[Contribution from the University Chemical Laboratories. University of the Punjab]

Equilibrium of the Ternary System Bismuth–Lead–Zinc

By S. D. Muzaffar and Ram Chand

This system has been investigated to study the influence of zinc on the miscibility of bismuth and lead. It has been partially attempted by H. Fincke.[1] It involves the three binary systems: bismuth–lead, bismuth–zinc, and lead–zinc, which have been investigated, and their thermal diagrams are given in Fig. 1.

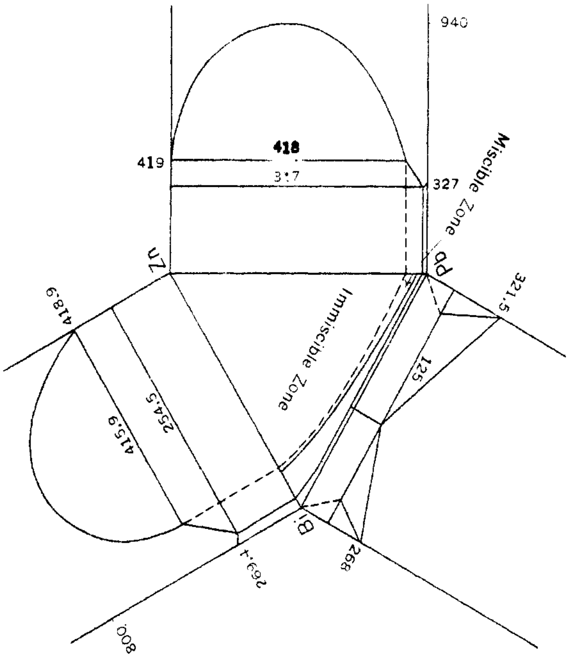


Fig. 1.—The three binary system invol ved in the ternary system Bi–Pb–Zn.

Bismuth–Zinc System.[2]—At 425° the two metals are immiscible but as the temperature is raised their mutual solubility increases, resulting in complete miscibility at 850°.

Lead–Zinc System.[2]—These two metals are also immiscible at 425° and they also become completely miscible at 940°.

Bismuth–Lead System.[3]—These are miscible in all proportions at 300°. They form a eutectic (with 56.6% bismuth and 43.5% lead), the freezing point of which is 125°.

Thermal Analysis.—Pure metals were employed throughout the work: bismuth (99.9%), lead (99.5%) and zinc (Merck Reagent). Their purity was confirmed by chemical analysis and their freezing points were found to be the same as the standards. Thermal arrests were determined by the method described by S. D. Muzaffar[4] in an earlier study on the ternary system bismuth–tin–zinc; one hundred and fifty grams of each alloy was prepared by accurately weighing out the requisite quantities of each metal on a sensitive balance. The alloys were protected from oxidation during melting by a layer of charcoal on their surface. In the case of certain alloys the composition was determined by chemical analysis after the thermal analysis. Results of the thermal analysis are given in Table I.

