[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

A Thermal Investigation of the Ternary System Mg–Na–Pb. II. The Compound MgNaPb and Several Cross Sections

BY GEORGE CALINGAERT, HYMIN SHAPIRO AND IVAR T. KROHN

In a recent note,[1] it was disclosed that the compound $Mg_4Na_4Pb_3$ had been discovered in the course of a thermal investigation of the ternary system Mg–Na–Pb. The investigation has now resulted in the discovery of a second compound and the partial elucidation of several important cross sections. The new compound, MgNaPb, was shown to be of the peritectic type rather than of the open maximum type, as the first compound, $Mg_4Na_4Pb_3$.

Method of Investigation

In this thermal study, two principal methods of attack were used: the investigation of cross sections of the ternary diagram, and the investigation of alloys having atomic ratios of small whole numbers. The first method was used mostly for determining the locations of ternary eutectic points and binary eutectic curves, and in the regions close to the binary compounds—in other words, for clarifying the general structure of the equilibrium diagram. The choice of cross sections was limited to those between binary compounds, between a compound and an element, and at a fixed concentration of one of the elements. The second method was used in spot attempts to discover ternary compounds, since compounds are usually characterized by atomic ratios of small whole numbers. Of course, the usefulness of this method is limited to compounds having open maxima. For peritectic compounds it is necessary to correlate several types of data, as will be discussed later.

The thermal analysis data for each alloy were plotted with millivolts and time as the coördinates. The cooling curves were interpreted after the manner of Tammann.[2] The differences in millivolts between successive readings were sometimes plotted against time in order to evaluate the precision of the results.

Experimental

Chemicals, Apparatus and Procedure.—All alloy melts were prepared from mixtures of magnesium, lead and NaPb or Na_4Pb alloy. The magnesium was Dow extruded bar of purity over 99.9%, and the lead was Asarco brand, over 99.95% pure. The NaPb was alloy from the stock used for the manufacture of tetraethyllead. The Na_4Pb was prepared from sodium and the Asarco lead, and analyzed 30.96% sodium as compared with the theoretical of 30.74%. The analytical figures were used in computing the quantities of alloy ingredients required.

The alloy melts were made in 200- to 300-g. batches under an atmosphere of nitrogen or helium purified over hot copper filings; the gases seemed to be equally effective up to about 550°, but above this temperature helium was

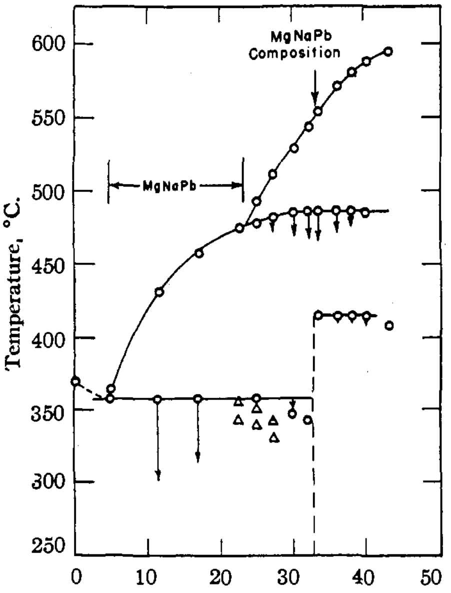

Fig. 1.—NaPb–Mg cross section (passing through 50% Na–50% Pb): time scale for temperature breaks, 50° = twenty minutes.

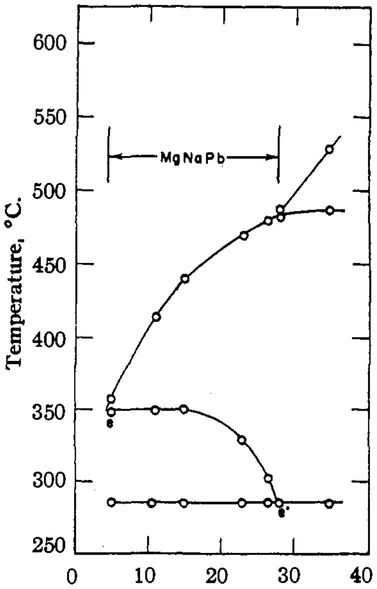

Fig. 2.—Cross section parallel to NaPb–Mg cross section and passing through 47.5% Na–52.5% Pb.

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[1] Calingaert, Shapiro and Krohn, THIS JOURNAL, 68, 520 (1946).

[2] Tammann, "A Textbook of Metallography," The Chemical Catalog Co., Inc., New York, N. Y., 1925, p. 181.

