COMPARISON OF THE GRAIN-REFINING CHARACTERISTICS
OF ZIRCONIUM AND CALCIUM ON MAGNESIUM

by

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INTRODUCTION

Magnesium is the lightest of all structural metals, and this low specific gravity endows many novel applications to engineering. Magnesium, like aluminum some years ago, has lately advanced from the position of being a "curiosity" metal to one of vast industrial and military importance, with a production running into many thousands of tons per annum.

During World War II great expansions were made to meet the need of war requirements. The aircraft industry alone used thousands of tons of magnesium. In the field of pyrotechnics immense quantities of magnesium ribbon, powder, and metal were used. If the magnesium industry is to improve, now that the war is over, research must be conducted on every phase of the product.

The purpose of this investigation was to study and make a comparison of the relative effects of calcium and zirconium upon the grain size and physical properties of magnesium and magnesium zinc alloys. Binary and ternary alloys were studied; i. e., magnesium with 4 per cent zinc, with additions up to 1.25 per cent calcium and then additions up to 1 per cent zirconium. This conviction was developed in a survey of the literature on grain refinement due to alloying elements.

REVIEW OF LITERATURE

It was found after thorough checking of the library facilities, that there are very few articles pertaining to grain-size

refinement in magnesium by the use of calcium and zirconium. The material that has been written will be found under the heading metallography. Sauerwald, Eisenreich, and Holub (16) have several patents covering various percentages of zirconium in magnesium, but these are very brief and contain no information as to the quantity of zirconium used to get various effects.

METALLOGRAPHY

Although much research has been conducted on this entire system, considerable disagreement still exists concerning the reactions and phases of many of the equilibrium diagrams.

Mg - Zn Alloy System

Magnesium is slightly strengthened by additions of zinc, but not to the same degree as with aluminum. Magnesium with a zinc content up to 2 per cent softens more readily when heated and can be worked at lower temperatures than other alloys. This is because of the lower eutectic melting temperature of 645.8° F. As in the binary aluminum alloys, hot-shortness occurs well below the eutectic temperature. Zinc improves the ductility of magnesium up to a content of about 3 per cent. Age hardening was observed from 2 per cent and up by McDonald (10).

Figure 1 shows the constitution diagram of the magnesium-rich alloys of the magnesium-zinc system according to the careful investigation of Chadwick (4). Chadwick's diagram is modified to include the MgZn compound reported by Hume-Rothery and Rounsefell (19). This portion of the diagram shows a simple eutectic
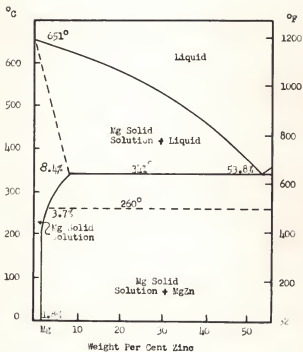
Fig. 1. Magnesium – Zinc constitution diagram.

system of alloys except for the solubility of zinc in magnesium and the polymorphic transformation of the MgZn compound. The eutectic point falls at 53.8 per cent by weight of zinc and at 341° C. (645.8° F.). The solubility of zinc in Alpha(Mg) is 1.8 per cent at 0° C. and increases to 8.4 per cent at the eutectic temperature.

The intermetallic compound MgZn in binary magnesium-zinc alloys cannot be distinguished microscopically from Beta(Mg-Al). However, in the commercial alloys zinc is added only in conjunction with aluminum and in lesser amounts than the aluminum additions. Zinc is used in magnesium alloys to increase their corrosion resistance.

Mg - Ca Alloy System

Probably the greatest benefit of calcium additions to magnesium is its strong grain refining and grain growth inhibiting powers. This not only toughens magnesium at ordinary temperatures, but also improves its mechanical properties at elevated temperatures. This grain refinement is brought about by such small amounts as 0.1 to 0.2 per cent calcium. These small additions also reduce the tendency of magnesium and its alloys to burn in casting, and appreciably reduce the amount of scale formed during annealing. McDonald (10) investigated the effects of calcium additions on the tensile properties of magnesium, and his findings show fair agreement. A rapid rise in ductility is seen up to 0.1 per cent calcium which is maintained to 0.3 per cent calcium after which it slowly decreases. The rise of strength is rapid up to 0.3 per cent, but still increases at a

good rate beyond this.

The Mg - Ca system was first investigated by Baar (2) in 1911, who constructed the first equilibrium diagram. He reported a compound of Mg_4Ca_3 whose melting temperature was 715° C. and a $Mg-Mg_4Ca_3$ eutectic at 18.7 per cent calcium. Second to publish information about his work was Paris (14) in 1934, who contended the compound was Mg_5Ca_3 which had a melting point of 725° C. He listed a $Mg-Mg_5Ca_3$ eutectic at 17 per cent calcium and at 528° C.