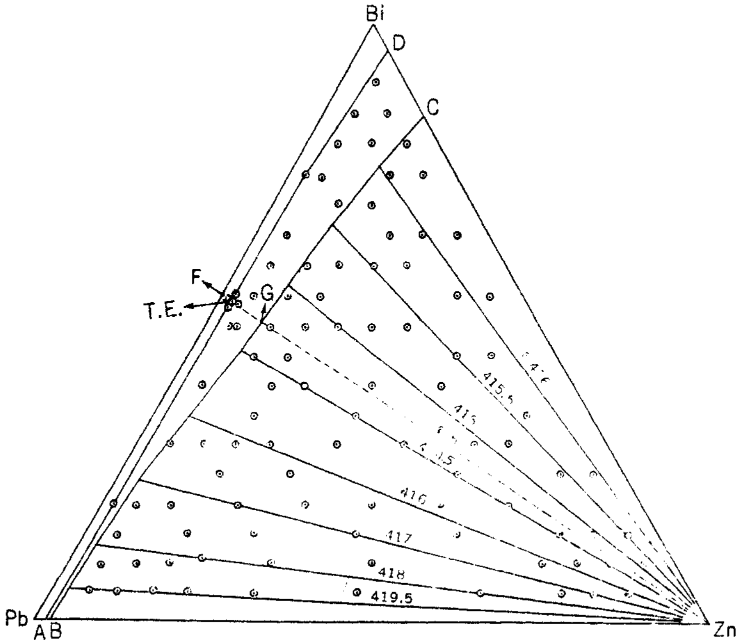


Fig. 2.—The phase diagram of the system Bi–Pb–Zn. The tie-lines represent freezing temperatures of the lower layer of two-liquid alloys in the zinc field.

Freezing Points of the Alloys.—All alloys whose compositions lie in the area Bi–Pb–A–B–C–D–Bi (as marked in Fig. 2) form a single liquid layer at all temperatures above their melting points while those whose compositions lie in the area B–C–Zn form two liquid layers upon melting. The boundary line B–C has been established by the observations of the clear-cut cross sections of the alloys on either side of the line. The immiscible alloys show a distinct layer of zinc on the top of the frozen alloy. Compositions of the alloys on either

---

[1] Fincke, *Metalbrose*, **17**, 2581 (1927).

[2] W. Spring and L. Romenhoff, *Z. anorg. Chem.*, **13**, 29 (1896).

[3] A. Kapp, *Ann. Physik*, **18**, 29 (1897).

[4] Muzaffar, *J. Chem. Soc.*, London, **123**, 2341 (1923).

side of the B–C line have been confirmed by chemical analysis.

In Fig. 2 is also shown the position of the *ternary eutectic* at TE. Its freezing point is 124° and its composition is 55% Bi, 2% Zn, and 43% Pb. The three binary valleys TE–A, TE–D and TE–F ascend from it to the three binary eutectics situated at A, D and F, respectively. The binary valley TE–A is essentially parallel to the Bi–Pb side as both the ternary eutectic and the binary eutectic of Pb–Zn contain about 2% of Zn.

The Freezing Process.—All alloys whose compositions lie in the immiscible zone (B–C–Zn in Fig. 2) separate out in two layers on freezing. The upper layer consists of almost pure zinc as this metal is lighter than the other two. Zinc is the first to freeze, as its freezing point is the highest.

With the separation of zinc, the composition of the lower layer shifts along a line (see Fig. 2), starting from zinc, passing through the position of the alloy in question and ending at the boundary line B–C. When the composition of the lower layer becomes the same

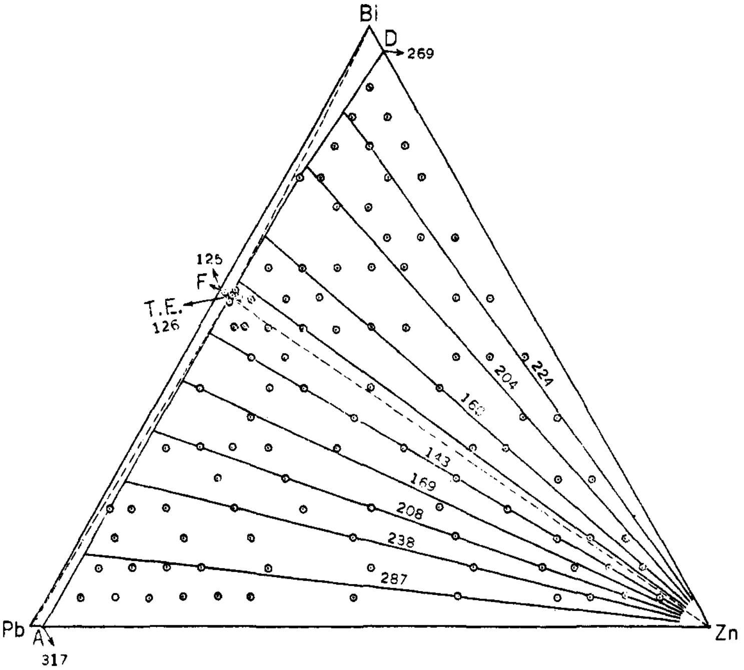


Fig. 3.—Isothermals of secondary (binary) arrests.