TABLE I

THERMAL ANALYSIS OF CROSS SECTIONS PARALLEL TO NaPb-Mg CROSS SECTION

Cooling method	Atom per cent.		Temperature breaks					
			I		II		III	
	Mg	Na	T. °C.	Min.	T. °C.	Min.	T. °C.	Min.
			NaPb-Mg Cross Section					
S. C.	5.00	47.50	365.6	9	...	..	357.2	30
S. C.	11.50	44.24	432.2	5	...	..	358.9	38
S. C.	17.00	41.50	455.9	6	...	..	355.7	33
R. T.	22.50	38.75	476.1	4	...	..	343.0–356.1	[a]
R. T.	25.00	37.50	493.0	[b]	479.2	4.5	339.8–351.1	[a]
R. T.	27.27	36.36	512.3	[b]	482.5	5	331.1–341.8	[a]
R. T.	30.00	35.00	528	[b]	485	6.5	348	3
R. T.	32.00	34.00	544	[b]	486	7	342.5	1.5
S. C.	33.33	33.33	555.0	[b]	486.1	14[c]	415.1	2
R. T.	36.00	32.00	571.8	[b]	486.2	5.5	416.4	>2
R. T.	38.00	31.00	580.8	[b]	486.0	5	415.6	1.8
R. T.	40.00	30.00	588.2	[b]	485.2	2	416.4	2.5
S. C.	42.85	28.57	594.2	>8	407.2	3	404.2–439.5	[a]
R. T.	50.00	25.00	587.9	7	521.0	4	411.2–424.9	[a]
			Cross Section Passing through 47.5% Na–52.5% Pb					
S. C.	23.00	36.00	470.8	5	329.6	7	284.6	11
R. T.	26.50	34.25	480.6	2.5	303.6	[b]	284.6	5
R. T.	28.00	33.50	485.2	[b]	482.8	3	283.8	4.2
R. T.	35.00	30.00	529.2	[b]	486.6	7	284.2	3
			Cross Section Passing through 52.5% Na–47.5% Pb					
S. C.	12.00	46.50	436.8	3	345.6	19	329.2	10
R. T.	15.00	45.00	454.9	2.5	339.4–349.1	[a]	331.4	3
R. T.	18.00	43.50	473.8	[b]	460.9	3.5	331.9	[d]
R. T.	20.00	42.50	483.8	[b]	465.4	3.5	329.2–336.9	[a]
R. T.	25.00	40.00	521.4	[b]	472.8	4	328.6	5.5
S. C.	35.00	35.00	583.0	<1	476.8	3	407.9	<1

[a] Supercooled break. Initial and maximum temperatures are given. [b] The break was indicated by a sudden change in the slope of the curve. [c] The time value of 14 minutes is equivalent to 7.8 minutes at the R.T. cooling rate. [d] Time of break difficult to estimate because of supercooled nature. There was some levelling off at 331.9°.

TABLE II

THERMAL ANALYSIS OF NaPb–Mg_2Pb CROSS SECTION

Cooling method	Atom per cent.		Temperature breaks					
			I		II		III	
	Mg	Na	T. °C.	Min.	T. °C.	Min.	T. °C.	Min.
R. T.	66.66	...	552.5	22	...	..	...	..
R. T.	57.48	6.90	552.3	10	...	..	...	..
R. T.	45.25	16.06	524.7	7	...	..	...	..
S. C.	44.00	17.00	531.9	5	405.5	1	287.1	11
S. C.	40.00	20.00	519.0	6	426.7	1	287.5	12
S. C.	37.33	22.00	509.0	4	438.0	2	287.1	11
R. T.	31.58	26.32	477.0	3	...	..	282.7	12
R. T.	29.83	27.63	474.4	3	453.1	1	284.0	16
R. T.	28.06	28.96	464.9	2	452.1	1	284.9	17
R. T.	26.98	29.76	460.2	1	455.4	1	286.1	16
R. T.	26.26	30.31	462	1	...	..	286.0	17
R. T.	22.57	33.07	453.3	6	352	1	281.9	19
S. C.	21.60	33.80	453.0	4	312	1	284.3	16
R. T.	20.67	34.49	452	[a]	...	..	284.5	13
R. T.	19.94	35.05	450.4	5	299.2	1	280	15
R. T.	18.77	35.92	447.1	6	309.1	6	285.4	15
R. T.	16.82	37.39	443.5	3	330.7	7	281.0	15
R. T.	14.84	38.87	428.6	3	336.1	9	281.5	11
R. T.	12.82	40.38	426.7	2	345.7	10	283.9	10
R. T.	8.69	43.48	397.9	2	353.0	17	285.5	8
R. T.	6.58	45.07	381.5	3	353.5	19	281.9	6
R. T.	4.42	46.68	355.7	28	...	..	282.7	6
R. T.	2.24	48.32	359	19	356	12	283.6	3
R. T.	0.91	49.32	364.3	27	...	..	...	..
R. T.	...	50.00	370.0	31	...	..	...	..

[a] The break was indicated by a sudden change in the slope of the curve.

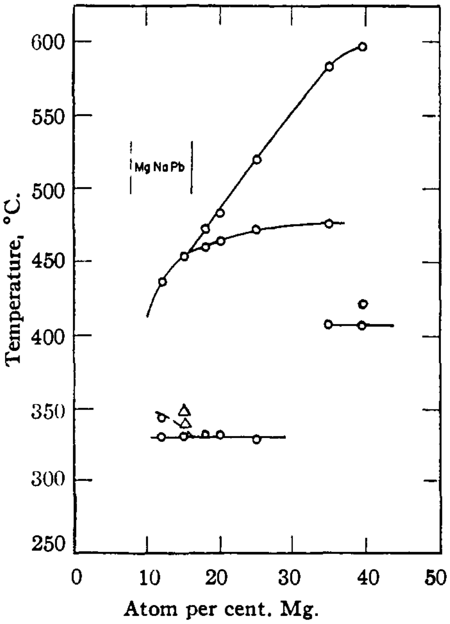

Fig. 3.—Cross section parallel to NaPb–Mg cross section and passing through 52.5% Na–47.5% Pb.