In 1937 the work of Vosskuhler (19) and Witte (20) was published. Vosskuhler carried out the most exhaustive investigation of the Mg-Ca system, and his equilibrium diagram is shown in Fig. 2. Vosskuhler used thermal and microscopic means of analysis. His work shows a compound at 45.2 per cent by weight calcium of Mg_2Ca which has a melting point of 714° C. The $Mg-Mg_2Ca$ eutectic was found to fall at 16.3 per cent by weight of calcium and at 516° C. The solubility of calcium in magnesium Vosskuhler reports to be .18 per cent at 300° C. and .78 per cent at the eutectic temperature.

Mg - Zr Alloy System

The important literature concerning zirconium in magnesium-base alloys is predominately contained in patent references. Sauerwald, Eisenreich, and Holub (16) discovered the profound grain-refining influence of small amounts of zirconium on cast magnesium and the attendant increases in strength and ductility. They extended their work to reveal that limited amounts of certain other elements, including aluminum and zinc, could be added
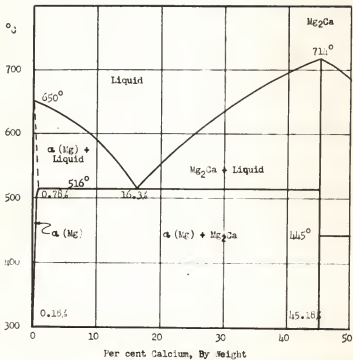
Fig. 2. Magnesium end of the magnesium-calcium constitutional
diagram.

for further improvement in strength and hardness. Doan and An-
sel (5) carried out extensive work on the extrusion of the Mg-Zn-
Zr alloys. They found that zirconium greatly increases the ex-
trudability of Mg-Zn alloys, and greatly refines the grain size
and inhibits grain growth, which in turn strengthens these al-
loys and gives a high ratio of compressiveness to tensile strength.

The author could locate no satisfactory constitution diagram
for the Mg-Zr system. According to Beck (3), a peritectic reac-
tion takes place in the system at a temperature close to the
melting point of magnesium. The liquidus meets the peritectic
temperature at 0.26 per cent zirconium; and then rises very
steeply with increase of zirconium until the neighborhood of
1000° C. (1632° F.) is reached, where it curves away toward the
horizontal. Using electrical conductivity measurements, Beck (3)
reports solid solubility of zirconium in magnesium as 0.8 per
cent or more at 500° C. and less than 0.1 per cent at 400° C.

GRAIN-SIZE THEORY AND DETERMINATION

Almost as soon as the microscope was directed at metallic
bodies, it was found that they consisted of minute grains. It
was not until 1898, however, that studies of etching pits ac-
tually revealed that the small grains were in reality crystals.
The name "crystals" had until then been applied only to mineral
crystals, with their symmetrical form and regular cleavage. When
Laue began the study of crystals structures with X-ray in 1912,
the fact that metals were crystalline became a familiar circum-
stance. It is now known further that even those properties of

crystals which are associated with minerals (regularity of out-
line and manner of cleavage) may be observed also in metals.

The subject of grain size of metals has been the object of
intensive interest for a number of years. It has been more thor-
oughly investigated in steels than in the nonferrous alloys; how-
ever, extensive research has been done on wrought copper alloys.
The influence of grain size on the properties of steels has been
well recognized and accepted.

In general, grains are of irregular shape. Even in a single
small piece of metal there may be considerable variation in the
size of neighboring grains. In estimating their average size,
however, it is convenient to idealize and regard them as cubical
or spherical. On a cubical basis, the edge length of a cube of
average volume is called the "grain size". The physical proper-
ties of metals and other solids are closely related to the grain
size. Two pieces of metal of identical chemical composition will
differ in their physical properties if their grain size differ.
Consequently, grain size is one of the features commonly measured
by metallographers.

A grain is, of course, a three-dimensional affair, and a
plane section through the grain, as through any of those photo-
graphed, shows but two of these; indirectly, however, if the num-
ber of grains present is sufficient to permit a statistical dis-
tribution, the section tells something about the "missing" dimen-
sion. A properly chosen section through a crystalline mass
should then give one a fair idea of the average grain size of
the sample. This, in fact, is the way that grain size is com-
monly determined, and size is reported in area units, as for

example, square millimeters. Plainly, such a measuring method cannot be applied safely to areas which have a small number of unequally sized grains. A reliable evaluation of size in such specimens requires the exploration of large areas.

It is well to recognize clearly that some difference may exist between the mechanism and laws of crystal growth as these pertain to the birth and growth of crystals in melts during freezing, and those which control recrystallization in the solid state, as for example, the recrystallization of strain-hardened metal. In both cases, however, the primary reason is the same; the tendency of all matter to assume the most stable form; i. e., the one possessing the least internal energy. This is, indeed, the precise reason that crystallization occurs in the first place, for the crystalline state represents a condition of lower energy content than the liquid state. In the former state of matter, the particular geometrical form of least internal energy is the one having least surface area per unit mass, that is to say, that the limiting condition of crystalline matter, with regard to its energy state, is a single crystal of spherical shape.