TABLE I

THERMAL ARRESTS OF ALLOYS IN THE SYSTEM Pb–Bi–Zn

Alloy no.	Composition in % by weight Bi	Pb	Zn	Thermal arrests, °C. 1	II	III	Number of layers in the solidified alloy
1	90	5	5	375	243	126	One
2	85	10	5	391	224	125	One
3	85	5	10	...	241	125	One
4	80	15	5	...	210	124	One
5	80	10	10	396	224	125	One
6	80	5	15	416	240	125	Two
7	75	23	2	...	200	124	One
8	75	20	5	...	205	125	One
9	75	10	15	416	222	125	Two
10	75	5	20	416.5	240	126	Two
11	70	20	10	...	198	125	One
12	70	15	15	416	214	124	Two
13	65	15	20	415.5	210	125	Two
14	65	10	25	416	220	125	Two
15	65	5	30	416.5	238	124	Two
16	60	35	5	...	...	126	One
17	60	30	10	415.5	160	125	Two
18	60	25	15	415.5	179	125	Two
19	60	20	20	415.5	193	124	Two
20	60	15	25	415.5	208	125	Two
21	57	41	2	...	...	124	One
22	56.5	42.5	1	...	...	124	One
23	56	42	2	...	...	124	One
24	56	41	3	...	...	124	One
25	55	40	5	...	...	124	One
26	55	35	10	415	...	126	Two
27	55	30	15	415	144	125	Two
28	55	10	35	416	210	124	Two
29	55	5	40	416.5	231	125	Two
30	50	45	5	...	...	126	One
31	50	44	6	...	...	126	One
32	50	40	10	414.5	...	125	Two
33	50	35	15	415	130	124	Two
34	50	30	20	415	127	123	Two
35	50	25	25	415	160	123	Two
36	50	20	30	415	170	124	Two
37	45	45	10	...	145	125	Two
38	45	40	15	415	...	124	Two
39	45	15	40	415.5	190	123	Two
40	45	10	45	416	210	124	Two
41	45	5	50	416.5	226	123	Two
42	40	55	5	...	169	125	One
43	40	45	15	415	149	125	Two
44	40	40	20	414.5	143	123	Two
45	40	30	30	415	...	124	Two
46	40	20	40	415.5	161	125	Two
47	35	50	15	416	162	124	Two
48	35	35	30	414	144	125	Two
49	35	10	55	415.5	203	124	Two
50	35	5	60	416.5	223	124	Two
51	30	65	5	...	220	124	One
52	30	60	10	...	210	123	Two
53	30	55	15	416	200	125	Two
54	30	50	20	415.5	170	124	Two
55	30	40	30	415	152	123	Two
56	30	30	40	414.5	142	124	Two
57	30	20	50	414.5	...	126	Two
58	30	15	55	414.0	158	...	Two
59	25	60	15	...	221	124	Two
60	25	50	25	417	208	123	Two
61	25	25	50	414.5	143	122	Two
62	25	10	65	415.5	176	...	Two
63	25	5	70	416.5	212	...	Two

TABLE I (*Concluded*)