TABLE III

THERMAL ANALYSIS OF 15 ATOM PER CENT. MAGNESIUM CROSS SECTION

Cooling method	Atom per cent.		Temperature breaks							
			I		II		III		IV	
	Mg	Na	T, °C.	Min.	T, °C.	Min.	T, °C.	Min.	T, °C.	Min.
S. C.	15.00	15.00	303.1	2	286.0	18	256.0	8	...	
S. C.	15.00	22.14	331.4	[a]			295.6	34	...	..
R. T.	15.00	27.00	359.9	2	288.0	<1	287.1	29	...	..
S. C.	15.00	29.00	372.1	2	311.7	<1	287.5	39	...	..
S. C.	15.00	32.00	384.9	4	291.5	<1	286.0	31.5	...	..
S. C.	15.00	35.00	411.8	3	292	<1	285.9	28.5	...	..
S. C.	15.00	37.00	423.5	4	315.5	7	284.7	27	...	..
S. C.	15.00	38.00	428.1	3	327.5	7	283.2	27	...	..
S. C.	15.00	40.00	443	<1	351	20	287	12	...	..
S. C.	15.00	41.50	444.3	4	355.5	21	284.9	7.5	...	..
S. C.	15.00	45.00	451.5	7	348.5	17	328.9	8	321.9	2

[a] The break was indicated by a sudden change in the slope of the curve.

TABLE IV

THERMAL ANALYSIS OF Na_4Pb–Mg_2Pb CROSS SECTION

Cooling method	Atom per cent.		Temperature breaks							
			I		II		III		IV	
	Mg	Na	T, °C.	Min.	T, °C.	Min.	T, °C.	Min.	T, °C.	Min.
S. C.	65.00	2.00	550.7	20	531.0	4	466.3	1	....	..
S. C.	63.64	3.64	552.4	16	514.0	2	502.2	1	467.5	3
S. C.	60.83	7.00	553.5	20	500.4	2.5	465.9	3	....	..
S. C.	59.58	8.50	554.1	21	547	<1	501.0	1	466.1	5
S. C.	58.33	10.00	553.5	18	547	<1	478.0	4	....	..
S. C.	57.14	11.43	551.9	16	542.4	3	478.8	6	396.7–397.7[a]	..
S. C.	55.00	14.00	551.0	<1	546.5	18	475.9	2	395.7–400.0[a]	..
S. C.	53.30	16.00	553.7	<1	547.0	16	477.9	3	397.5–409.7[a]	..
S. C.	50.83	19.00	566.0	<1	546.7	10	476.7	2	398.3–412.7[a]	..
S. C.	50.00	20.00	567.2	<1	542.0	5	474.4	1	396.4–411.5[a]	..
S. C.	49.17	21.00	572.1	3	546.6	8	471.9	<1	397.1–412.6[a]	..
S. C.	48.33	22.00	574.3	3	547.2	12	...		414.0–434.9[a]	..
S. C.	46.67	24.00	580.6	8	...	..	...	..	404.7–427.8[a]	..
S. C.	42.85	28.57	594.2	>8	407.2	<1	...	..	404.2–439.5[a]	..
S. C.	41.72	29.94	592.5	19	405.2	7	...	..	395.1–400.2[a]	..
S. C.	40.50	31.40	596.3	14	455.9	<1	407.1	10	....	..
S. C.	39.46	32.65	596.7	22	419.6	<1	408.0	5	....	..
S. C.	38.32	34.00	596.9	22	...	..	398.9	3	....	..
S. C.	36.36	36.36	600.7	23	...	..	383.8	1	....	..
S. C.	34.16	39.00	596.5	15	...	..	...	..	....	..
S. C.	30.83	43.00	594.0	16	...	..	...	..	....	..
S. C.	27.49	47.00	587.4	11	...	..	...	..	....	..
S. C.	25.00	50.00	582.0	5	...	..	...	..	....	..
S. C.	21.66	54.00	571.4	4.5	...	..	...	..	....	..
S. C.	16.67	60.00	551.2	4.5	...	..	...	..	....	..
S. C.	11.11	66.66	516.8	<1	430.7	4.5	341.5–342.5[a]	..	....	..
S. C.	7.50	71.00	475.2	<1	434.0	6	343.9–346.8[a]	..	....	..
S. C.	5.00	74.00	439.2	<1	356.9	<1	352.2–361.6[a]	..	....	..
S. C.	2.50	77.00	400.1	<1	363.7	6	356.9–375.6[a]	..	....	..

[a] Supercooled break. Initial and maximum temperatures are given.

used exclusively. Both open iron crucibles and closed iron bombs were employed. Iron was used because the binary equilibrium diagrams show that iron does not interact with any of the three metals in the system within the temperature range of this study; examination of the vessels after many experiments substantiated this fact. Above 600° the closed bombs were used exclusively on account of the substantial vapor pressure of the alloy at the higher temperatures. These bombs, 2 in. i.d. and 2.125 in. inside height, were threaded on the upper outside edge for 0.75 in., and fitted with 0.5-in. thermocouple wells extending in through the bottom. For easy removal, the screw covers were hexagonal in shape.

