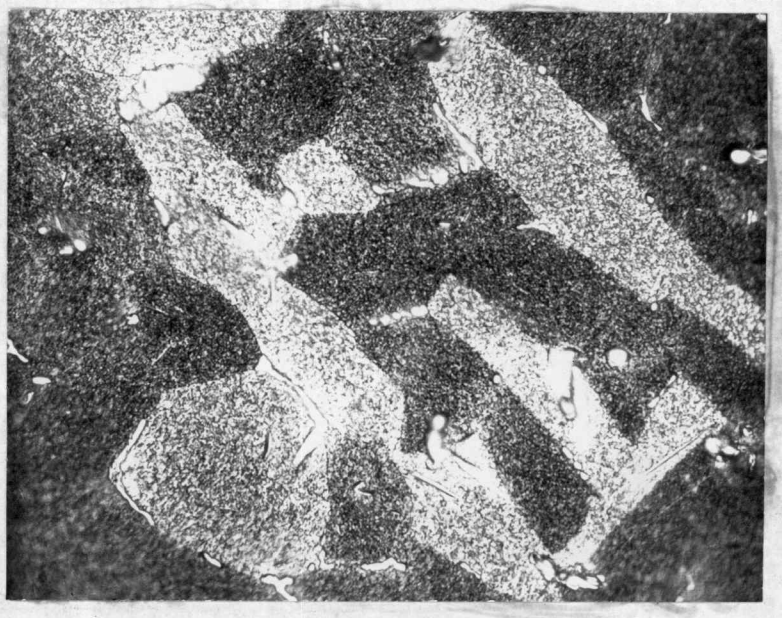

Figure 17. Ductile Zirconium (99.5% Zr, 0.1% C, 0.1% Fe) Showing Alpha Grain Structure and Zirconium-Carbide Particles, 10% HF - 60% Alcohol - 30% Glycerin Etch, 750x.

X-ray Diffraction. X-ray diffraction methods did not adapt themselves to the study of the magnesium-zirconium system. Very fine measurements are necessary to distinguish between the diffraction pattern for magnesium and the diffraction pattern for zirconium because of the similarity of the two metals' lattice dimensions. (Lattice constants for the two metals are given in Table) Diffraction patterns of three representative alloys of magnesium-zirconium were made, and in all cases the diffraction pattern was nearly identical to the diffraction pattern for either of the parent metals. Thus, the x-ray diffraction experiments made show no other phases beside magnesium, zirconium, and various mixtures of the two.

Segregation of Alloys. All of the alloys containing less than about 35 per cent zirconium showed a strong tendency to segregate into a layer of alloy containing about 2 per cent zirconium and another layer of alloy containing about 35 per cent zirconium. This may indicate formation of an unstable intermetallic compound in alloys containing about 35 per cent zirconium.

CONCLUSIONS

Further Research. Results from the three alloying techniques used in this investigation brought the author to the following conclusions:

1. Further research should be conducted at high pressures, so that temperatures above the boiling point of magnesium may be used. Leitgebel's graph (Figure 5) shows that equipment built to stand 100 atmospheres pressure would be necessary to retain the magnesium in the liquid form at the melting temperature of zirconium.

2. Long soaking periods at elevated temperature seem to promote segregation rather than help it. A positive stirring action is necessary to get an unsegregated structure in alloys containing less than about 35 per cent zirconium. Heating in an induction furnace would probably supply adequate stirring action.

3. A vacuum treatment, of alloys made with zirconium-hydride, is not satisfactory for the removal of hydrogen as most of the magnesium leaves with the hydrogen. Melting in a flow of helium would remove the hydrogen without distilling away the magnesium.

Constitution Diagram. A study of the magnesium-zirconium alloys, made during this investigation, has generally confirmed the constitution diagram as drawn by

Sauerwald (Figure 1-a). The author bases his confirmation of Sauerwald's work on the following factors:

1. A metallographic study of the alloys showed that molten magnesium at a temperature of 700 C has a definite action on zirconium, as attested to, by the disintegration of shavings to small globules (Figures 13 and 14). This factor was interpreted by the author to show that a peritectic reaction takes place at a temperature between 650 C and 700 C.

2. Magnesium will dissolve at least 1.8% zirconium. Metallographic observation of alloys containing 1.8% zirconium showed no different structure than pure magnesium other than a grain refinement.

3. Micro-hardness tests reveal an increase in average hardness in the magnesium solid solution from Knoop 25, for pure magnesium to Knoop 37, for a 1.8% zirconium alloy. Pure zirconium and the zirconium globules in the alloys all had the same hardness of Knoop 220.

4. X-ray diffraction patterns of three alloys varied insignificantly from the diffraction patterns for pure magnesium and pure zirconium.

5. A study by the author of the "factors-of-alloying," given in the Introduction, was corroborated in one respect by the experimental evidence just outlined. A comparison of the constitution diagrams of many alloys

of both magnesium and zirconium generally disclosed low solubility limits for both metals. The maximum solubility of zirconium in magnesium found in this investigation was 1.8%.

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