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The Age-Hardening of Magnesium with Aluminum and Zinc

K. DeAtley Loughridge

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THE AGE-HARDENING OF MAGNESIUM
WITH
ALUMINUM AND ZINC

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By

K. DeAtley Loughridge

Butte, Montana

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A Thesis,
Submitted to the Department of Metallurgy in
Partial Fulfillment of the Requirements for
the Degree of Bachelor of Science in Metallurgical Engineering.

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Montana School of Mines

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THE AGE HARDENING OF MAGNESIUM

MAGNESIUM

Magnesium is one of the most active elements and forms oxides, nitrides, and carbides, but not hydrides. Due to its activity, low melting point, low strength when unalloyed, and the difficulty with which it is worked, magnesium has not been and is not at present well developed. At the present time, a great deal of work is being done with magnesium and its alloys for the following reasons:

1. Due to its low specific gravity of approximately 1.74, magnesium is in great demand for the manufacture of streamlined trains, automobiles, aeroplanes, boats, and many other articles where a saving in weight means an increase in profit.

2. Magnesium is being developed in Germany, Italy, and other deficient nations in an attempt to become self sufficient. Germany is lacking in iron and many other metallics, but has a large supply of carnallite from which magnesium is easily obtained. In 1938, Germany produced over 14,000 metric tons of magnesium, or more than half of the

world's production, which was 25,000 metric tons.

Magnesium is rather plentiful in the earth's crust, but at present the chloride is the only ore. It has a melting point of 651° C. and a boiling point of 1050° C. In 1914, the metal was worth two dollars a pound, but at present is down to thirty cents a pound, and with new developments, it will undoubtedly become a very economical metal to use.

With the exception of iron, chromium, and, to a limited extent, manganese, magnesium alloys with most of the common metals. Many of these combinations do not give useful alloys, but aluminum and zinc, or both, give an alloy with satisfactory strength and forming properties. These alloying ingredients are generally well below 10 per cent. The alloys may be had on the market as castings, extruded shapes, and rolled shapes.

One of the most important properties of the cold-worked alloys is that they may be appreciably hardened below their melting point and after annealing, by heating to a low temperature for a short length of time. This process is called age-hardening.

THEORY OF AGE-HARDENING

There is still considerable controversy as to the exact nature of the mechanism of age-hardening, but for the purposes of this paper, I will assume the simple theory of precipitation or "dispersion hardening" as proposed by Merica, Waltenberg, and Scott,(1) in conjunction with the theory of age-hardening by distorted groups or "knots" of hardening atoms, as proposed by Merica.(2)

The precipitation type of hardening occurs only in alloys of the solid solution type where the solubility increases with temperature (See Figs. 2 & 3). When the alloy is brought into the solid solution field, and then cooled quickly, or quenched to a temperature below the solid solution field, it becomes supersaturated with a second phase. This second phase precipitates out along the slip planes, keying the metal in place. This decomposition takes place the fastest at high temperatures and decreases as the temperature is lowered.

Age-hardening by distorted groups is the formation of "knots" or segregations of different lattice structure throughout, giving a distorted lattice in the solid solution itself. Merica gives a rather comprehensive discussion of this theory.(2)

Although not all combinations of metals are the solid solution type, it is easy to see that with any one metal, another metal could be found that would form the solid solution type alloy.

It is interesting to note that the increases of hardness and of strength possible by age-hardening are of the same magnitude as those obtained by substantial cold working. This brings out the facts that in both cases (1) the increases are brought about by obstructions along the slip planes, and (2) there is a limit to the increases by the same basic characteristics of the parent lattice. The age-hardening effect on any alloy will be based on the following three facts:

1. The hardness of the hardening constituent itself.
2. The quantity of the hardening constiuent present.
3. The size of dispersion of the hardening constituent.

The alloy will reach a maximum hardness and then decrease as the test is continued. This is best shown by Fig. 6 from Merica.(2)

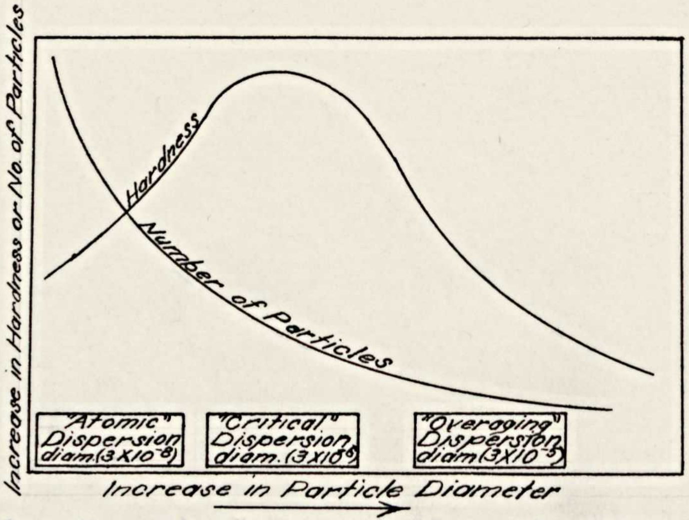


Fig. 6 - Simple conception of effect of particle size and number on hardening power of a constant amount of hardening constituent.