The open crucibles, of $^{1}/_{32}$-in. wall thickness, were covered with a slotted iron disc which centered a stirrer and thermocouple in the melt. The thermocouple was encased in 4-mm. Pyrex tubing, which was not attacked at the temperatures employed. The stirrer consisted of a $^{1}/_{16}$-in. iron rod welded perpendicularly to a 1-in. iron disc. The crucible was centered in an iron pot by means of a triangular tripod. The pot, cylindrical in shape and of 0.125-in. thickness, was fitted with a special cover

TABLE V

THERMAL ANALYSIS OF 50 ATOM PER CENT. LEAD CROSS SECTION

Cooling method	Atom per cent.		Temperature breaks					
			I		II		III	
	Mg	Na	T, °C.	Min.	T, °C.	Min.	T, °C.	Min.
S. C.	4.54	45.45	352.3	<1	348.0	<1	285.1	12
R. T.	12.50	37.50	384.9	2	320.0	7	286.0	23
S. C.	15.00	35.00	411.8	3	292	<1	285.9	28.5
S. C.	16.66	33.33	414.0	3	331	<1	284.0	36
S. C.	18.50	31.50	413.1	2	398	<1	286.5	33
S. C.	20.00	30.00	422.9	<1	398.2	2	288.0	30
R. T.	25.00	25.00	432.1	2	[a]	...	285.0	29
S. C.	27.50	22.50	451.9	2	302	<1	288.1	42
S. C.	33.00	17.00	463.7	<1	...	...	248.8	11
S. C.	35.00	15.00	474.1	3	...	...	295.5	20
S. C.	37.50	12.50	455.4	3	289.4	15	252	<1
R. T.	42.50	7.50	465.7	2	254.1	<1	253.3	<1
R. T.	45.00	5.00	467.3	<1	253.3	<1	252.8	<1

[a] Break of doubtful validity.

which was fastened to the pot by screws and contained two holes corresponding to those in the crucible cover. The cover was also fitted with a steel gas inlet tube. The entire pot assembly could be lifted by means of two bolts screwed into the cover. The pot fitted closely into a Hoskins electric furnace, whereas the bomb assembly was centered in the furnace by means of a magnesia block.

The alloy was cooled either against room temperature, with the heat turned off, or at a constant cooling rate of 1°/minute. For the latter, a calibrated electrical system was used consisting of a Variac and a variable resistor connected in parallel to the furnace. During heating, the resistor was by-passed.

The crucible or bomb was charged with the proper mixture of magnesium, lead, and NaPb or Na_4Pb, in a box flushed for a minimum of one hour with inert gas. The assembly of the apparatus was completed under inert gas, after which it was placed in the furnace chamber and fitted with an iron-constantan thermocouple. When the crucible was used, nitrogen or helium was passed through the iron pot at the rate of 1 or 2 liters/min. With the bomb, an inert atmosphere was not required in the furnace chamber.

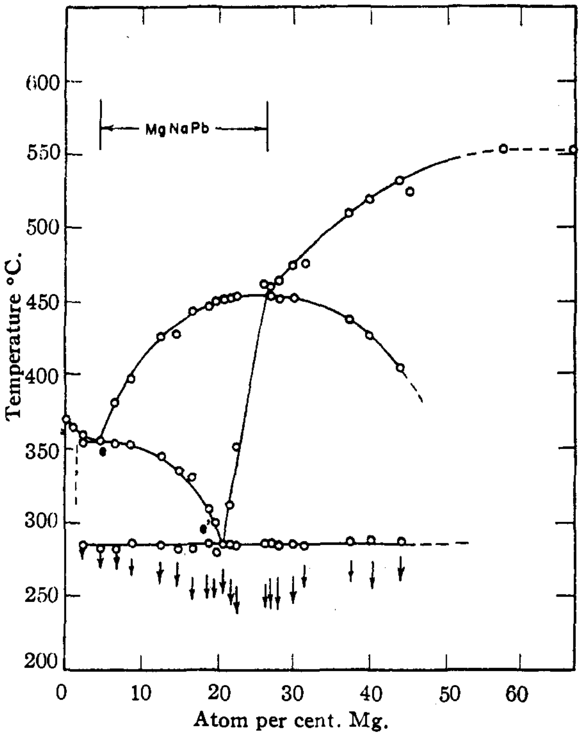

Fig. 4.—NaPb-Mg_2Pb cross section: time scale for temperature breaks, 50° = twenty minutes.

The constituents of the alloy were heated to a temperature 75 to 100° above the predicted temperature of the primary break in the cooling curve of the alloy, if above 450°. For alloys with lower primary breaks, it

TABLE VI

THERMAL ANALYSIS OF MISCELLANEOUS ALLOYS

Cooling method	Atom per cent.		Temperature breaks							
			I		II		III		IV	
	Mg	Na	T, °C.	Min.	T, °C.	Min	T, °C.	Min.	T, °C.	Min.
S. C.	3.00	27.28	312.4	25	...	...	291.6	6	...	..
S. C.	9.00	24.71	...	...	...	...	295.4	37	...	..
S. C.	12.00	23.43	317.2	2	...	...	295.6	34	...	..
S. C.	15.00	22.14	331.4	3	...	...	295.6	34	...	..
S. C.	30.00	15.71	434	5	...	...	294.9	23	...	..
S. C.	14.73	4.78	...	...	...	...	252.9	36	...	..
S. C.	14.28	28.57	370.8	<1	294.0	<1	288.6	30	....	..
S. C.	5.00	55.00	331.6	1	...	...	326.2	36	...	..
S. C.	10.00	55.00	339.1	<1	...	...	326.4	29	...	..
S. C.	37.50	37.50	589.8	11	...	...	559.9	11	...	..
S. C.	44.44	33.33	596	<1	570.9	7	561.2	25	...	..
R. T.	19.25	21.14	372.0	<1	294.9	4	284.6	12	...	..
S. C.	15.58	51.08	408.4	2	...	...	329.2	22	...	..
S. C.	45.27	14.72	461.3	<1	290.5	<1	287.1	<1	...	..
S. C.	9.00	50.00	420.9	5	337.7[a]	...	332.9	11	326.9	5
R. T.	12.50	50.00	457.9	<1	421.2	<1	330.9	23[a]	...	..
R. T.	20.51	39.11	471.0	5	354	13	285.5	4	...	..
R. T.	27.50	32.50	478.1	2	...	...	285.8	5	...	..
R. T.	30.00	30.00	477.8	3	...	...	286.9	7	...	..
R. T.	32.50	35.00	564.4	...	484.9	7	329	<1	...	..
R. T.	35.00	27.50	502.0	2	486.0	2	286.8	5	...	..