Alloy no.	Composition in % by weight			Terminal arrests, °C.			Number of layers in the solidified alloy
	Bi	Pb	Zn	I	II	III	
64	20	78	2	. . .	260	123	One
65	20	75	5	. . .	256	121	One
66	20	70	10	417	248	124	Two
67	20	60	20	417	241	123	Two
68	20	50	30	416	223	123	Two
69	20	40	40	416	206	124	Two
70	20	30	50	416	164	123	Two
71	20	20	60	414	143	. . .	Two
72	15	80	5	. . .	272	124	One
73	15	70	15	418.5	271	123	Two
74	15	60	25	418.0	260	122	Two
75	15	45	40	418	238	124	Two
76	15	30	55	417	208	125	Two
77	15	15	70	414.5	142	. . .	Two
78	15	10	75	414.5	. . .	. . .	Two
79	15	5	80	415.5	206	. . .	Two
80	10	85	5	. . .	292	124	One
81	10	80	10	. . .	292	. . .	Two
82	10	75	15	418.5	290	124	Two
83	10	70	20	418.5	287	. . .	Two
84	10	60	30	418	280	. . .	Two
85	10	45	45	418	265	124	Two
86	10	30	60	417.5	240	123	Two
87	10	20	70	417.5	208	124	Two
88	10	15	75	416.5	. . .	. . .	Two
89	10	10	80	414.5	141	. . .	Two
90	10	5	85	415.5	. . .	124	Two
91	5	90	5	. . .	310	. . .	One
92	5	85	10	420	306	. . .	Two
93	5	80	15	419.5	305	. . .	Two
94	5	75	20	419.5	303	. . .	Two
95	5	65	30	419	301	121	Two
96	5	50	45	419	297	. . .	Two
97	5	35	60	418.5	288	. . .	Two
98	5	20	75	418.5	257	. . .	Two
99	5	15	80	418.0	236	. . .	Two
100	5	10	85	417.0	210	. . .	Two
101	5	5	90	415.0	185	. . .	One
T.E.	55	43	2	. . .	. . .	124	One

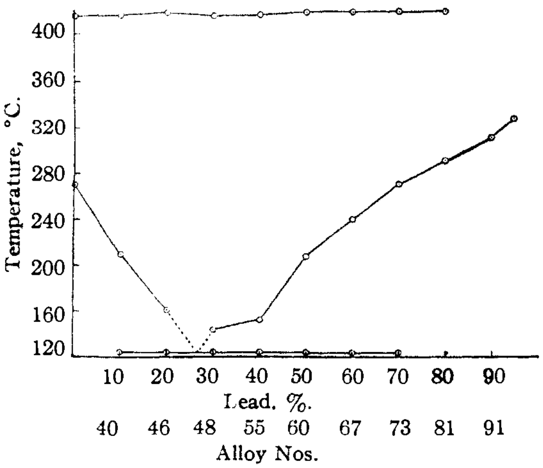


Fig. 4.—Cross section showing median through lead.

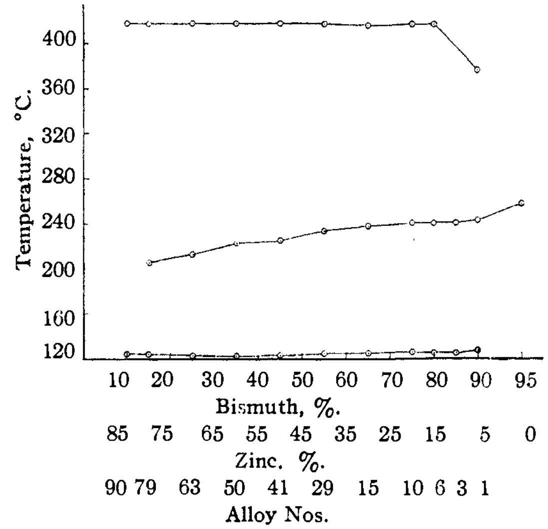


Fig. 5.—Section of thermal diagram (Fig. 2) through 5% lead.

as that of the point at which the line from zinc meets the line B–C the lower layer starts freezing. Thus all alloys whose composition lies on a line joining zinc and a point on B–C yield lower layers of the same composition represented by the said point on the line B–C. This is the significance of the thick lines diverging from zinc in Fig. 2. The binary arrest of all alloys lying on such a line is therefore the same (see Fig. 3).

