Magnesium-Rich Side of the Magnesium-Zirconium Constitution Diagram

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The magnesium-rich side of the magnesium-zirconium constitution diagram has been studied for the purpose of improving the previous work on this subject. A diagram has been developed that is similar in form to that found by previous investigators, but the phase boundaries differ as to temperatures and alloy compositions. The peritectic reaction was found to take place at 654° C, beginning at 0.58 percent of zirconium.

1. Introduction

The rapid expansion of the aircraft industry during World War II set the pace for the production and the development of magnesium alloys. Zirconium proved one of the most beneficial of the alloying elements used with magnesium. Additions of 0.4 to 0.8 percent of zirconium to magnesium impart a very fine grain size (0.02 mm diam.), relative insensitivity to notches, superior corrosion resistance, high strength, and ease of working.

The industrial utilization of zirconium in magnesium has proceeded more rapidly than the accumulation of basic data on the magnesium-zirconium system. Siebel [1] found a peritectic reaction at a temperature close to the melting point of magnesium. The liquidus and the peritectic temperatures coincided at 0.26 percent of zirconium, and then the liquidus rose very steeply with increase of zirconium until temperatures in the neighborhood of 1,000° C were reached, at which point the liquidus curved away toward the horizontal.

Nowotny [2] and his associates showed an alpha phase region with a maximum solubility of 0.87 percent of zirconium at 700° C. Adjacent to this zone was a two-phase region containing magnesium-rich alpha solid solution plus zirconium-rich beta solid solution. The structure became entirely beta when zirconium exceeded 30.3 weight percent. Volume curves for the beta phase showed a minimum in the region of 34.5 weight percent, possibly arising from a chemical affinity that forms Mg_2Zr, a valence bond type of compound analogous to Mg_2Si. The tendency for valence compound formation grew weaker with the increasing solubility of magnesium in zirconium. The results of this work are open to question because raw materials containing over 12 percent of impurities were used.

Sauerwald [3] melted magnesium and powdered zirconium in a steel crucible under an atmosphere of argon and determined the diagram shown in figure 1. Solution of iron by the melt affected the results adversely. By use of solid diffusion techniques, more zirconium was dissolved in the solid magnesium than in the liquid.

Recently, G. A. Mellor [4] of the National Physical Laboratory published a magnesium-zirconium diagram, figure 2, based on the addition of a "chloride-master-alloy" to melts made in iron and magnesia crucibles. Determining solid solubility by electrical resistivity measurements was hindered by contamination from atmospheric elements.

In all of these previous efforts, the inherent difficulties of obtaining accurate and reproducible results were apparent in the limited data obtained and the wide spread of compositions used in determining the points on the resulting diagrams. Nevertheless, figures 1 and 2 show that Sauerwald and Mellor are in fair agreement as to the general form of the magnesium-rich end of the diagram and differ only in degree.

A comparison of the fundamental characteristics of significance in studying the magnesium-zirconium system are summarized in table 1. Since the atomic diameter of magnesium is 3.20 and of zirconium 3.19 (crystal angstroms), the latter may be said to have an almost perfect "favorable-size factor" for alloying with magnesium. Solid solubility of zirconium in magnesium is also favored by the fact that both elements have a hexagonal-close-packed crystal structure. However, magnesium is in group II with a valence of 2, whereas zirconium is a transition element in group IV with zero alloying valency. As the valency between solvent, magnesium, and solute metals becomes more unequal, solid solutions become more restricted. Zirconium, therefore, has an unfavorable valence for solid solution in mag-

TABLE 1. *Comparison of physical constants of magnesium and zirconium*

	Mg	Zr
Atomic number	12	40
Group	IIA	IVA
Period	3	5
Crystal structure	HCP	α-HCP
Do	HCP	β-BCC
Atomic diameter (crystal angstroms)	3.20	3.19
Atomic weight	24.32	91.22
Density (g/cm³)	1.74	6.4
Melting point (° C)	650 ±2	1,750 ±700
Boiling point (° C)	1,110	
Latent heat of fusion (cal/g)	70.0	
Alloying valence	2	0
Electrical potential (referred to H⁺)	+2.34	+1.53
Electrical resistivity (microhm/cm)	4.33 (18° C)	41.0 (0° C)
Modulus of elasticity (psi×10⁶)	6.5	10.7

[1] G. Siebel, Unpublished work, referred to in The Technology of Magnesium and Its Alloys, by Adolph Beck p. 77 (F. A. Hughes & Co., Ltd., London, England 1941).

[2] H. Nowotny, E. Wormnes, and A. Mohrnheim, Investigations of Al-Ca, Mg-Ca, and Mg-Zr; Z. Metallkunde **32**, Heft 2, 39–42 (February 1940).

[3] Von F. Sauerwald, Das Zustandsdiagramm Magnesium-Zirkonium, Z. Anorg, Chem., **255**, Heft 1–3, 212–220 (December 1950).