[a] Supercooling.

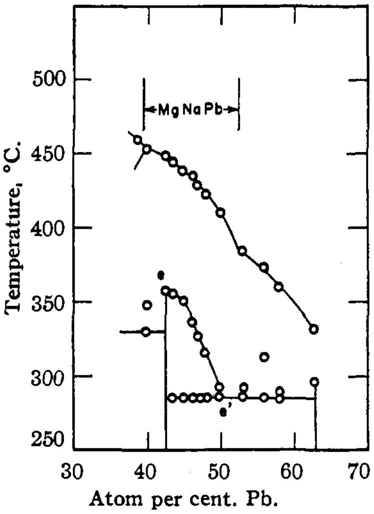

Fig. 5.—Cross section at 15 atom per cent. magnesium.

was necessary to raise the temperature to approximately 500° to dissolve the magnesium. Alloys made in crucibles were stirred for a minimum of forty-five minutes to ensure complete solution of the ingredients at the maximum heating temperature. Similarly, alloys made in bombs were vigorously shaken by means of tongs for at least five minutes over a forty-five minute heating period. No trouble was encountered in dissolving the alloy metals in the bombs since the temperatures were usually above 650°, the melting point of magnesium, the highest melting ingredient.

After the alloy was thoroughly mixed, shredded magnesia insulation was placed over the furnace to a depth of about 3 in. If the crucible was being used, the stirrer was lifted out of the molten alloy and fixed in this position by a small clamp. The temperature of the furnace was held constant for about thirty minutes to bring the insulation to temperature equilibrium.

Most of the alloys were cooled at the constant rate of 1°/minute to give a more easily interpreted cooling curve and to favor the establishment of equilibrium conditions in the alloy. Cooling against room temperature was used as a check on roughly half of the alloys cooled at the constant cooling rate, and sometimes when the necessary time for constant rate cooling (about five hours) was lacking.

The cooling rates for cooling against room temperature varied from approximately 4°/minute at 500° to approximately 1°/minute at 250°. For a few alloys, heating curves were taken, in order to detect temperature breaks below 200° and to confirm temperature breaks obtained on cooling. The heating rates varied from 1°/minute to 4°/minute, the former rate being used on alloys of special interest.

After the cooling curve was obtained, the alloy apparatus was cooled to room temperature and opened in an inert atmosphere. The alloy was coarsely crushed and was inspected for undissolved constituents, if any, crystallinity, color, and brittleness. It was then stored in paraffin-sealed bottles for microscopic examination. Thirty alloy specimens were polished and photomicrographed.

Results and Discussion

The results of thermal analysis are given in Tables I–VI. Two abbreviations are used: R. T., denoting cooling against room temperature; and S. C., cooling at a constant rate of 1° per min. The alloys are classified as belonging either to a specific cross section, such as Na_4Pb–Mg_2Pb, NaPb–Mg_2Pb, NaPb–Mg, Na_2Pb_5–Mg_2Pb, 15% atom magnesium, or 50% atom lead, or to a region, such as the lead corner. An alloy located at the intersection of two cross sections is found in the tables for both cross sections.

For alloys in the various cross sections of Tables I–IV, the temperature breaks are plotted in Fig. 1–6. The length of the solid vertical line immediately below an isothermal break is proportional to the time of the break. In several cross sections, notably the Na_4Pb–Mg_2Pb cross section, the final temperature breaks were characterized by a sharp rise and fall in temperature, which indicates a high degree of supercooling. This type of break is designated in the plots by triangles, which show both the beginning and the end of the temperature rise.

MgNaPb Surface of Primary Crystallization.—The surface of primary crystallization of the compound MgNaPb is bounded in part by the two incomplete binary eutectic curves and the one peritectic curve (GG′) shown in Fig. 7. The temperatures along the curves are given at various points. The loci of the curves were determined from Fig. 1–5 and also from several other cross-sectional plots not shown in this paper.[3] The lim-