From Fig. 2, it is seen that the hardening constituent in the case of the magnesium aluminum alloy is , a solid solution of magnesium in $Al_2 Mg_3$, and in the case of the magnesium zinc alloy, Fig. 3, is MgZn. Both of these hardening constituents must be fairly hard, as they increase the hardness of the alloy considerably.

There is one structural defect from which all age-hardening alloys suffer to a greater or less extent. Precipitation of the hardening constituent under optimum aging conditions is probably always accompanied by some intergranular precipitation. This probably explains the difference in properties of different specimens of the same composition and treatment.

PREVIOUS WORK ON MAGNESIUM

Merica, Waltenberg, and Scott(1) proposed the precipitation theory of age-hardening in 1919, and in 1932, Merica(2) proposed a second age-hardening to explain the two hardness peaks shown on most curves. This result was confirmed in this investigation.

Meissener(3), Archer(4), and Gann(5) have investigated the changes in mechanical properties of magnesium-aluminum alloys during aging and have shown the optimum condition for the age-hardening treatment. Meissener's results are particularly interesting, because when replotted so they represent hardness as a function of aging time, the curves at 125° and 150° C. show two hardness peaks, thus substantiating Merica's second hardening theory.

A. M. Talbot and John T. Norton(6) made rather extensive tests on 10 per cent aluminum alloys at 100°, 150°, and 175° C. Hardness, x-ray, and resistivity were measured. These results did not show a double hardness peak when hardness was plotted against time, and in other ways did not agree with Merica's second hardening theory.

Schmid and Liebel(7) have reported an investigation similar to that of Talbot and Norton. These authors compared the changes in mechanical properties during aging with the amount of precipitation as measured by x-ray. These two reports show agreement where the results overlap.

In the last few years, a great many investigations have been carried out on the different metal combinations. Most of these done in this country may be found in the A. I. M. E. publications.

PREPARATION OF ALLOYS

The alloys were prepared of magnesium supplied by the Dow Chemical Company, electrolytic zinc supplied by the Anaconda Copper Mining Company, and aluminum supplied by the Aluminum Company of America, all of high purity. The magnesium-aluminum alloys were made of 6 and 10 per cent aluminum by weight, and the magnesium-zinc specimens of 3 and 6 per cent zinc by weight. 20-gram specimens were made of each alloy.

The metals were melted in a clay crucible under a flux made up of 42 per cent magnesium chloride, 30 per cent calcium chloride, and 28 per cent sodium chloride. This flux has a melting point of about 600° C. and a specific gravity slightly higher than the alloy, but due to capillary action, a thin layer of flux will cover the metal. Melting was tried in both a gas-fired, muffle furnace and an electric, carbon-resistance furnace, but good temperature control could not be effected with either of these, and a small, electric, crucible furnace was used, as shown in Fig. 1. With this arrangement, it is easy to mix the alloy and keep a fair temperature control, within 15 or 20 degrees, depending somewhat on the rheostate used.

Casting was tried by several different methods with more or less success. First, the alloy was poured on an iron cupel tray, but the alloy would not separate from the flux by gravity, and since the metal has a rather high surface tension, while the surface tension of the flux is low, the cast mass was flux, shot through with spherical-shaped alloy particles. No more luck was had when a carbon mould was used for the same reason. Finally, a rather ingenious method was hit upon, whereby a flux-metal separation was effected, and the flux was saved for the next melt. This was done by pouring on to a warm wire gauze where the flux ran through, while the alloy, with a relatively high surface tension, remained on top. The separate metal particles were then caused to coalesce by puddling with a steel rod; after which, the metal was poured on to a cupel tray to solidify. The casting was flattened slightly with a spatula while still in the mushy state.

The ingots were extremely difficult to homogenize. Severe, hot working at about 300° C. by rolling and subsequent cold rolling was necessary if a satisfactory structure was to be obtained. All of the specimens rolled well hot, and the three per cent alloys rolled well cold; the six per cent alloys rolled with some difficulty; and the 10 per cent alloys were rather brittle and showed a marked tendency to crack on cold working. The cold rolling was done by taking a large number of thin passes in various directions with respect to the speciman. The zinc alloys were somewhat more brittle than the corresponding aluminum alloys. Sheets 1-1/2 inches wide, 2 inches long, and 3/16 inches thick were thus obtained. These were cut into specimens about an inch long and 5/8 inches wide for testing purposes.