With respect to the ultimate grain size of a cast metal (or alloy), there are two determining factors at work during the solidification process: one of these is the rate of nuclear formation and the other is the rate of crystal growth. Whenever crystal growth, for any reason, becomes the more predominant factor in the process, there are relatively few centers of crystallization, but these few nuclei grow rapidly into a few large grains, and the resulting solid will possess a generally coarse-grained
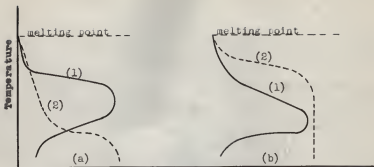
Fig. 3. Two possible relationships between the nucleation rate (1) and the crystal growth rate (2).

structure. On the other hand, if the rate of nucleation is rapid as compared with the growth rate, a large number of growing crystallites marks the progress of freezing almost from the start, and the final solid will be fine-grained. The rate at which nucleation proceeds in a melt--the nuclei number--is small immediately below the freezing point, but increases with the degree of undercooling to a maximum, Fig. 3 (curves 1 of a and b). The value of the nuclei number for the metals is very large, while for slags and glasses it is low. With the former it is impossible, by varying the conditions of solidification (as for example its speed), to secure anything but a crystallized aggregate; while, with the latter class of nonmetallic materials, the production of an undercooled liquid is more frequent than otherwise.

The second step concerned in crystallization is the growth of the several nuclei. The nuclear growth rate also increases

as the temperature falls below the freezing point, attaining eventually a maximum which may be, as regards temperature, either below or above the maximum on the nuclei number curve, Fig. 3 (curve 2 of a and b). When the maximum growth rate is, in point of temperature, below the maximum rate of nucleation as in (a) of Fig. 3, a large number of nuclei form, but any marked growth is delayed until somewhat lower temperatures are attained. A slow rate of cooling of the melt, therefore, brings a large number of nuclear crystals into the maximum growth range, and a fast rate only a small number. The first procedure obviously results in the production of the finer grained aggregate. When the maximum growth rate occurs earlier than the maximum rate at which the nuclei will grow, as in (b) of Fig. 3, nuclei start growing vigorously as fast as they form. A rapid rate of cooling of the melt is, then, conducive to a smaller average grain size, since the sooner the maximum-nucleation-rate range is reached, the more prominent nuclear formation becomes in comparison with nuclear growth.

The above statement that the final grain size of cast metals depends chiefly on the relative predominance of the rates of nucleation and crystal growth does not apply to cases where polymorphic changes occur in the metal or alloy, since these later changes are of some consequence in determining the final grain size of the material. The process whereby a new crystalline form, or even a new set of crystals of like form, is created from preexisting crystalline matter is known as recrystallisation, a name which precisely describes the phenomenon. One common

cause of recrystallization in metals and alloys is the occurrence of a polymorphic change.

Magnesium alloys, as they are now generally understood, differ in some important respects from most other structural alloys, but it is a matter of general understanding that the finer grain structures possess superior mechanical properties, enhanced amenability to solution treatment, and improved machinability. In these respects, the metal is somewhat similar to the austenitic steels and some of the aluminum alloys. A peculiarity of this metal is that frequently the fine grain resulting from superheating is preserved in subsequent remelting. One school of thought is that small magnesium oxide particles are formed during superheating; these particles then serve as nucleolating agents for the formation of fine grains during solidification. While this phenomenon has apparently not received the attention and study that it may well deserve, and as a result is little understood, its circumstance has been confirmed.

The recognition of the influence of grain-size in austenitic steels resulted in the need for correlation between grain-size and mechanical properties and a clear-cut means of reporting grain-size for analytical purposes. Since the grain-size of magnesium has such an important bearing on the mechanical properties of its alloys, it would seem of appreciable importance to establish a recognized and standard method for its recording and correlation to the mechanical properties. Its effect on mechanical properties and on possible heat-treating requirements is a highly important factor, and it is economically desirable

that the magnesium producers and fabricators be able to control the grain-size in the finished product and to correlate intelligently that size to necessary heat treatment and anticipated results.

In the United States there is a method of grain-size measurements outlined in the A. S. T. M. Tentative Methods of Preparation of Micrographs of Metals and Alloys (E 2 - 39 T). A planimetric or direct comparison of a micrograph or projected image with standard micrographs or network charts is recommended for material in which the grains are to be judged. There are standard photomicrographs provided by this Society for this purpose. When wrought and cast magnesium alloys are studied, they are usually graded in various grain-sizes at 100 magnifications, Plate I. This proposed system starts with the largest grains and proceeds higher numerically with decreasing grain-size and increasing number of grains per unit of area. The A. S. T. M. grain-size number used is given by the following formula:

$$n = 2^{N-1}$$

where: n is the number of grains in each square inch at 100 magnification.

N is the A. S. T. M. grain size number.