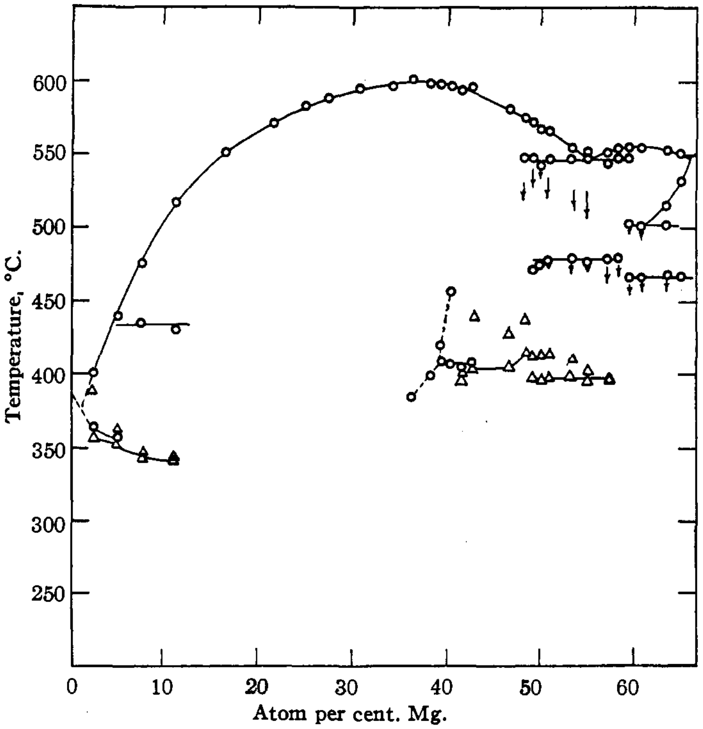

Fig. 6.—Na_4Pb–Mg_2Pb cross section. Time scale for temperature breaks, 50° = twenty minutes.

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[3] The complete experimental data are given in Ethyl Corporation reports LTD 46-22 and LTD 47-32, which are available on request.

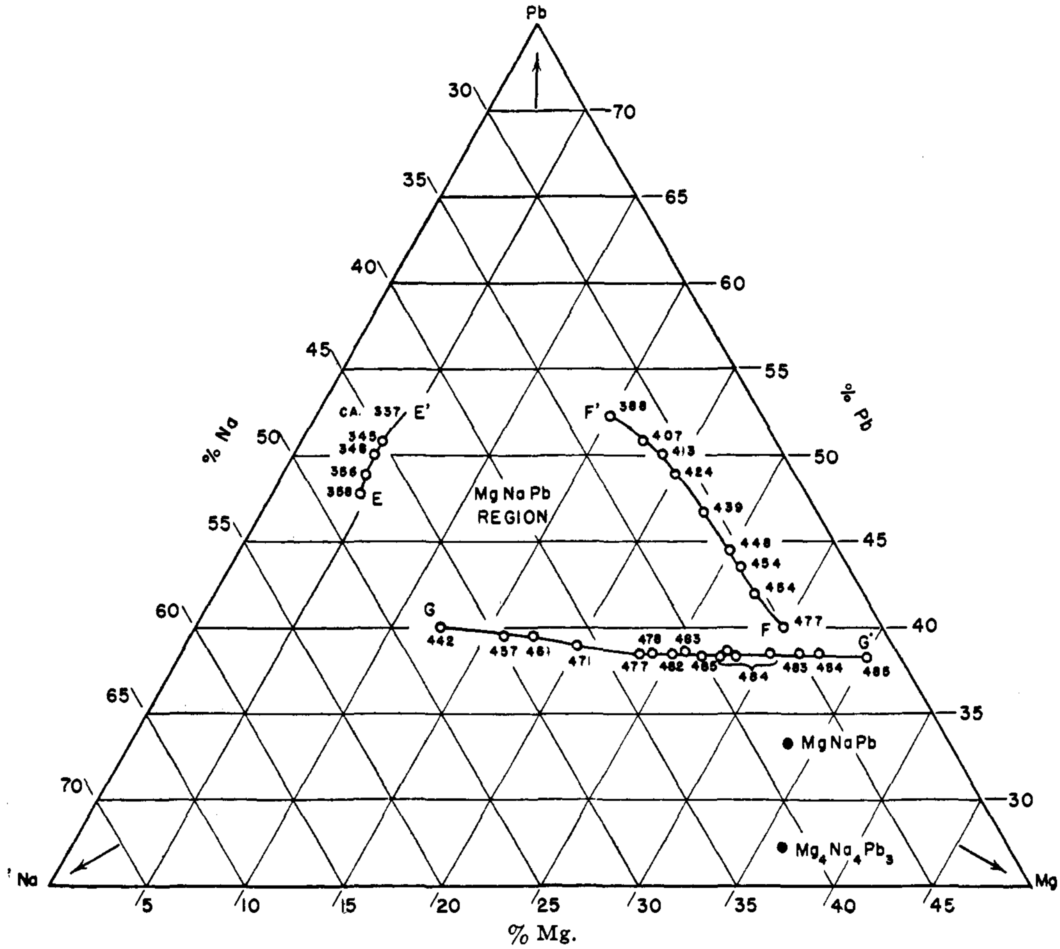

Fig. 7.—Binary eutectic curves of the region of primary crystallization of MgNaPb.

its of the surface of primary crystallization of MgNaPb are also indicated in Fig. 1–5.

From the cross-sectional shapes of the surface of primary crystallization of the compound (Fig. 1–5) and the isothermal plots of the primary temperature breaks (Fig. 8), it is evident that the surface of primary crystallization possesses no open-maximum point. It should be noted that the alloys in this region exhibited two or three temperature breaks; in general, the primary break was represented by a sharp change in the slope of the cooling curve and not by an isothermal flat.