HARDENING MAGNESIUM

Annealing was accomplished in a bomb made of a 1-1/4 inch by 2 inch nipple with a plate welded on one end and a cap on the other. The specimens were packed in the bomb with magnesium powder, and the cap was loosely screwed in place. The bomb was then placed in the crucible furnace and annealed for about 24 hours at 450° C. for magnesium-aluminum alloys, and 350° C. for magnesium-zinc alloys. The bomb was then removed from the furnace, the cap taken off, and the specimens quenched in cold water. In the furnace, unprotected, some specimens oxidized to a gray-white mass of the oxide and nitride. Very little air got into the bomb, and this was taken up by the magnesium dust, so there was no action on the specimens. The temperature was read with a chromel-alumel thermocouple in direct contact with the bomb and connected with a direct-reading millivoltmeter. As the 10 per cent aluminum alloy has a very short temperature range in the solid solution field, temperature control was very important.

The aging was done in an electric tube-furnace with a chromel-alumel thermocouple with a direct-reading millivoltmeter and rheostat control (Fig. 1). The aging temperatures were 200° and 250° C., and the tests were run for 150 hours, taking hardness readings with a Rockwell Superficial Hardness Tester at short intervals at first, and increasing to 24 hours for the last part of the test. No less than four Rockwell-15T readings were taken at each time on each specimen, and an average was taken to get the final reading.

EXPERIMENTAL RESULTS

The first series of experiments were performed on alloys containing 6 and 10 per cent of aluminum by weight. These samples were aged at 200° and 250° C. for 150 hours. The results are given in Tables I and II. The second series of experiments were performed on alloys containing 3 and 6 per cent of zinc by weight, and the same aging times and temperatures were used, but the 3 per cent zinc alloy didn't show any age-hardening at 250° C.; evidently, it is in the solid solution field at this temperature. These results are given in Tables III and IV.

DISCUSSION OF RESULTS

The graphs (Figs. 4 & 5) show clearly that the age-hardening cannot be explained by the simple precipitation hardness theory, as all curves, without exception, showed a double maximum which cannot be explained by this theory. I believe this first maximum was due to structural alteration other than that of the precipitation of excess solute. It has been proposed by Merica(2) that this preliminary hardening is due to a distortion of the crystal lattice in the solid solution itself. As this would have to be studied by x-ray, I did not do anything to prove or disprove the theory, but it is certain that there was some other system of hardening, except precipitation hardening, which was probably responsible for the first maximum.

From the same curves, it was seen that hardening took place in a shorter time with an increase in the per cent of aluminum or zinc, as the case may be, as long as the solid solution field was not exceeded. Also, the critical hardness increases as the per cent of alloying element increases; at least until the maximum solid solution composition was reached. After the maximum was reached, the hardness began to drop, due to the gathering of the critically dispersed particles into larger particles by diffusion. This phènomenon is called averaging.

TABLE V

SHOWING THE CRITICAL TEMPERATURES AND TIMES OF THE VARIOUS ALLOYS TESTED

% Alloying Metal	Aging Temp. deg. C.	Critical Time in hr..	Critical Hardness Rockwell 15T
3% zinc	200	120	57
6% zinc	200	60	65
6% zinc	250	45	62
6% aluminum	200	35	61
6% aluminum	250	60	66
10% aluminum	200	55	64
10% aluminum	250	45	66

All of the aluminum curves tended to converge, and at 150 hours, the hardness was practically identical for the 6 and 10 per cent alloys at 200 and 250° C. This seems natural, as the rate of flocculation or gathering of the dispersed particles increases with the concentration of these particles, and, hence, averaging was faster.

CONCLUSIONS

1. The age-hardening of magnesium with aluminum and with zinc had a double maximum and the first one was caused by some system other than precipitation hardening.

2. Hardening took place very unevenly and went to completion in one region before a neighboring region.

3. The rate of age-hardening of magnesium with aluminum and with zinc increased rapidly as the aging temperature was raised.

4. The maximum hardness increased with an increase of aluminum or zinc present as long as its composition wasn't out of the solid solution field at the annealing temperature.

5. The ease of mechanical work, either hot or cold, decreased as the per cent of either aluminum or zinc increased.

SUGGESTIONS FOR FURTHER STUDY

From the experience gained by my work on this subject, I offer the following suggestions:

1. The first and most important suggestion that I have is that a good deal of library research be done before going into the laboratory work, and much time will be saved.

2. The crucible furnace used for melting worked fairly well, but, perhaps, an induction furnace would be more satisfactory.

3. A better method of casting could be devised and a bottom pouring iron crucible might be the answer.

4. Although annealing is fairly satisfactory, using the bomb method already described, I believe a tube-furnace with an atmosphere of hydrogen could be used to better advantage.

5. An oil bath, thermostatically controlled, or anyway a thermostat on a tube furnace, is almost necessary to get good, accurate, consistent aging results, as the room temperature fluctuates, and the temperature in an uncontrolled furnace fluctuates with it.