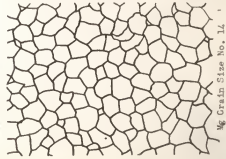EXPLANATION OF PLATE I

Proposed magnesium network chart

PLATE III

Mg Grain Size No. 13

Mg Grain Size No. 17

Mg Grain Size No. 12

Mg Grain Size No. 16

Mg Grain Size No. 11

Mg Grain Size No. 15

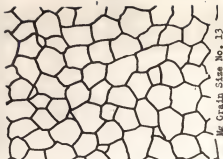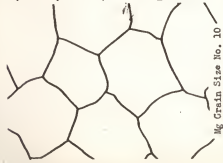Mg Grain Size No. 10

Mg Grain Size No. 14
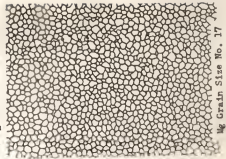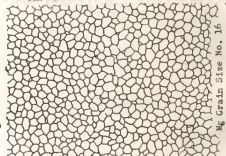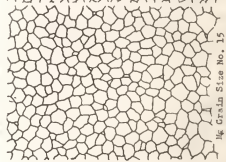
Table 1. A comparison between A. S. T. M. austenitic steel
grain-size numbers and the proposed grain-size
numbers for magnesium.

Magnesium grain-size number	:	Corresponding A. S. T. M. grain-size number
1	:	-8
2	:	-7
3	:	-6
4	:	-5
5	:	-4
6	:	-3
7	:	-2
8	:	-1
9	:	0
10	:	1
11	:	2
12	:	3
13	:	4
14	:	5
15	:	6
16	:	7
17	:	8
18	:	9
19	:	10

The system that is presented has been the outgrowth of an in-
dustrial requirement, and in its various stages of development has
been applied in operation over the past years. It is readily ap-
parent that this system is a modification of the Society's stan-
dards for austenitic grain-sizes, and that the standard network
charts presented are from that source.

MELTING REFINING AND CASTING

For a complete and comprehensive discussion of melting and
refining of magnesium the reader is referred to the excellent
paper prepared by Nelson (13).

Refining and Melting

In the following few pages it might be well to outline the common melting and refining practices especially adaptable to individual research. The processes to be discussed will be limited to primary magnesium. In general, there are two types of primary magnesium: one, the well-known ingot, made by electrolytic reduction process, and the second a crystalline condensed product, which is a newly-introduced reduction process such as the ferro-silicon-dolomite reaction.

The use of crystalline magnesium is quite limited in the field as the melting and the refining of the crystalline material are somewhat difficult. Crystalline magnesium is finely divided and hence oxidized readily. Furthermore, a variable and sometimes appreciable amount of oxide, nitrides, and other impurities are occulded with the crystals. Inasmuch as the ingot is more readily obtained and in a more desirable form, it shall be considered to be our supply of primary magnesium.

The melting and refining of secondary magnesium such as light scrap, dross, turnings, etc., will not be discussed in this thesis.

Little special description need be given to the magnesium ingot, since this product is a solid ingot that is already in a well-refined state. The only significant impurity in this metal is iron, which at saturation is 0.030 per cent when at the temperature of the electreytic cell.

The melting and refining processes for magnesium and its alloys require the use of fluxes. These fluxes have a magnesium chloride base, and other halide salts or oxides are added to give a density or behavior exactly suited to the particular melting practice. The successful handling of magnesium depends upon the proper use of the correct fluxes.

There are two general methods of melting magnesium. They are as follows: open pot method and the crucible process.

The crucible process was the one adopted, and was found to have considerable merit over other types for private research. This process makes use of No. 310 flux, the composition being 20.0 per cent KCl, 50.0 per cent $MgCl_2$, 15.0 per cent CaF_2, and 15.0 per cent MgO. This flux has the property of being thinly fluid at the start to provide protection and refining qualities, and then drying out or thickening after a time, leaving a protecting crust on the pot surface until the time of casting. At that time it can be readily skimmed off or held back, thus allowing the contents of the crucible to be poured out directly into castings without fear of flux contamination. This flux is not self-healing in its film protection, hence is not suitable for hand-ladling operations.

Crucible melting is one of the methods commonly used for the production of sand and permanent-mold castings. The steps in the process are as follows:

1. Steel crucibles in the size range of 10 to 100 pounds of magnesium are commonly used.

2. The crucible is placed in the setting, heated, and dusted with 310 flux.

3. Solid ingot of the correct composition is introduced into the crucible.

4. No. 310 flux is carefully sprinkled over the entire charge.

5. After the charge is melted down and raised to a temperature of approximately 1325° F., a quantity of fresh 310 flux (approximately 0.5 per cent) is added and allowed to melt, after which it is vigorously stirred through the metal. This refining operation should take about one minute, and serves to agglomerate the dross so that part of it rises to the surface of the metal and the remainder goes to the bottom into the sludge.

6. The clinker-like dross that rises to the surface should be carefully skimmed off and fresh 310 flux immediately dusted behind the skimmer to prevent reoxidation. Some of the sludge is removed with the skimmings, and the rest of the sludge remains in the bottom of the crucible. If there is any question as to the quality of the refining treatment, a little more flux should be added, the stirring operation repeated, and the melt again skimmed. The absence of substantial quantities of dross on the second skimming indicates that the refining treatment was adequate.

7. A moderate quantity (0.5 to 1 per cent) of 310 flux should then be spread over the surface of the crucible, the temperature raised to 1600° F. to 1650° F., and held for about 15 minutes. This treatment refines the grain in the alloy and causes the flux to "cure" or dry out, so that when the metal cools to the required casting temperature the flux either can be pushed back away from the lip or entirely skimmed off before pouring.