MgNaPb Composition.—The method used to locate the compound MgNaPb is based on the fact that within the region of primary crystallization of a compound all alloys along a straight line passing through the compound composition will give the same secondary break, representing the intersection of the line with a binary eutectic curve bounding the region. Several such lines, each representing a simple secondary temperature break on the same binary eutectic curve, must themselves intersect at the location of the ternary compound.

Of the available data on the two eutectic curves (EE', FF') shown in Fig. 7, only that portion of the curve EE' descending in temperature from the NaPb–Mg cross section in the direction of the Pb corner was used to locate the MgNaPb compound. The curve GG' cannot be used for this purpose, since it cannot be reached *via* the primary precipitation of this compound.

In Fig. 2, 4 and 5, the curves for the secondary temperature breaks corresponding to the curve EE' are indicated by ee'. By and large, the curves ee' are well established. They show a gradual but sufficient change in temperature to define the lines of interest (the alloy compositions having the same secondary temperature break). Figure 9 shows four such lines, for the secondary breaks of 358, 340, 320 and 285°. (The 285° line gives, in reality, those compositions which show a second and final temperature break corresponding to a 285° eutectic.) On extrapolation, these lines intersect at the alloy composition $33^1/_3$ atom per cent. Mg, $33^1/_3$ atom per cent. Na and $33^1/_3$ atom per cent. Pb, or MgNaPb.

From the aforementioned analysis curves EE' and FF' in Fig. 7 are binary eutectic curves char-

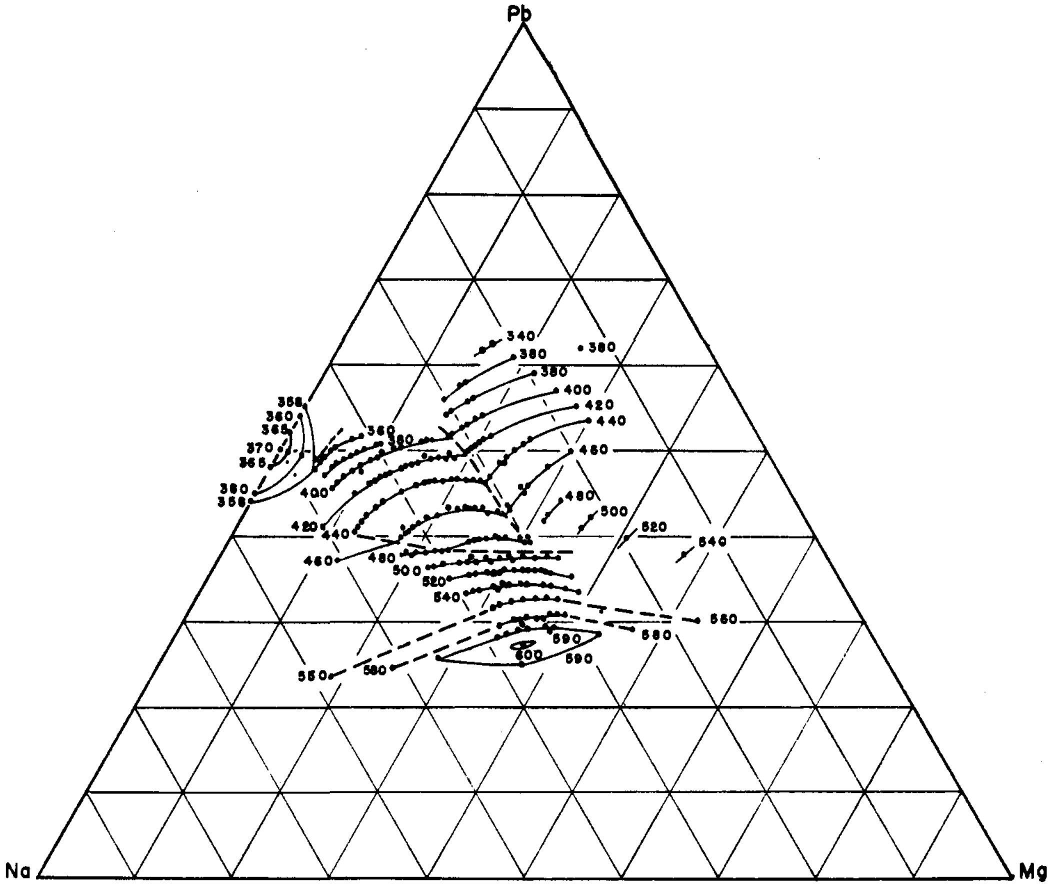

Fig. 8.—Isothermal curves of primary crystallization of the MgNaPb region and surrounding area.

acterized by the simultaneous crystallization of two different species. On the other hand, curve GG′ is apparently a binary peritectic curve at which solid and liquid react to give a second solid phase. The reaction must be

$$Mg_4Na_4Pb_3 + \text{liq.} \longrightarrow MgNaPb$$

Microscopic examination of the polished surface of the alloy MgNaPb revealed two regions. The main phase was dark-colored and constituted more than 90% of the surface area. The minor region was silver in color. Other alloys examined in the neighborhood of the alloy MgNaPb disclosed two or three regions, with the main phase being present in amounts below 90%.