6. The hot rolling should be done at about 300° C., and thin passes should be taken, with frequent reheatings.

7. I suggest that 3 and 6 per cent alloys with zinc, 3, 6, and 10 per cent alloys with aluminum, and also alloys with the compound of zinc and aluminum be used and tests be run at 100, 150, 200, and 250° C. The 3 per cent alloy of aluminum will not age-harden at 200 or 250° C., and the 3 per cent alloy of zinc will not age-harden at 250° C.

8. To use the time most efficiently, two or three complete aging apparatuses should be available.

* * * *

I wish to acknowledge the help of Dr. C. L. Wilson, Professor of Metallurgy, and Dr. E. A. Peretti, Assistant Professor of Metallurgy, at the Montana School of Mines, under whose direction this work was performed.

TABLE I

ROCKWELL HARDNESS (15T) OF A MAGNESIUM ALLOY CONTAINING 6 PER CENT OF ALUMINUM BY WEIGHT

AT 250° C.		AT 200° C.	
Aging Time, Hr.	Hardness, Rockwell 15 T	Aging Time, Hr.	Hardness, Rockwell 15 T
0.	*52.25	0.	49.5
0.5	55.75	0.5	53.33
1.25	57.66	1.5	55.5
2.75	60.0	2.5	58.66
4.0	60.5	4.5	57.25
5.50	60.25	9.5	58.
7.5	61.0	19.5	57.25
13.5	61.25	29.5	60.25
21.	60.66	41.5	60.75
32.5	62.66	66.	59.75
46.5	65.0	90.	60.5
70.5	65.75	114.	63.25
93.5	65.66	167.	64.75
117.	65.25		
141.	65.0		
150.	65.0		

TABLE II

ROCKWELL HARDNESS (15T) OF A MAGNESIUM ALLOY CONTAINING 10 PER CENT OF ALUMINUM BY WEIGHT

AT 250° C.		AT 200° C.	
Aging Time, Hr.	Hardness, Rockwell 15 T	Aging Time, Hr.	Hardness, Rockwell 15 T.
0.	53.		
0.5	58.66	0.	51.5
1.25	59.5	0.5	55.0
2.75	63.	1.5	59.
4.	64.75	2.5	58.75
5.5	67.25	4.5	62.25
7.5	67.5	9.5	63.75
13.5	69.8	19.5	63.25
21.	70.25	29.5	63.
32.5	66.25	41.5	63.5
46.5	66.5	66.	64.
70.5	65.5	90.	65.
93.5	66.	114.	66.
117.	66.5	167.	65.25
141.	65.75		
150.	65.50		

TABLE III

ROCKWELL HARDNESS (15T) OF A MAGNESIUM ALLOY CONTAINING 3 PER CENT OF ZINC BY WEIGHT

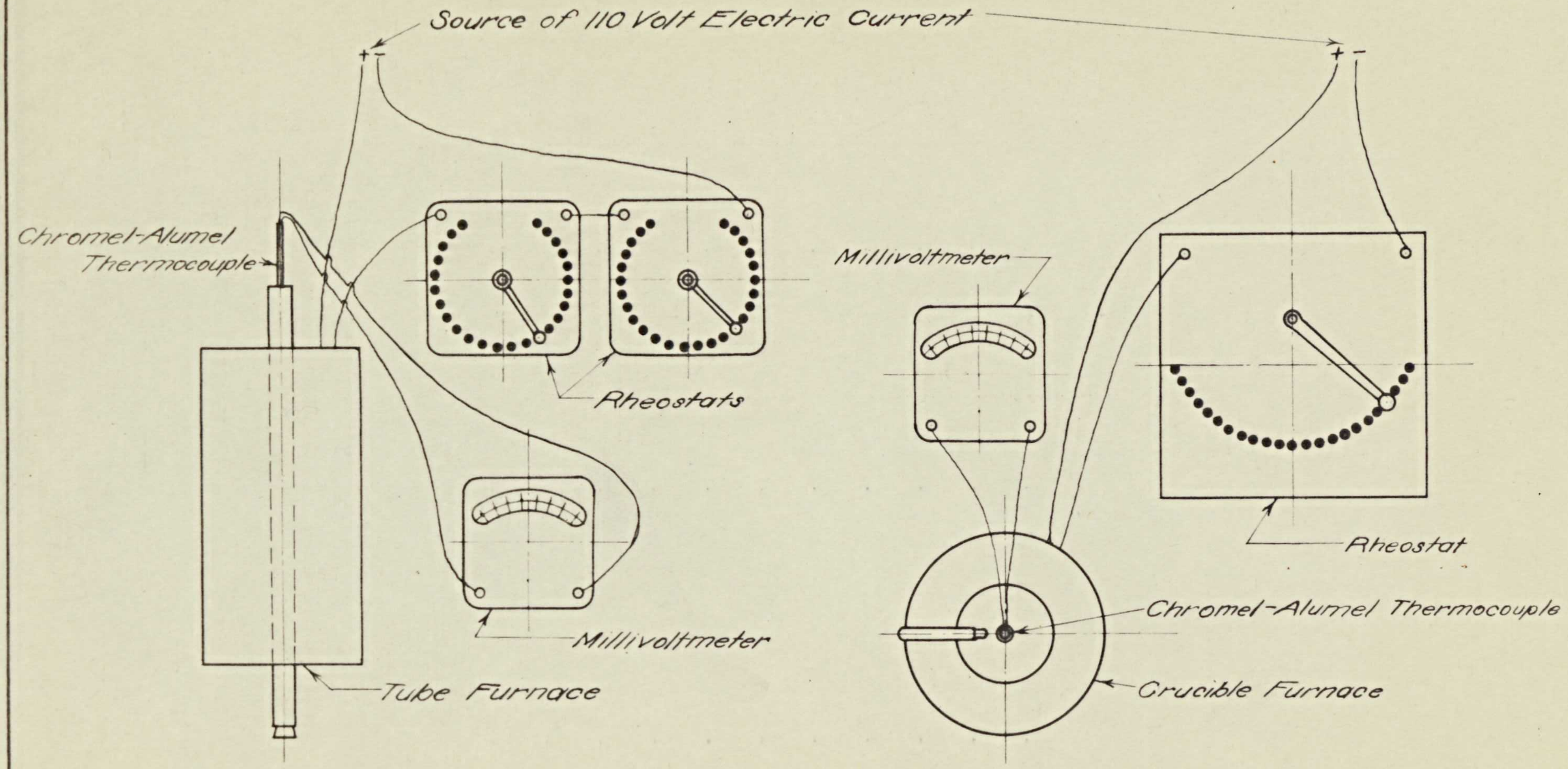
AT 200° C.	
Aging Time, Hr.	Hardness, Rockwell 15T
0.	40.
0.5	51.
1.75	50.5
3.5	54.5
11.5	56.75
19.5	57.50
35.5	55.5
60.0	55.75
84.0	56.5
137.	58.5
161.	58.5