[4] G. A. Mellor, The constitution of magnesium-rich alloys of magnesium and zirconium, J. Inst. Metals **77**, part 2 (1950).
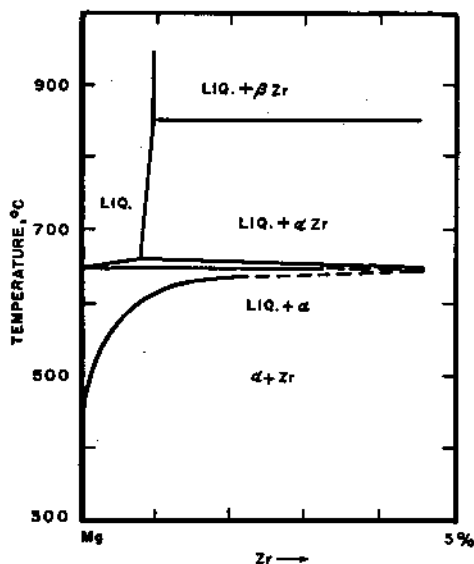
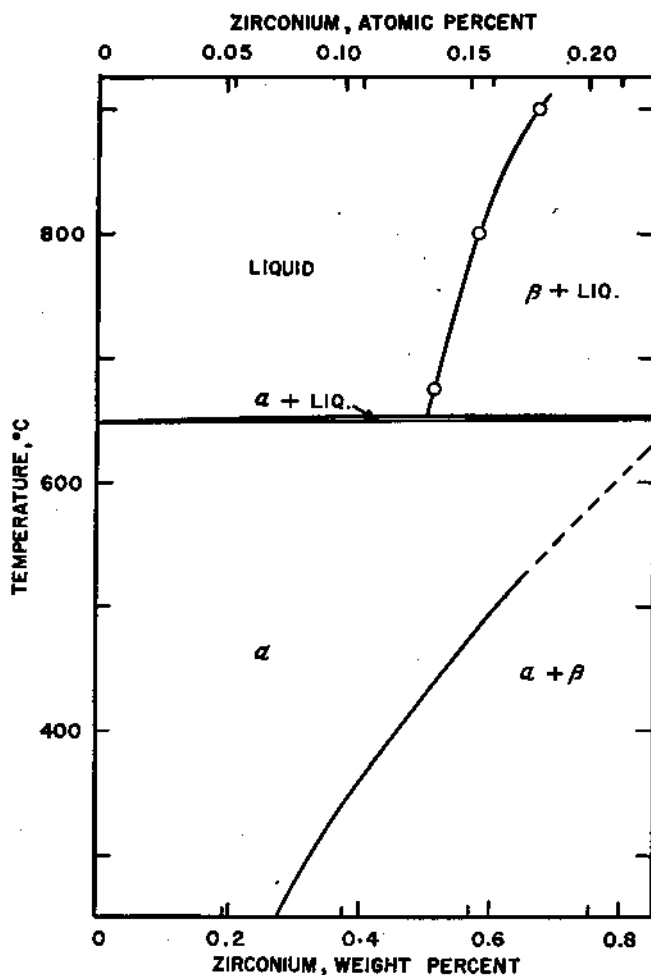FIGURE 1. *Magnesium-zirconium constitution diagram.*

By Sauerwald [3]

FIGURE 2. *Magnesium-zirconium constitution diagram.*

By Mellor [4]

nesium. Also, the more unequal the respective valency factors, the steeper is the slope of the liquidus and solidus curves, the latter being affected the most. A metal of lower valency tends to dissolve a metal of higher valency more readily than vice versa. This explains the low solubility of zirconium in magnesium and the high solubility of magnesium in zirconium. Zirconium is unique in that it is the only commercially significant transition element in groups III, IV, V, and VI used in magnesium-base alloys.

The more electropositive the solvent metal and the more electronegative the solute metal, the greater is the tendency to restrict solid solubility and form stable intermetallic compounds. If the solute atom, zirconium, has a choice of entering solid solution or forming a stable compound, it will form the latter.

Since the solubility of zirconium in magnesium is low and increases with temperature, it would be expected to manifest age-hardening properties.

Transition elements, such as zirconium, tend to form electron compounds, which are actually phases with wide ranges of homogeneity (like brass), in contrast to the restricted ranges of general intermetallic compounds. For zero valence type elements, such as zirconium, the valency electron concentration will vary from 2.0 to 1.5 when the atomic percent of solute varies from 0 to 25 percent.

Some doubt appears to exist as to the exact melting point of pure magnesium. The accepted figure is 651° C, but competent workers have obtained values from 647 to 652° C. This spread is quite small compared to the values of 1,750°±700° C reported for the melting point of zirconium.

2. Experimental Procedures

2.1. Survey of Raw Materials

As a preliminary step to actual study of the phase diagram, a survey of the purity and alloying characteristics of the available raw materials was made. Table 2 lists the spectrochemical analyses of the raw materials used. Because of the technical difficulties of removing hafnium from its "Siamese twin" zirconium, practically all commercial zirconium contains two to four percent of hafnium. Hafnium-free zirconium has only recently become available in quantity. The hardeners, such as 60 percent Zr-40 percent Mg and 40 percent Zr-60 percent Mg alloys, and the proprietary compound, TAM flux,[5] contained the most impurities. Spectrochemical analyses of the magnesium-zirconium alloys made from these raw materials showed no discernible increase in impurities beyond those already present in the commercially pure magnesium. The highest contents of zirconium in the alloys resulted when the hardeners and the flux were used. In subsequent heats it was discovered that the hardeners were very heterogenous in composition because they were mechanical mixtures of magnesium and zirconium. It was difficult

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[5] Contains 50 percent of ZrCl₄, 25 percent of NaCl, and 25 percent of KCl.