Na_4Pb–Mg_2Pb Cross Section.—The Na_4Pb–Mg_2Pb cross section is shown in Fig. 6. The range of primary crystallization of the ternary compound $Mg_4Na_4Pb_3$ (at 36.36 atom per cent. magnesium in the Na_4Pb–Mg_2Pb cross section) appears to be quite large. The absence of lower breaks within part of the range is suggestive of solid solution in the compound. On the other hand, the ranges of primary crystallization of the binary compounds within the ternary system are very limited. Na_4Pb extends into the ternary diagram for less than 2.5 atom per cent. magnesium and Mg_2Pb for less than 2.0 atom per cent. sodium (approximately equivalent to 65 atom per cent. magnesium). The approximate equality of the initial temperature breaks between 55 and 65 atom per cent. magnesium might suggest a very flat surface of primary crystallization for Mg_2Pb. However, the existence in this region of non-isothermal breaks and of several lower temperature breaks precludes this possibility, which ordinarily would require a single secondary temperature break. The long duration of the initial temperature breaks for these alloys (Table IV) suggests that a ternary compound of high magnesium-to-sodium ratio may exist close to the cross section.

Temperature breaks characterized by a sharp rise were observed principally in the Na_4Pb–Mg_2Pb cross section.

Solid Solubility in the NaPb–Mg_2Pb Cross Section.—The NaPb–Mg_2Pb cross section, shown in Fig. 4, is well defined up to 45 atom per cent. magnesium. The limit of solid solubility in NaPb lies somewhere between 0.91 and 2.24 atom per cent. magnesium as measured along the cross section. With the former alloy, only a single temperature break was obtained and the presence of a single phase was confirmed by micro-

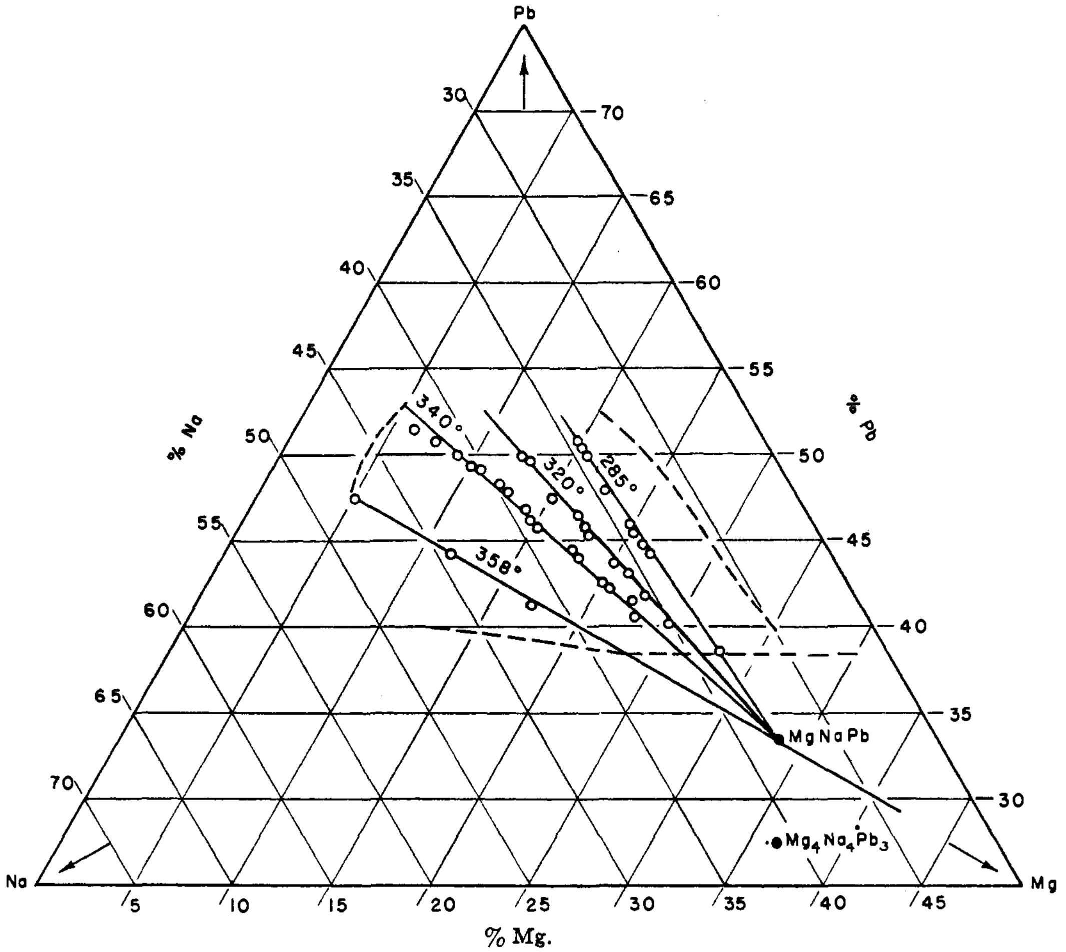

Fig. 9.—Method of locating the compound MgNaPb.

scopic investigation. With the latter alloy, three temperature breaks were obtained. No further attempt was made to establish more exactly the limits of solubility.

Summary

Approximately 120 individual alloy compositions within the ternary system Mg–Na–Pb were investigated by thermal analysis. The system was shown to be complex. A second compound, MgNaPb, was discovered, but unlike the first compound, $Mg_4Na_4Pb_3$ (which is of the open maximum type), it is of the peritectic type.

Several important cross sections of the system were partly elucidated. The lead corner was indicated to be the simplest region, while solid solutions were discovered in two regions and supercooling in others. Thirty alloys were photomicrographed, including the compound MgNaPb.

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