TABLE IV

ROCKWELL HARDNESS (15T) OF A MAGNESIUM ALLOY CONTAINING 6 PER CENT OF ZINC BY WEIGHT

AT 250° C.		AT 200° C.	
Aging Time, Hr.	Hardness, Rockwell 15T	Aging Time, Hr.	Hardness, Rockwell 15T
0.	40.	0.	39.25
0.5	48.	0,5	50.5
1.5	58.	1.75	59.75
2.5	59.	3.5	63.25
4.	62.5	11.5	65.75
13.	62.5	19.5	63.75
37.	59.75	35.5	64.75
60.	61.25	60.	64.50
83.	60.	84.	65.
107.	59.50	137.	65.
137.	58.5	161.	65.
150.	57.		

* Note: All tests are an average of at least three readings.



Age Hardening Furnace Set Up

Casting And Annealing Furnace Set Up

Fig 1

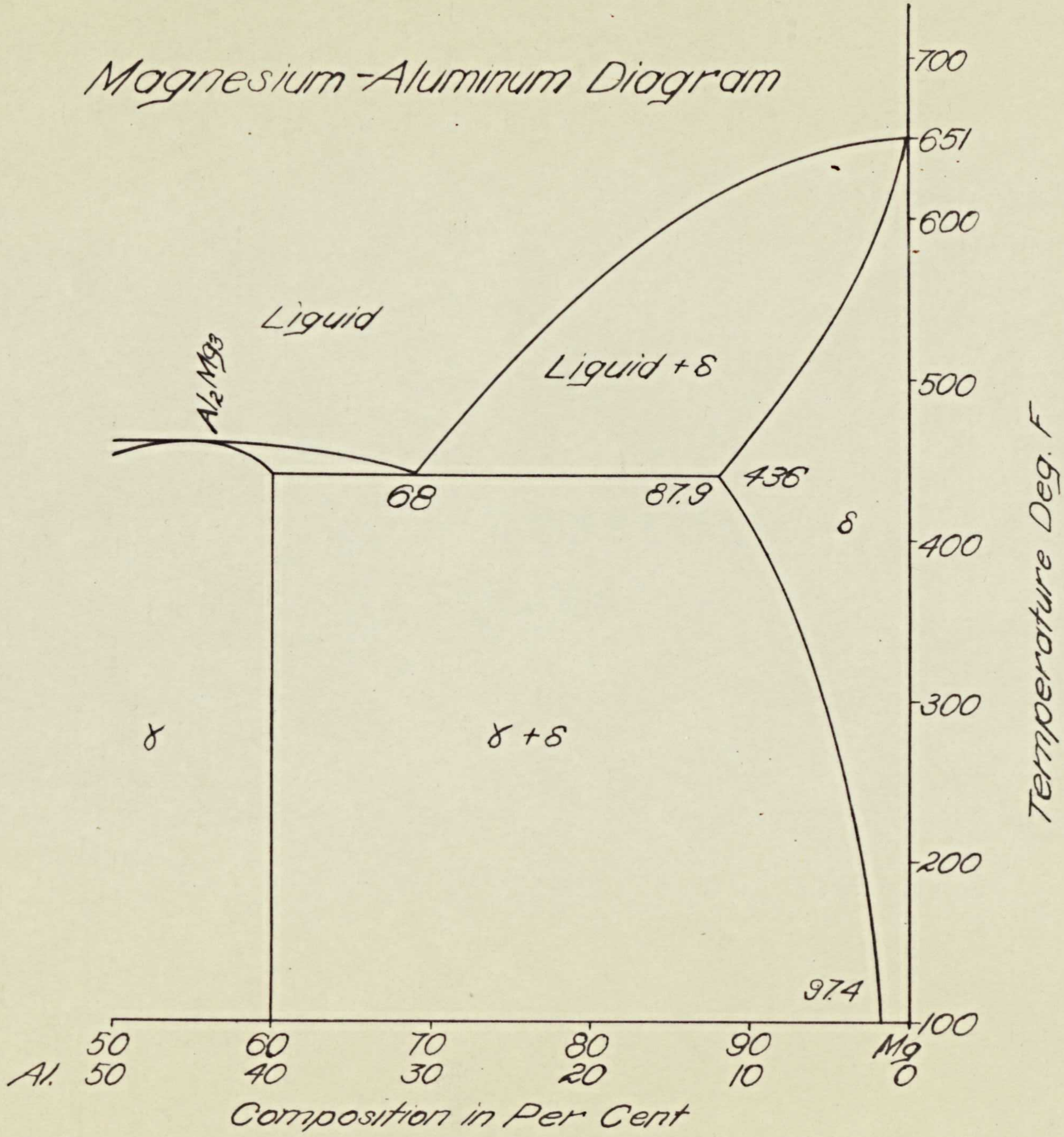

Magnesium-Aluminum Diagram

Fig 2

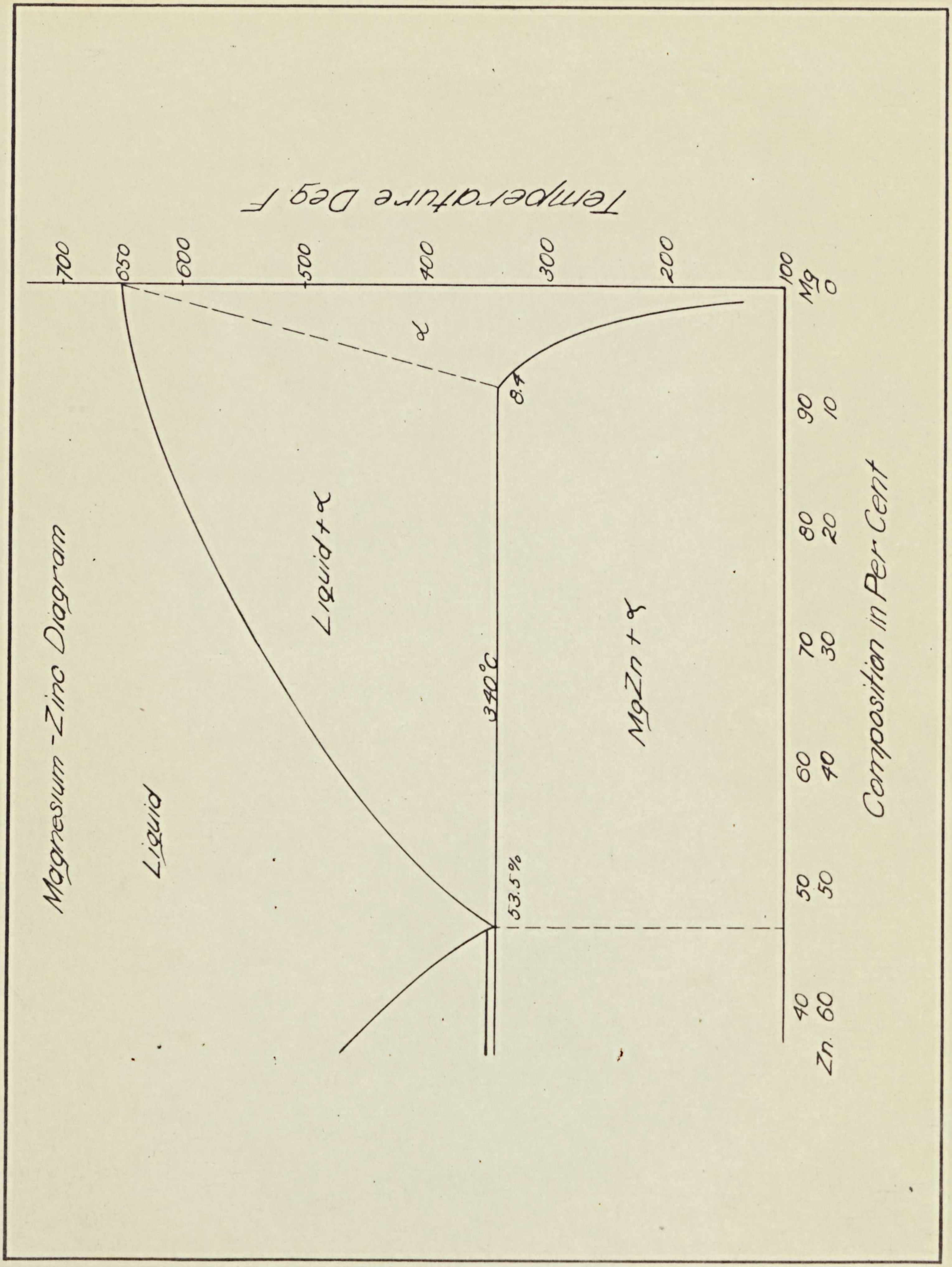

Magnesium -Zinc Diagram
Temperature Deg. F
700
650
600
500
400
300
200
100
Liquid
Liquid + α
α
8.4
340°C
53.5%
MgZn + α
Mg 0
90 10
80 20
70 30
60 40
50 50
40 60
Zn.
Composition in Per Cent