Table 2. *Spectrochemical analyses of raw materials*

VS=10 to 100%; S=1 to 10%; M=0.1 to 1.0%; W=0.01 to 0.1%; VW=0.001 to 0.01%; T=0.0001 to 0.001%; FT=0.00001 to 0.0001%

Raw material	Chemical elements																				
	Ag	Al	B	Ba	Ca	Cr	Cu	Fe	Hf	K	Mg	Mn	Mo	Na	Ni	Pb	Si	Sr	Sn	Ti	Zr
Dow commercially pure magnesium		T		T	T		VW	W			VS	W					VW			T	
Zr metal	FT	T	W		W		W	M	8		VW				M		T		T	T	VS
TAM flux [1]	T	W	W		M	T	VW	W	W	M	VW	T	T	VS	W	T	W	M		T	VS

[1] Contains 50% of ZrCl₄, 25% of NaCl, and 25% of KCl.

to avoid inclusions in alloys made with the flux because of the formation of a large amount of slag and dross. Zirconium tetrachloride was unsatisfactory because it reacted too readily with the atmosphere and was ineffective in introducing zirconium into the molten magnesium because of the violence of its dissociation. Zirconium hydride floated on the surface of the melt, was pyrophoric, and formed considerable slag. Powdered zirconium also oxidized rapidly. Despite its slow rate of solution, the high purity and low reactivity of zirconium sheet made it the preferable material for most of the subsequent work.

2.2. Melting Techniques

In the course of this investigation various melting procedures were evaluated and modifications were adapted to fit the special requirements unique to phase-diagram studies. In screening the raw materials, described in the preceding section, approximately 350 g of magnesium were placed in an ingot-iron crucible, covered with a graphite lid, and melted by means of a 35-kva high-frequency induction furnace. One percent of zirconium, in the various raw material forms tested, was added to the molten magnesium at 760° C, superheated to 960° C, cooled to 800° C, and poured into a graphite-ingot mold.

Because zirconium is so much heavier than magnesium, some heats were stirred with a graphite rod attached to the shaft of an electric motor. This procedure proved undesirable because it stirred many inclusions into the alloy and tended to emulsify the zirconium in the magnesium, making a mechanical mixture with a highly insoluble zirconium constituent.

Induction melting was not used extensively in the project because it was difficult to hold melts at constant temperature for long periods of time with this type of melting.

In order to have accurately controlled heating, cooling, melting, and holding cycles, an electric resistance furnace was built. Nichrome wire was wound around a 3-in.-diameter Alundum tube, coated with Alundum cement, placed within another larger Alundum tube, and then packed in diatomaceous earth for thermal insulation. Partial on and off controls were incorporated into the electrical system by the use of a variable transformer, slide wire resistances, and an electronic high-speed controller-recorder. A Chromel-Alumel thermocouple was located between the two Alundum tubes, adjacent to the Nichrome coil, and connected to the controller. Graphite and ingot-iron crucibles, measuring 2½ in. in diameter by 8 in. high, were used for melting without protective atmosphere. A brick of diatomaceous earth on top of the furnace tube reduced heat loss by radiation.

In order to melt the alloys under a protective atmosphere, a steel bomb-type container was designed, as shown in figure 3. A 2-in.-diameter graphite crucible held the melt in the bomb. Water-cooling of the lid and flange protected the rubber gasket between them. A steel tube sheathed the Chromel-Alumel thermocouple used in measuring melt temperatures and taking cooling curves. An inlet pipe was connected to a system of valves and gages that permitted the bomb to be evacuated with a vacuum pump and filled with helium. Another opening in the lid was provided for removing molten alloy samples.

Limited stirring of melts was effected by attaching a mechanical vibrator to the steel thermocouple protection tube.
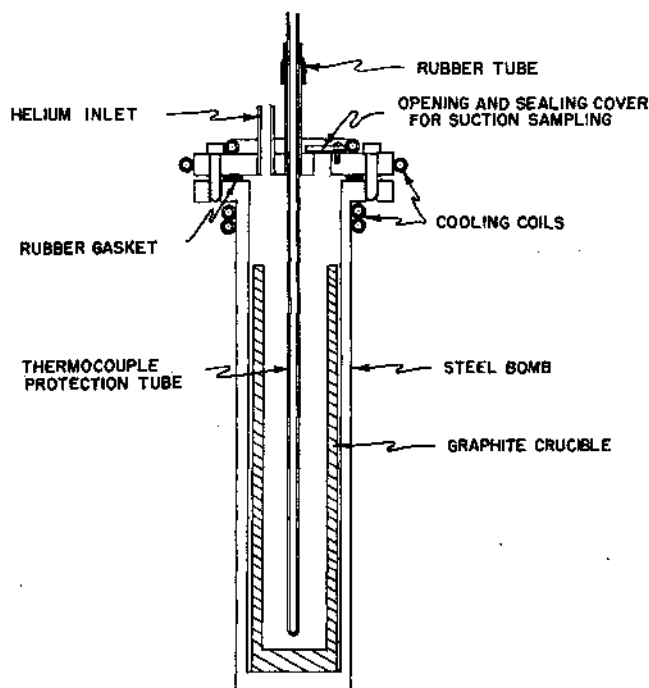

FIGURE 3. *Steel bomb for melting under protective atmosphere.*

2.3. Chemical Analysis

One of the difficulties encountered in studies of the magnesium-zirconium system is the tendency for zirconium, elemental or combined, to become mechanically entrapped as an extremely fine colloidal suspension. It is necessary, then, to distinguish between zirconium in solution in the magnesium and zirconium mechanically suspended as inclusions. Some of the disagreement in the results of previous investigations may be attributed to variation in the effectiveness of analytical procedures in distinguishing between the dissolved and the undissolved constituents of the alloys. The insoluble zirconium can be observed in the microstructure but its quantitative evaluation has required analytical techniques involving differential solubility in acid. Hydrochloric acid, nitric acid, and sulfuric acid of various concentrations have been used for this purpose with varying results and degrees of success.