Again sulphur, or a mixture of sulphur and boric acid, is used for protection during pouring. If the proper refining and fluxing technique is not followed, the flux occasionally may dry out or crumble after superheating, thus allowing oxidation. A very light dusting at the exact point of oxidation is permissible, but the general remedy is better refining and the use of more flux at the refining stage. It is quite important that no prolonged delay is allowed between the time the metal is at the superheating temperature--that is, 1600° F. or above--and the time of pour off. The superheating treatment causes a desirable grain refinement, which is lost rapidly on standing at lower temperatures.

8. The crucible size should be selected for a given casting job so that a small heel of metal will always be left in the crucible. After the pour off is finished, the crucible is returned to the melting room and the sides spudded down, fresh flux being added when required to inhibit oxidation, and the dross and sludge skimmed out of the bottom of the crucible. The heel of flux and metal then remaining may be used as a starter for the next charge.

Casting

The magnesium alloys were cast into a permanent mold which was preheated to 800° F., Plate IV. The castings were made horizontally and had the approximate dimensions of $1\frac{1}{2}$ inches in diameter by 9 inches in length. This was found to be a very nice size casting, as a grain-size sample and a tensile test specimen could be obtained from each casting.

EXPERIMENTAL PROCEDURE

Procedure

The crucible, well-cleaned, was heated and dusted with No. 310 flux equivalent to about one per cent of the charge to be melted. The magnesium ingot was charged into this flux bath, and additional flux was dusted over the charged and on the sides of the crucible. This procedure was quite time-consuming, as it took approximately two hours for the melt down. After the magnesium had become molten, which is above 1204° F., the crucible was closely watched in order to observe and dust over any burning spots that might appear. When the melt had reached a temperature of 1300° F. a refinement of the pure magnesium was performed. This refinement was accomplished by adding a small amount of 310 flux and stirring vigorously. This refining operation took about one minute and served to agglomerate the dross so that most of it floated to the surface of the metal and the remainder settled to the bottom into the sludge. The clinker-like dross that accumulated on the surface was skimmed off, discarded, and new 310 flux dusted on the surface to prevent reoxidation.

Once the magnesium has been refined, one may add various alloying elements. In the research that was carried out, the author used the following elements: zinc, calcium, and zirconium. The zinc was added as mossy metallic zinc. The calcium was added as a master alloy. The zirconium was added as a zirconium bearing flux listed as TAM.

The calcium alloy was added to the pure magnesium when the temperature reached 1350° F. The required amount of master alloy was thrust through the surface and held under the flux covering by means of steel tongs until the master alloy was dissolved. After the master alloy had been added, the temperature was raised to 1450° F. and then cast. This alloy was not superheated, as superheating tends to oxidize out the calcium.

When zinc was to be added to make it a ternary alloy, it was added about 15 minutes before the pour by use of ladle with small amount of stirring.

The zirconium flux was added when the temperature was between 1350° F. and 1450° F. The flux was washed in by use of a small basket or ladle, and the melt very carefully stirred while adding the flux. The percentage of TAM flux to get maximum grain refinement was approximately 10 per cent. After the zirconium flux had been added, it was advisable to go to 1450 - 1550° F. for thirty minutes. During this period, CaF_2 was used to thicken the flux. The zinc was added as described for the calcium alloy if a ternary alloy was wanted. The melt was let cool to approximately 1425° F. before casting.

The casting as shown on Plate V was then used to make a study of the grain size and physical properties. First the risers and sprues were sawed off, then the casting was machined to standard A. S. T. M. specifications for tensile specimens. The tensile test specimens were pulled to determine ultimate strength. Photomicrographs of the original castings were taken as a means of studying grain size.

Apparatus

Melting was done in a crucible made from 11-inch length of heavy 6-inch low carbon steel pipe, to which a steel plate was welded to form the bottom of the crucible, Plate III. A small baffle was introduced and welded to the inside of the crucible. This was found to be an aid to pouring as it held back much of the flux while pouring into the mold. The crucible sealed considerably on the outside, but the flux and metal prevented undue sealing on the inside.

The crucible was heated in a vertical type tubular electric resistance furnace, Plate II. The temperature of the heating element in the furnace was controlled by a Wheelco automatic controller. A chromel-alumel thermocouple, insulated by silica beads and sheathed in a small diameter low carbon steel pipe, which was sealed at the bottom, was used in conjunction with a Leeds and Northrup controller to indicate the temperature of the molten magnesium. This steel tube sheath should not be used as a stirring rod for refining the melt if the thermocouple is still in place, as stirring fractures the silica beads surrounding the thermocouple leads.

Materials

The magnesium used was a commercial grade metal in the form of 20-pound cast ingots. This magnesium was secured from a government agency.

The calcium master alloy was made by carefully weighing out both calcium and magnesium to give an alloy of 20 per cent calcium. The calcium used was of commercial stick quality, and was purchased from Metal Hydride Inc. The master alloy was used to facilitate fast solution and diffusion of the calcium in the molten magnesium to minimize oxidation losses.