The formation of immiscible liquid layers is limited to the area C–B–Zn, which lies entirely in the zinc field, D–TE–A–Zn. The alloys in the first-mentioned area form a two-liquid system on cooling before beginning to precipitate zinc. Upon complete solidification all the alloys in the zinc field (D–TE–A–Zn) will in general consist of three structures: (1) pure zinc, which crystallizes out first; (2) one of the binary "eutectics" (or mixtures), *i. e.*, Pb–Zn eutectic in the area

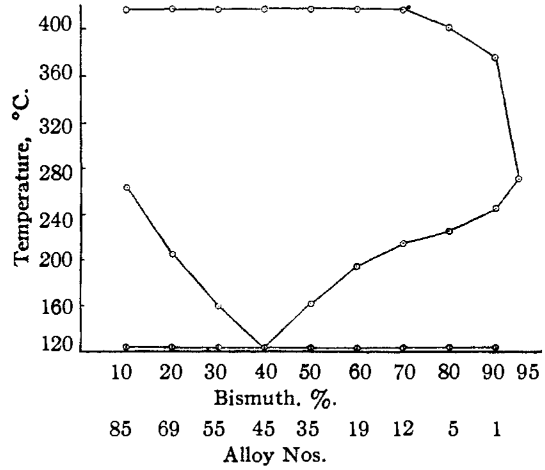


Fig. 6.—Section of thermal diagram showing median through bismuth.

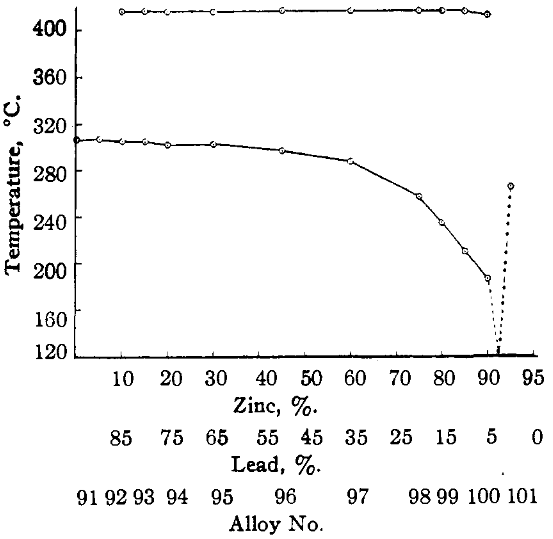


Fig. 7.—Section of thermal diagram (Fig. 2) through 5% bismuth.

TE–A–Zn and Bi–Zn eutectic in the area TE–D–Zn; (3) the ternary eutectic. Similar considerations apply to alloys with compositions in the bismuth or lead fields. Alloys with compositions lying on the two-solid curves, F–TE, A–TE and D–TE, show only two structures, a binary and a ternary eutectic. Furthermore, the line joining TE and Zn through G forms a valley in itself. In alloys 32, 45 and 57, whose compositions lie almost on this line, no binary eutectic is formed; they have only two structures, zinc and the ternary eutectic. Similarly the alloys on lines joining the corners Bi and Pb with TE will consist only of bismuth or lead, respectively, and ternary eutectic.

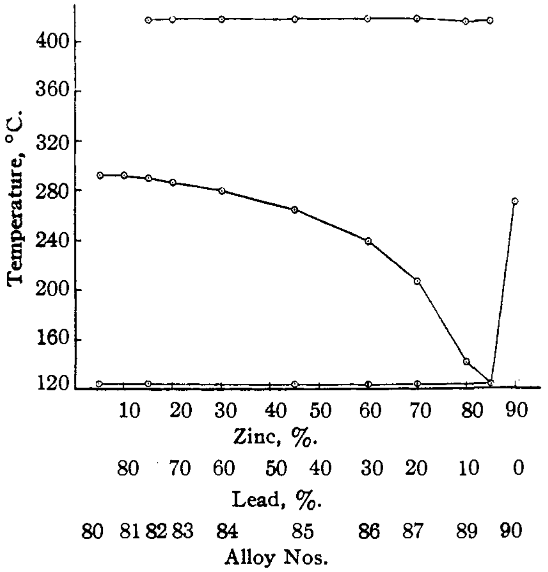


Fig. 8.—Section of thermal diagram (Fig. 2) through 10% bismuth.