The Analytical Chemistry Section of the Bureau cooperated by developing the analytical procedure used and compared the results with those of other investigators. Because the chemical-analysis technique is an important factor in the development of the diagram, it is given in detail in the Appendix, section 5. In brief, the magnesium-zirconium alloy sample was dissolved in 15-percent hydrochloric acid and filtered. As only the soluble zirconium constituent of the alloy dissolved in the acid, the amount was determined by precipitating it from the filtrate with ammonium phosphate. The insoluble zirconium constituent of the alloy remaining on the filter paper was put in solution by fusion with potassium bisulfate and sulfuric acid and the zirconium determined by precipitation as the di-ammonium phosphate.

Because of the conflict of opinion concerning the best acid and concentration to use for dissolving the alloy samples, tests were made in which duplicate magnesium-zirconium specimens were treated with 10-percent HCl, 15-percent HCl, 4.8-percent H_2SO_4, and 11-percent HNO_3 solutions. The latter three acids were all the same normality, that is, 1.7 N. Soluble and insoluble zirconium were then determined according to steps II and III described in the Appendix. No significant difference in soluble and insoluble zirconium contents were obtained from the different acids or concentrations used in the tests.

2.4. Electrical Resistance Measurements

Because the electrical resistance of an alloy changes abruptly as melting occurs, this method was used to determine both the solidus and liquidus of some of the alloys. Electrical resistance test specimens were made by pouring magnesium, or its alloys with zirconium, into a graphite mold containing four Nichrome wires inserted at the corner positions. Two of these wires carried the current to and from the specimen; the other two were used to measure the potential drop across it. The specimen was cast as a slab measuring 1 3/4 in. long, 1 in. wide, and 3/16 in. thick, and was sawed as shown in figure 4. Figure 5
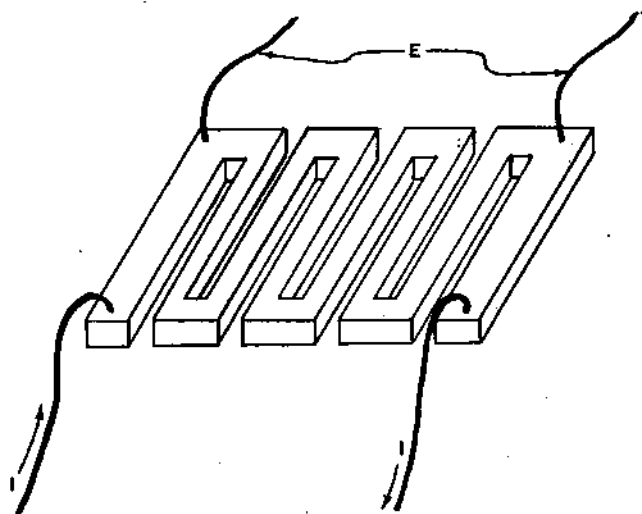

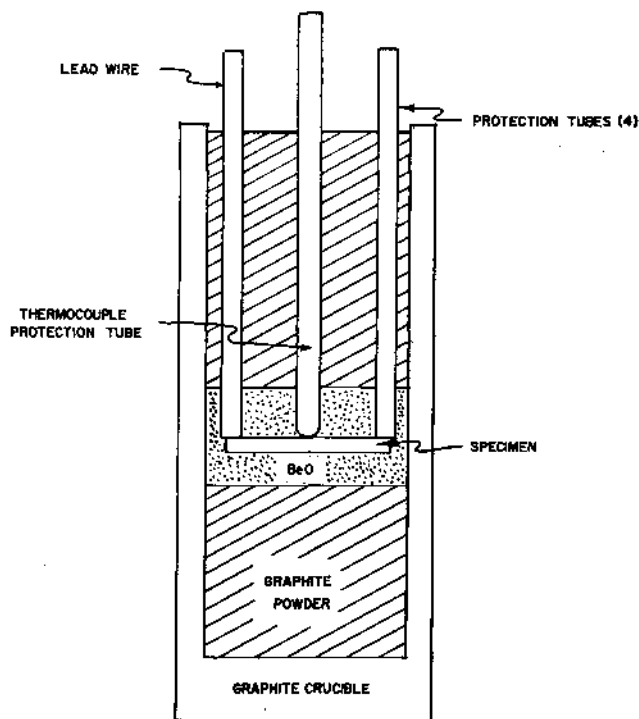FIGURE 4. *Electrical resistance test specimen.*