The zirconium metal was obtained from TAM Fused Salt Zirconium Flux. This electrically fused flux has the following composition: 50 per cent zirconium tetrachloride, 25 per cent sodium chloride, and 25 per cent potassium chloride. The Titanium Alloy Manufacturing Company furnished this flux for the purpose of research.

EXPERIMENTAL RESULTS

The data obtained from the various alloys are presented in Table 2. The photomicrographs were the basis from which grain sizes were determined. The curves obtained were constructed from the data in Table 2.

The use of zirconium was found to have profound grain-refining capacity even though small quantities of zirconium were used. The series of photomicrographs containing zirconium are shown in Figs. 15, 16, 17, and 18.

The use of calcium as a grain refiner is shown in Figs. 19, 20, 21, and 22. It is very obvious calcium does not have the refining capacity that zirconium contains. Figures 20 and 22 show cold working and some twinning besides the grain boundaries.

The magnesium zinc alloy shows some grain refinement and a

Table 2. Mechanical properties of magnesium alloys.

Alloy	Yield strength p.s.i.	Tensile strength p.s.i.	% Elongation in 2 inches	% Reduct. of area	Grain size
Pure Mg	3000	12200	3.8	3.5	5
0.1% Ca	3000	12000	4.4	3.0	5
0.3% Ca	3200	12500	5.0	4.0	7
0.7% Ca	4500	18500	9.1	8.0	9
1.0% Ca	6000	12500	4.0	2.0	9
0.1% Zr	4500	16950	8.2	4.0	6
0.25% Zr	6500	20000	14.2	12.0	12
0.50% Zr	8000	20250	10.8	4.0	14
0.75% Zr	8000	19000	8.0	3.0	16
4% Zn	6500	14400	9.0	8.0	10
8% Zn	9500	17000	3.0	2.0	11
12% Zn	7500	13500	4.0	3.0	9
0.1% Ca 4.0% Zn	7000	21250	11.0	5.0	9
0.3% Ca 4.0% Zn	7250	11500	5.0	4.0	10
0.7% Ca 4.0% Zn	7500	9500	4.0	2.0	10
1.0% Ca 4.0% Zn	8000	9250	4.0	1.0	8
0.1% Zr 4.0% Zn	9000	15100	3.4	2.0	11
0.25% Zr 4.0% Zn	9500	18100	4.4	3.0	11
0.50% Zr 4.0% Zn	12000	20000	4.2	3.0	11
0.75% Zr 4.0% Zn	10000	16000	3.0	3.0	11

boost in tensile strength up to 12 per cent zinc where there is a fall in tensile properties. The zinc alloy castings were harder to get uniform results as the zinc seemed to form hard areas through the casting.

The magnesium, zinc, and calcium alloy showed good mechanical properties at low percentages of calcium, but very poor properties with increasing amounts of calcium. The calcium addition gave much better looking castings than either with zinc or zirconium additions.

The magnesium, zinc, and zirconium alloy had no visible change in grain size, but did increase in tensile strength with increase of zirconium.
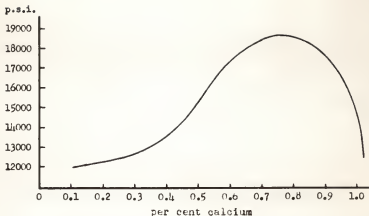
Fig. 4. Magnesium calcium alloy. Tensile strength vs. calcium content.
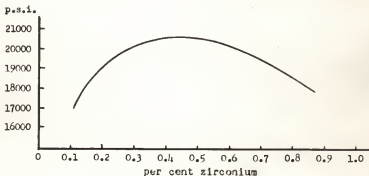
Fig. 5. Magnesium zirconium alloy. Tensile strength vs. zirconium content.
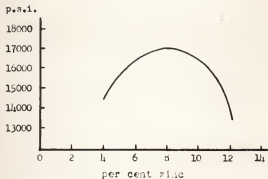
Fig. 6. Magnesium zinc alloy. Tensile strength vs.
zinc content.
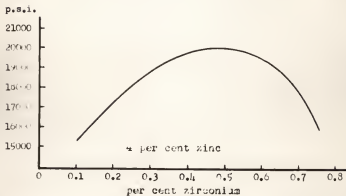
Fig. 7. Magnesium, zinc, and zirconium alloy. Tensile
strength vs. zirconium content.
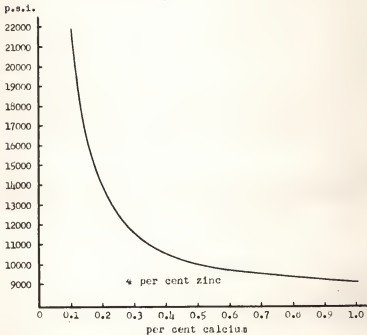
Fig. 8. Magnesium, zinc, and calcium alloy. Tensile
         strength vs. calcium content.
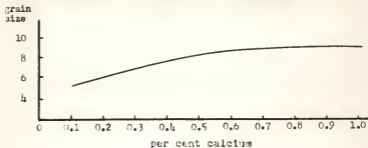
Fig. 9. Magnesium calcium alloy. Grain size vs. calcium content.
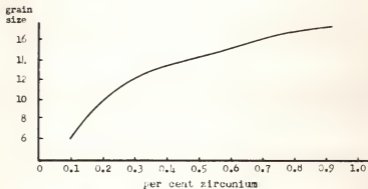
Fig. 10. Magnesium zirconium alloy. Grain size vs. zirconium content.
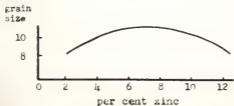
Fig. 11. Magnesium zinc alloy. Grain size vs. zinc content.
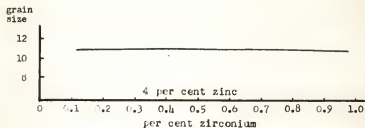
Fig. 12. Magnesium, zinc, and zirconium alloy. Grain size vs. zirconium content.
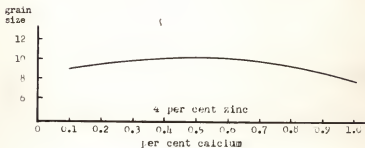
Fig. 13. Magnesium, zinc, and calcium alloy. Grain size vs. calcium content.