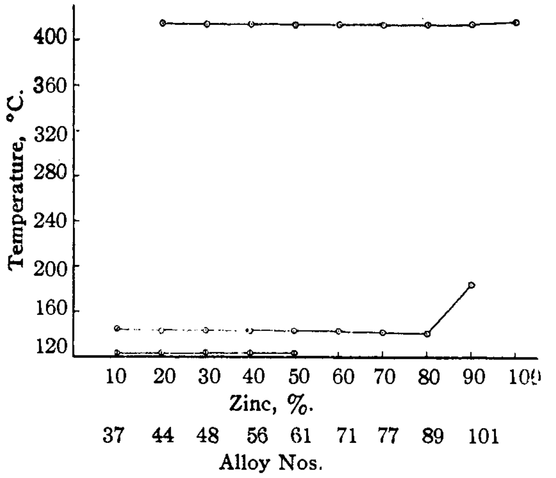


Fig. 9.—Section of thermal diagram showing median through zinc.

Isothermals of the Binary Arrests.—In Fig. 3 isothermals of the binary arrests of the various alloys of this system are given. As the line joining TE and Zn does not meet any of the binary valleys, the alloys whose compositions lie on this line have no binary eutectic and do not give any binary arrests. This line forms a valley by itself. The alloys with compositions farther and farther from this line give higher and higher binary arrests. Similar considerations apply to the configuration of the isothermals in both the bismuth and the lead fields.

Effect of Lead on the Partial Miscibility of Bismuth and Zinc (Median through Lead).—Figure 4 illustrates the effect of adding increasing quantities of lead to a mixture of equal proportions of bismuth and zinc by weight. This is a section through the middle point of the Zn–Bi base and the apex Pb of Fig. 2. The top line shows that up to 80% lead, zinc freezes out from these alloys at almost constant temperatures. With higher

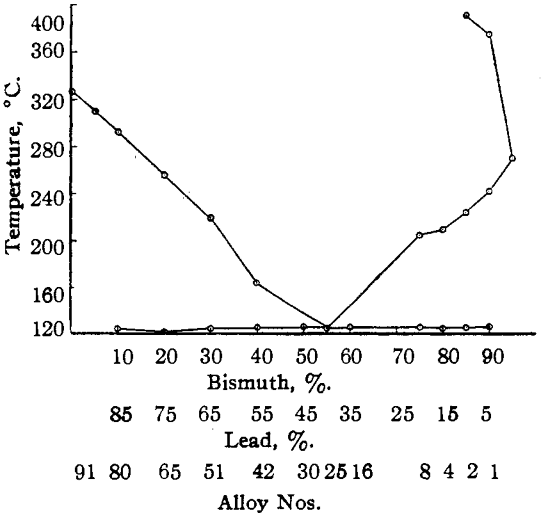
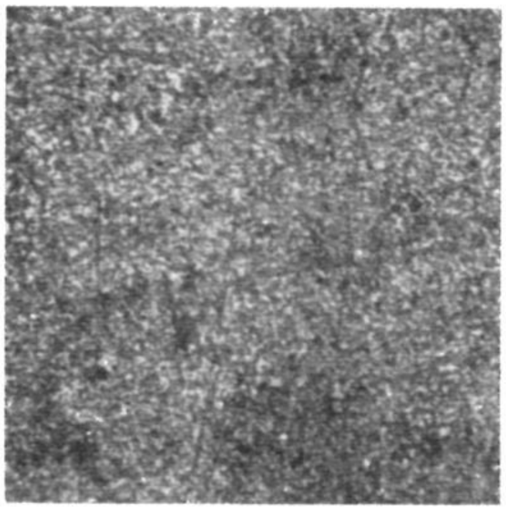