FIGURE 5. *Packing arrangement of resistance specimen in crucible.*

illustrates the manner in which the resistance grid was packed in a graphite crucible, and figure 6 is a schematic drawing of the electric circuits required. The crucible and contents were placed in the electric resistance furnace and heated at a rate of 0.5 deg C per minute. A steady current from a 6-volt battery was sent through the specimen, using the wires marked I, figure 4, during the period of the test, and the IR drop across the specimen was continuously recorded with an electric recorder, using the
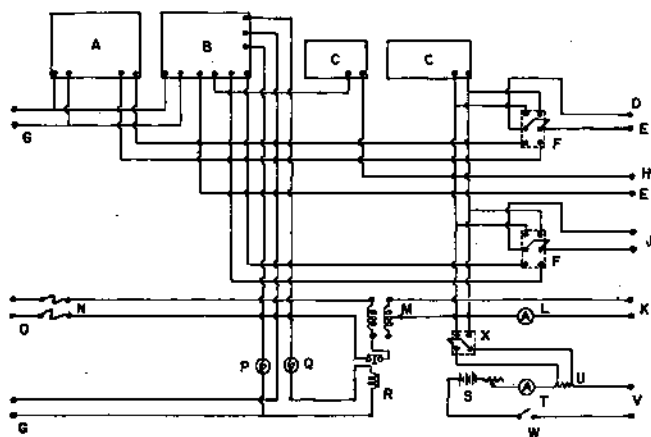
FIGURE 6. *Electrical circuits for resistance measurements.*

A, Recorder; B, controller recorder; C, potentiometers; D,E, specimen thermocouple; F, DPDT switch; G, 110-v a-c current; H,E, furnace thermocouple; J, unknown grid; K, furnace coil; L, 0 to 20-amp ammeter; M, variable transformer; N, 15-amp current; O, 220-v a-c current; P, green light; Q, red light, R, relay; S, 6-v battery; T, 0 to 1.5-amp ammeter; U, known 0.001 standard ohm; V, emf to grid; W, SPST switch; X, DPST switch.
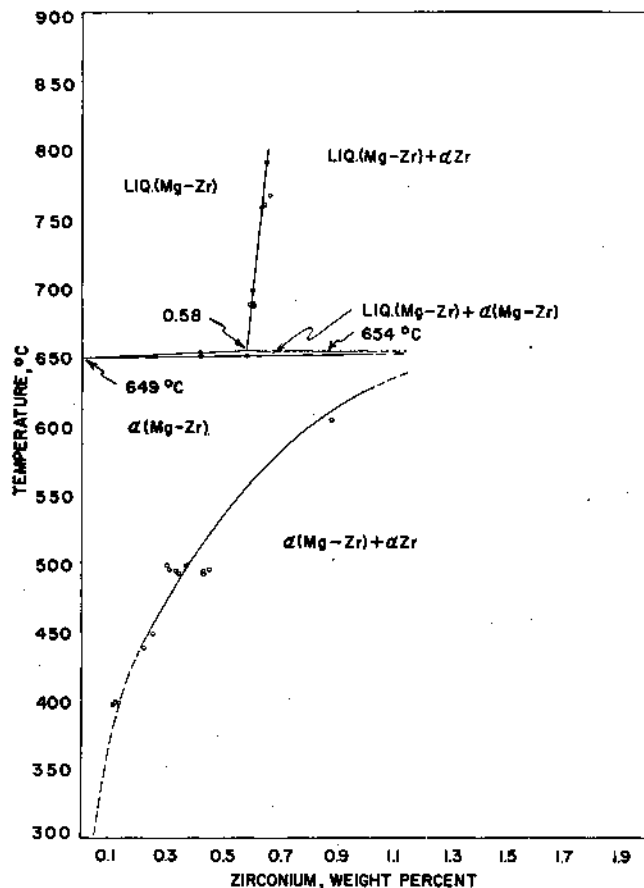

FIGURE 7. *NBS magnesium-zirconium constitution diagram.*

wires marked E. The temperature was simultaneously recorded with a second electronic recorder. A standard resistance was incorporated into the circuit to standardize the current during the course of an experiment and to permit conversion of millivolts to ohms when necessary. As the temperature of the specimen approached a critical point, temperature was measured with a semi-precision potentiometer. As the temperature increased, the resistance of the specimen gradually increased until a sharp increase in resistance indicated the beginning of melting. Careful packing in beryllia held the grid in shape and prevented short circuits even when the specimen was molten.

2.5. Suction Sampling

Previous investigators found that the liquidus above the peritectic line had an almost vertical slope and consequently precluded the use of cooling curves for locating its position. As an alternative, dip samples of the molten alloys were analyzed to find the solubility limits.

In this project, points on the liquidus were determined in the following manner. One hundred grams of commercially pure magnesium were charged into a graphite crucible with 2 percent of zirconium as narrow strips of pure zirconium sheet. After the crucible was placed in the steel bomb and sealed, it was evacuated and flushed with helium several times as the temperature rose and finally held under helium pressure of about 5 lb/in ^{2}. When the alloy melted, the protection tube was lowered to the bottom of the crucible so that the thermocouple bead was located $1\frac{1}{2}$ in. from the bottom of the melt. This thermocouple was connected to a semiprecision potentiometer. Experimental data obtained but not included in this paper showed that 3 hr, the period for which the alloys were held molten, was adequate for the attainment of equilibrium between the liquid and the excess zirconium. The access lid on the top of the bomb was then slid open and a Pyrex glass tube (4-mm inside diam) was immersed in the melt to a point opposite the thermocouple bead. An alloy sample was quickly sucked out of the melt by the action of a rubber suction bulb on the other end of the tube. At the moment of sampling a temperature reading was made with the adjacent thermocouple. The samples obtained in this manner were analyzed for total zirconium because it was presumed that all the zirconium in the melt at the time of sampling would have to be in solution. The excess zirconium, not in solution, settles to the bottom of the melt because its density is 6.4 compared with 1.74 for magnesium.