PHOTOMICROGRAPHS
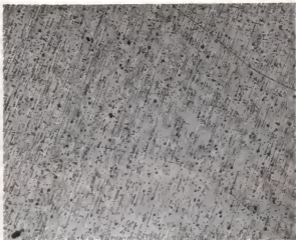
Fig. 14. Typical permanent mold pure magnesium casting.
Glycol etchant.* X 100.

In Fig. 14 the grains are uniformly large--so large, in
fact, that, even at the magnification employed, only a portion
of three grains can be included in the area photographed.

*Note - All samples photographed were etched with Glycol etchant.

	Per cent by volume
Ethylene glycol	60
Glacial acetic acid	20
Conc. nitric acid	1
Distilled water	19
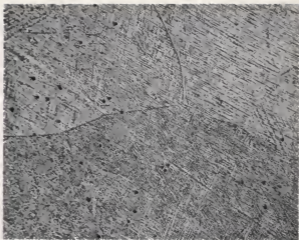
Fig. 15. Magnesium zirconium alloy.
0.1 per cent Zr. X 100.
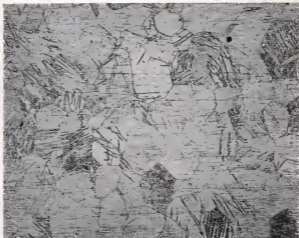
Fig. 16. Magnesium zirconium alloy.
0.25 per cent Zr. X 100.
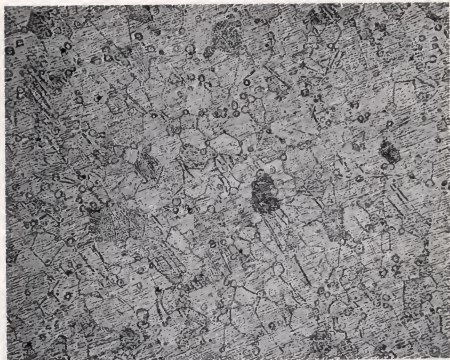
Fig. 17. Magnesium zirconium alloy.
0.5 per cent Zr. X 100.
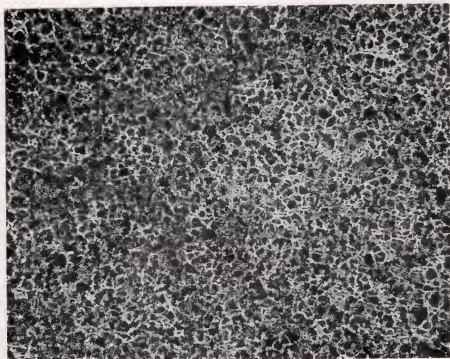
Fig. 18. Magnesium zirconium alloy.
0.75 per cent Zr. X 100.

Fig. 19. Magnesium calcium alloy.
0.1 per cent Ca. X 100.
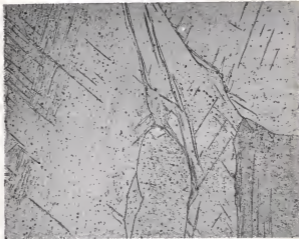
Fig. 20. Magnesium calcium alloy.
0.3 per cent Ca. X 100.
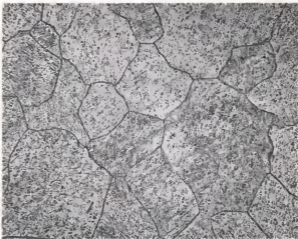
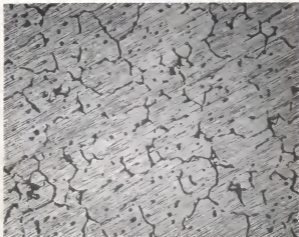Fig. 21. Magnesium calcium alloy.
0.7 per cent Ca. X 100.