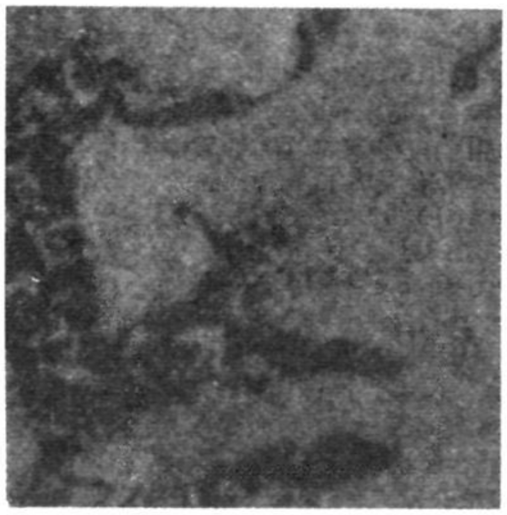
Fig. 10.—Section of thermal diagram through 5% zinc.

percentages of lead the freezing point rapidly falls. Binary arrests show a minimum at 30% lead, 35% bismuth, 35% zinc. This composition lies on the Zn–TE line (Fig. 2).



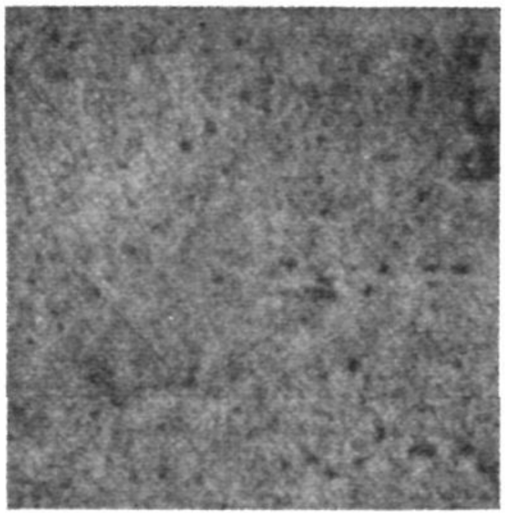
I. Ternary eutectic alloy TE (× 150) etched in HCl–$FeCl_3$.