An alternative procedure for obtaining suction samples proved quite successful and was used for locating six of the points shown on the diagram (fig. 7). In these heats 300 g of commercially pure magnesium were melted in a graphite crucible with Dow 310 flux for protection. At 760° C, 6 percent of zirconium in the form of the chloride flux was stirred into the melt and the alloy held at constant temperature for 3 hr. Suction samples were taken, as described in the previous technique, at a point opposite the thermocouple bead indicating the melt temperature.

2.6. Heat Treatment

Determination of points on the solvus are unusually difficult because the magnesium-zirconium alloys comprise a sluggish metastable system in the solid state. During heating or cooling there is no measurable heat of reaction when crossing the solvus line and apparently no change in soluble zirconium. Most of these alloys exist at room temperature with from 0.4 to 0.8 percent of zirconium in solid solution when theoretically zirconium is practically insoluble in magnesium at room temperature. Such pseudo-stability indicated the need for lengthy heat treatments in order to approach true stable equilibrium. The heat-treatment time required to reach equilibrium probably becomes longer as the temperature is lowered.

The stability of the alpha solid solution was demonstrated by heating alloys, in about one-half hour, to within 2 deg of the melting point, followed by water quenching. Chemical analysis showed no change in zirconium in solid solution. Microscopic examination revealed grain growth, as would be expected.

It was planned originally to follow the progress of zirconium solution into, or rejection from, the alpha solid solution by observing the change in electrical resistance of alloy grids held at constant temperature for extended periods of time. The extensive equipment required for this work (described in a previous section) and the long periods of time needed for the heat treatments led to the substitution of the following procedure for location of points on the solvus. Ingots of different analyses were sectioned and cold rolled to a reduction of 25 percent, the purpose of the cold-rolling being to reduce the stability of the zirconium in solid solution. Four small duplicate samples were cut from a rolled specimen with high soluble and low insoluble zirconium content and another four obtained from a specimen with low soluble and high insoluble zirconium. Nichrome wires were tied to each specimen to facilitate their removal at various stages of heat treatment. The samples were then packed with graphite dust in a graphite crucible and placed in an electric resistance furnace. Various sets of samples were subjected to isothermal heat treatments at temperatures ranging from 190° to 635° C for periods of 100 to 500 hr.

At the end of 50- or 100-hr intervals one specimen of each analysis was removed from the furnace by means of the Nichrome wire and water-quenched. These samples were analyzed for the amount of solid soluble and insoluble zirconium (as described in Appendix) to observe their progress toward reaching equilibrium.

Because of the low vaporization point of magnesium, the alloys were prone to evaporate, even below their melting point, given sufficient time. Also, a steady conversion of soluble zirconium to the insoluble form, with time and temperature, seemed to indicate the formation of an inert compound such as the carbide, nitride, or oxide. Both of these effects were reduced by covering the specimens with several coats of a wash made from a cristobalite investment material.

3. Results

3.1. Melting Point of Magnesium

The melting point of the basic raw material—Dow commercially pure magnesium—was determined by means of inverse-rate cooling curves taken on 450-g melts contained in a graphite crucible. Heating and cooling was controlled in the resistance furnace to give a rate of 2° C per minute. Three heating and cooling cycles indicated the melting point to be 648.7° ±0.2° C. The 22 gage Chromel-Alumel thermocouples used were standardized against the melting point of NBS Standard Temperature Sample 44d (pure aluminum, 659.7° C).

The melting point also was determined by using the electrical resistance technique described previously. Although less accurate than the cooling-curve results, the observed melting point of 648.5 ±0.5° C was in good agreement.

3.2. The Liquidus

Points on the liquidus were determined by analyzing the total zirconium content of samples removed from saturated melts by the suction technique described in section 2.5.

The data obtained in these tests are shown in table 3 and plotted in figure 7.

TABLE 3. *Points on the liquidus as determined by suction tests*

Temperature	Zirconium	Raw material
° C	*Percent*	
791	0.65	TAM flux.
767	.66	Zr sheet.
760	.64	TAM flux.
758	.63	Zr sheet.
698	.60	Do.
688	.59	TAM flux.
688	.59	Do.
688	.60	Do.
687	.60	Do.

The proximity of the solidus and the liquidus to the left of the peritectic line makes it difficult to distinguish between them. Although past investigators have claimed the location of the liquidus by arrests on the cooling and heating curves, examination of this portion of the diagram in figure 7 reveals that the change in heat evolution when crossing the liquidus is almost imperceptible, whereas the heat evolution at the solidus, as indicated by the lever-arm principle, is quite marked.