Fig. 22. Magnesium calcium alloy.
1.0 per cent Ca. X 100.
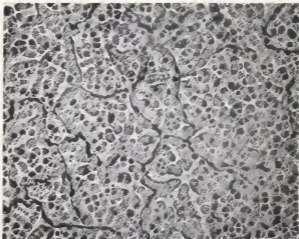
Fig. 23. Magnesium zinc alloy.
4 per cent Zn. X 100.

Fig. 24. Magnesium zinc alloy.
8 per cent Zn. X 100.
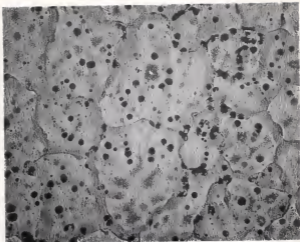
Fig. 25. Magnesium, zinc, and calcium alloy.
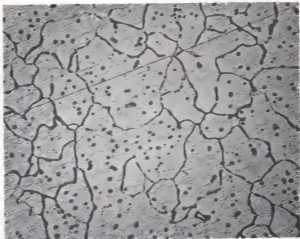4 per cent Zn., 0.1 per cent Ca. X 100.
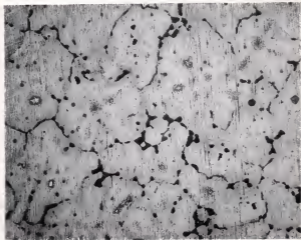
Fig. 26. Magnesium, zinc, and calcium alloy.
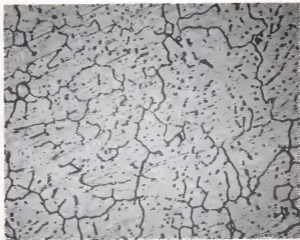4 per cent Zn., 0.3 per cent Ca. X 100.

Fig. 27. Magnesium, zinc, and calcium alloy.
4 per cent Zn., 0.7 per cent Ca. X 100.

Fig. 28. Magnesium, zinc, and calcium alloy.
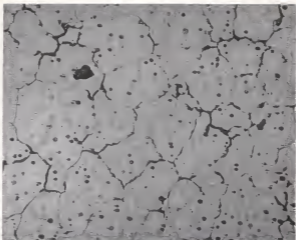4 per cent Zn., 1.0 per cent Ca. X 100.

Fig. 29. Magnesium, zinc, and zirconium alloy.
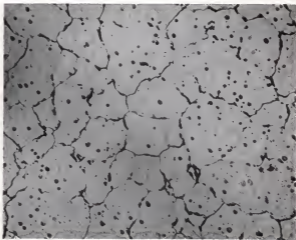4 per cent Zn., 0.1 per cent Zr. X 100.

Fig. 30. Magnesium, zinc, and zirconium alloy.
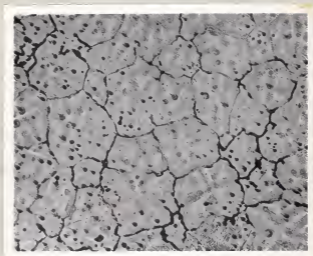4 per cent Zn., 0.25 per cent Zr. X 100.

Fig. 31. Magnesium, zinc, and zirconium alloy.
4 per cent Zn., 0.5 per cent Zr. X 100.

Fig. 32. Magnesium, zinc, and calcium alloy.
4 per cent Zn., 0.1 per cent Ca. X 100.
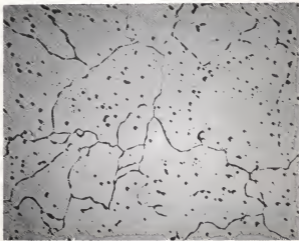Heat treated at 770° F.

Fig. 33. Magnesium, zinc, and calcium alloy.
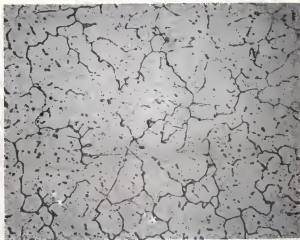4 per cent Zn., 0.7 per cent Ca. X 100.
Heat treated at 770° F.

Fig. 34.   Magnesium, zinc, and calcium alloy.
4 per cent Zn., 1.0 per cent Ca. X 100.
Heat treated at 770° F.

EXPLANATION OF PLATE II

Vertical type tubular electric resistance furnace

PLATE II   45

EXPLANATION OF PLATE III

Equipment used in casting: crucible, tongs, skimmer, wash basket, and pure magnesium

PLATE III

EXPLANATION OF PLATE IV

Cast iron permanent mold

PLATE IV

EXPLANATION OF PLATE V

Magnesium casting from permanent

mold and test specimen

PLATE V

CONCLUSIONS

1. The greatest refining capacity was exhibited by zirconium.

2. The zirconium in the magnesium zinc alloy had very little or no effect on grain refinement.

3. The magnesium calcium alloy showed grain refinement, but it did not have the grain refining capacity that zirconium contained.

4. The physical properties were increased by both calcium and zirconium additions.

5. The magnesium zinc alloy had poorer casting characteristics than the other alloys.

6. Figures 4 to 13 show the physical properties and degree of grain refinement.

ACKNOWLEDGMENT

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