Fig 3

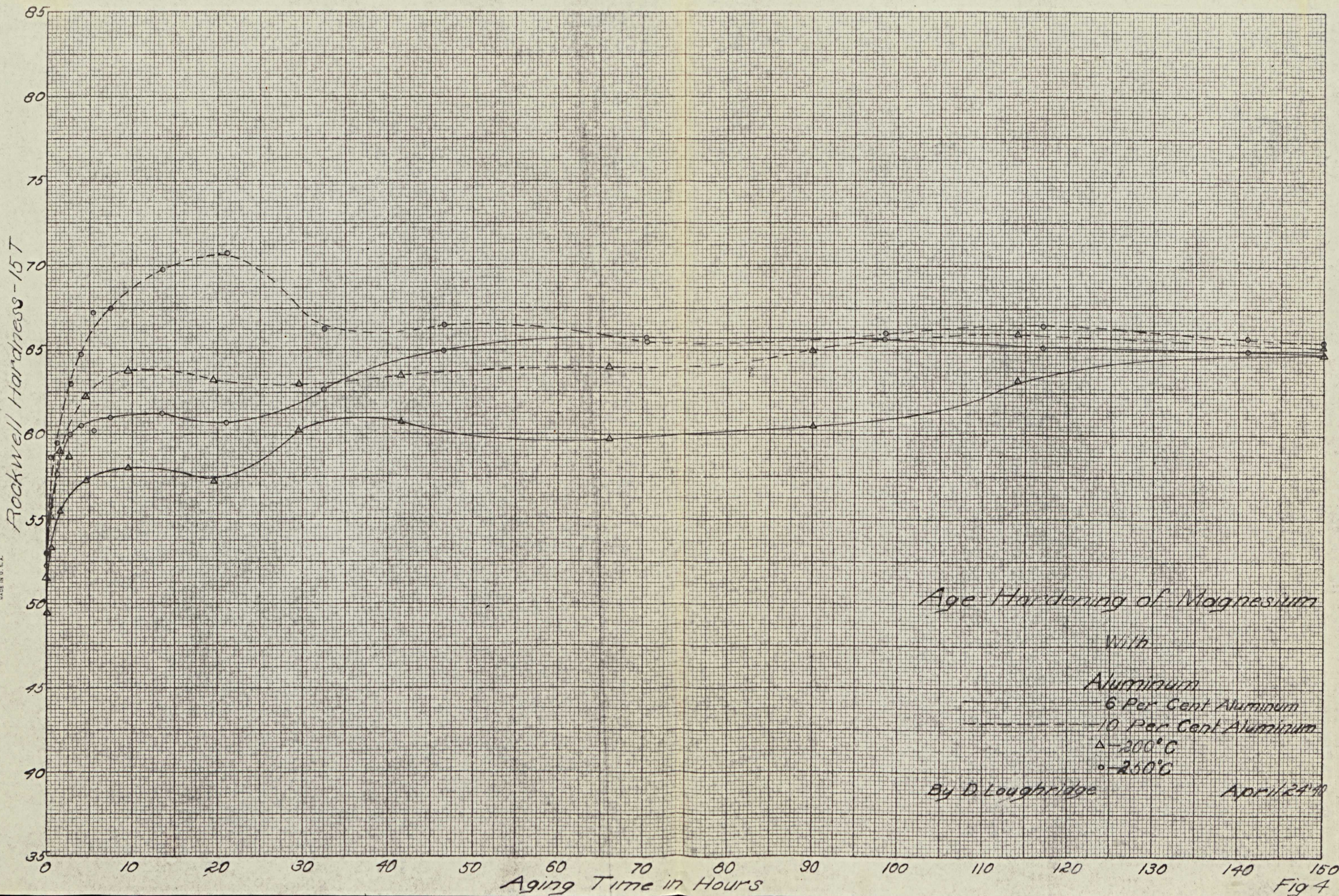
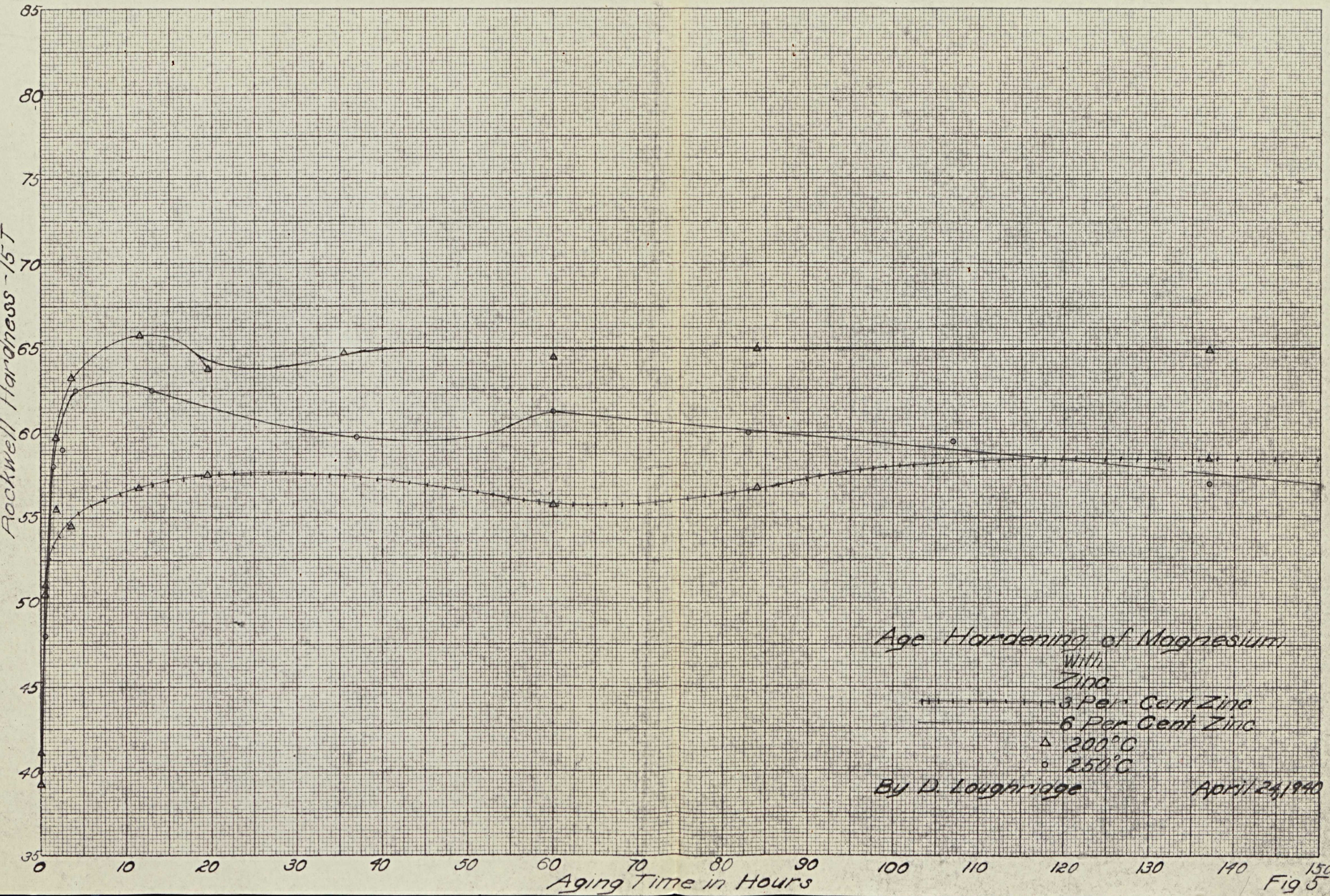

Age Hardening of Magnesium
With
Aluminum
6 Per Cent Aluminum
10 Per Cent Aluminum
△ 200°C
○ 250°C
By D. Loughridge
April 24 '40
Rockwell Hardness - 15 T
85
80
75
70
65
60
55
50
45
40
35
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Aging Time in Hours

Fig 4


Age Hardening of Magnesium
With
Zinc
3 Per Cent Zinc
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Rockwell Hardness -15T
85
80
75
70
65
60
55
50
45
40
35
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Aging Time in Hours

Fig 5

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