Electrical resistance measurements proved to be sufficiently sensitive to differentiate between the liquidus and solidus. Figure 8 is a plot of the temperature versus millivolt drop across an electrical resistance grid made from an alloy containing 0.42 percent of zirconium in solution. By slowly heating
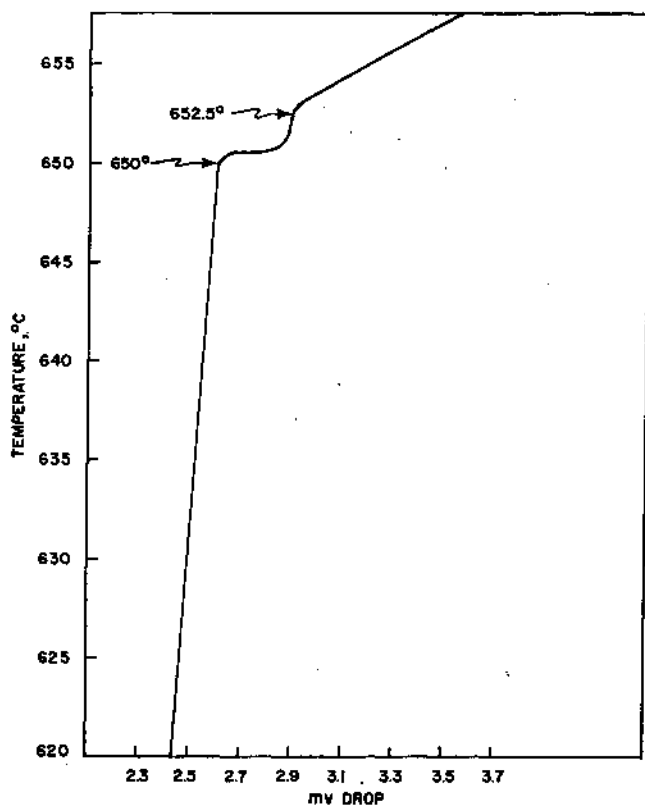
FIGURE 8. *Relation between temperature and electrical resistance on heating a magnesium-zirconium alloy containing 0.42 percent of zirconium in solution*

3.4. The Solvus

Points on the solvus were determined by lengthy isothermal heat treatments described in section 2.6. Table 4 contains data obtained in these experiments, and figure 7 shows the solvus line plotted from them.

Below 400° C the alloys were so stable that no change in soluble zirconium took place during the

TABLE 4. *Composition of alloys after isothermal heat treatment*

Temperature of heat treatment	Time held at temperature	Zirconium		
		Soluble	Insoluble	Total
°C	Hours	Percent	Percent	Percent
604	113	0.89	0.88	1.77
498	172	.37	.15	0.52
498	172	.32	.18	.50
495	387	.45	.11	.56
495	387	.31	.19	.50
494	292	.43	.11	.54
494	292	.33	.20	.53
492	196	.43	.11	.54
492	196	.34	.17	.51
449	363	.25	.31	.56
438	242	.22	.31	.53
398	156	(ᵃ)	(ᵃ)	(ᵃ)
305	503	(ᵃ)	(ᵃ)	(ᵃ)

ᵃ No change from original composition

entire heat treatment and above 500° C results were erratic because of the strong tendency for the alloys to react with environmental elements. It is of interest to note that there was always some insoluble zirconium present in the alloys regardless of the temperature or time of heat treatment.

3.5. Other Observations

The similarity of the lattice constants of magnesium and zirconium precluded the use of X-ray diffraction techniques. However, the two metals do differ sufficiently in their X-ray absorption characteristics to distinguish between them in microradiographs. A number of microradiographs were made but were of no value as an accurate quantitative measure of zirconium content. They were of interest, however, from a qualitative viewpoint to indicate distribution of insoluble zirconium and its compounds, as may be seen in figure 9A. The specimen shown in this microradiograph contained 0.09 percent of soluble zirconium plus 0.26 percent of insoluble zirconium. The dark background is the magnesium-zirconium solid solution containing 0.09 percent of zirconium and the light particles and clusters are the 0.26 percent of undissolved or insoluble zirconium.

Brinell-hardness measurements on a series of magnesium-zirconium alloys showed no correlation with total or soluble zirconium content.

Although photomicrographs were of no value in indicating the amount of zirconium in solid solution, the grain-refining influence of zirconium can be observed by comparing the grain size of unalloyed magnesium, figure 9, B, with that of an alloy containing 0.54 percent of zirconium in solution, figure 9, C.
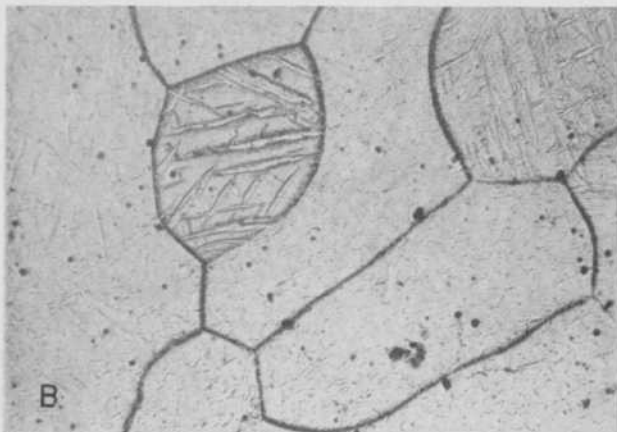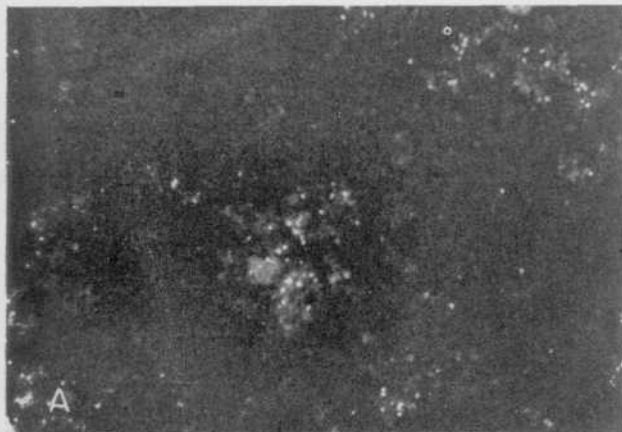
the alloy grid up to and beyond the melting point it was possible to observe both the solidus, at 650° C, and the liquidus, at 652.5° C.

By extrapolating a line from the melting point of magnesium through this one point on the liquidus to the intersection with a similar extension of the liquidus line above the peritectic, the beginning of the peritectic line was located at 0.58 percent of zirconium and 654° C.

3.3. The Solidus

Since the heat evolution at the solidus is quite marked, thermal analysis was utilized for locating its position. Three inverse-rate cooling curves and one heating curve of melts saturated with zirconium (from zirconium sheet) revealed the solidus thermal arrest at 650.5 ±0.5° C. This point is shown on figure 7, directly below the left end of the peritectic line.

An electrical resistance experiment, described in section 3.2, located the solidus of a sample containing 0.42 percent of soluble zirconium at 650° C. The complete solidus line is located in figure 7 by drawing a straight line from the melting point of magnesium through the two points noted above and extending it to the point of intersection with the horizontal peritectic line, determined as noted in section 3.2.

FIGURE 9. *Magnesium-zirconium alloys at ×100.*

A, Photomicroradiograph of an "as cast" magnesium-zirconium alloy containing 0.09 percent of soluble zirconium and 0.26 percent of insoluble; B, photomicrograph of "as cast" commercially pure magnesium; C, photomicrograph of "as cast" magnesium-zirconium alloy containing 0.54 percent of soluble and 0.06 percent of insoluble zirconium (B and C, etched with ethylene glycol).

4. Summary

As a result of the work described it was found that the magnesium-rich side of the magnesium-zirconium diagram, shown in figure 7, was similar in form to those developed by Sauerwald and Mellor.

The intersection of the liquidus and peritectic lines was located between the values reported by these two previous investigators. The peritectic reaction and the solidus were observed at higher temperatures than in the other two diagrams. Location of the solvus at high temperatures was handicapped by the vapor pressure of magnesium and the reactivity of zirconium. Heat treatments below 400° C apparently had no effect on the soluble zirconium constituent of the alloys. In order to distinguish accurately between the soluble and insoluble zirconium, an improved chemical-analysis technique was developed. All the alloys analyzed contained an insoluble zirconium constituent at room temperature. Microradiography proved useful for observing the distribution of insoluble zirconium and its compounds.

5. Appendix. Determination of "Soluble" and "Insoluble" Zirconium in Magnesium

R. K. Bell, B. B. Bendigo, and E. E. Maczkowskie

1. REAGENTS

(a) Ammonium phosphate solution, 15 percent: Dissolve 150 g of $(NH_4)_2HPO_4$ in about 800 ml of water and dilute to 1 liter.

(b) Hydrogen peroxide, 30 percent.

(c) Ammonium nitrate wash solution (50 g/liter).

2. PROCEDURE

I. Decomposition of Sample.

(a) Transfer a 1–g sample (approximately ¼-in. cubes) to a 600-ml beaker and add 300 ml of hydrochloric acid (15+85). (All the acid should be added at one stroke.) When the sample is decomposed, *immediately* filter through a tight paper, using paper pulp, and wash with hot water.

(b) Reserve the filtrate, (a), which contains the "soluble" zirconium. Place the paper, (B), which contains the insoluble zirconium, in a platinum crucible and reserve.

II. Determination of "soluble" zirconium.

(a) Add 60 ml of sulfuric acid (1+1) to the reserve filtrate (A), section 2 I(b), and heat to fumes of sulfuric acid. Fume for 5 to 10 min., cool, and dilute to 275 ml.

(b) Add 1 ml of H_2O_2 (30 percent) and 25 ml of the ammonium phosphate solution. Digest at 40° to 50° C for 2 hr or overnight if only a small amount of precipitate is visible.

(c) Cool and add a little paper pulp. Stir and allow the precipitate to settle. Filter through a tight paper containing a little paper pulp and wash about 10 times with the NH_4NO_3 wash solution. Discard the filtrate.

(d) Place the paper and contents in a weighed platinum crucible and ignite carefully under good oxidizing conditions until the carbon has been removed. Finally, ignite at 1,050° C for 20 min. Weigh as ZrP_2O_7.

$$\% \text{ Zr} = \frac{0.344 \times \text{wt of } ZrP_2O_7 \text{ in grams}}{\text{wt of sample in grams}} \times 100.$$

III. Determination of "insoluble" zirconium.

(a) Ignite the reserved paper and contents (B), section 2, I(b), at 500° C until the carbon is destroyed. Cool, and add 2 drops of sulfuric acid (1+1) and 5 ml of hydrofluoric acid (48 percent). Heat cautiously until fuming has ceased. Cool, and add just enough fused $KHSO_4$ to cover the residue and heat until the melt is clear. Cool, transfer the crucible and its lid to a 250-ml beaker, and add 40 ml of sulfuric acid (1+1). When the melt has dissolved, wash and remove the crucible and lid. Dilute to 175 ml.

(b) Continue as directed in section 2, II(b) to (d).

WASHINGTON, June 5, 1952.