II. Bismuth–zinc binary eutectic × 300.

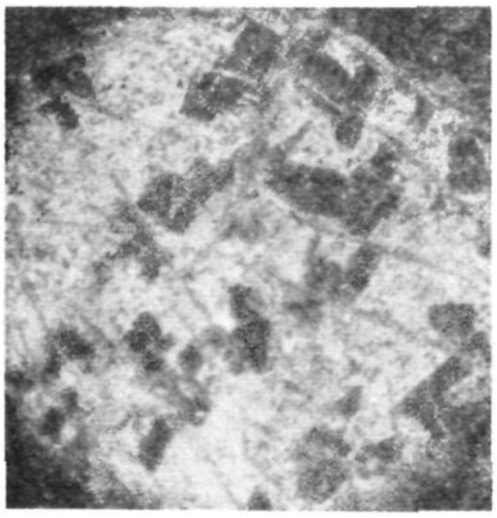


III. Ternary eutectic and bismuth–zinc binary eutectic alloy No. 8 (× 150).

IV. Alloy No. 39 (× 100), showing the upper and lower layers of the solidified alloy, the upper layer being zinc.

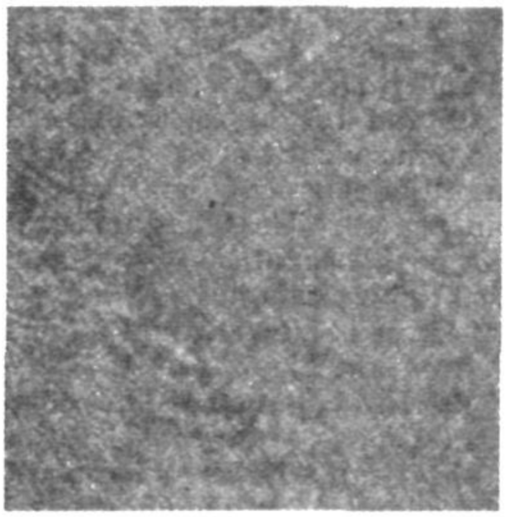


V. Showing the upper layer of the immiscible alloys consisting of almost pure zinc, × 200.

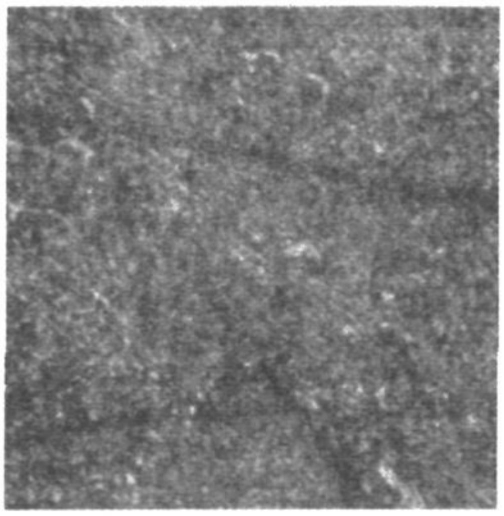


VI. Showing (× 100) the lower layer of the immiscible alloys consisting of three phases: (a) ternary eutectic (fine-grained background), (b) bismuth–zinc binary eutectic (dark blocks), and (c) pure zinc (dark lines).

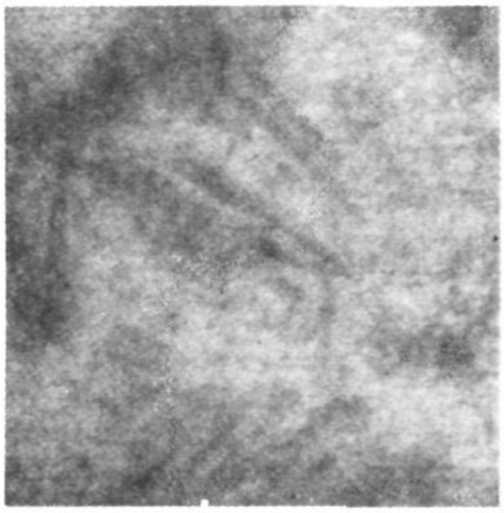
Fig. 11.—Photomicrographs of some of the alloys.



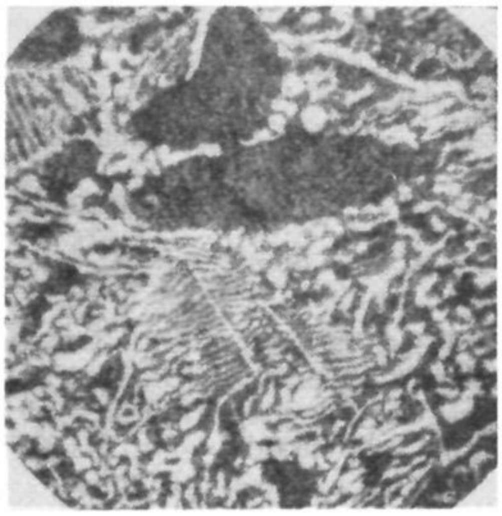
VII. Alloy No. 42 etched in iodine (× 150) and showing three phases: (a) ternary eutectic (fine-grained background), (b) lead–zinc binary eutectic (semi-dark blocks), (c) pure zinc (dark rods).



VIII. Alloy No. 45 (× 150) showing two phases: (a) ternary eutectic (black and white background), and (b) zinc (dark lines). This alloy lies on the line joining Zn and TE.

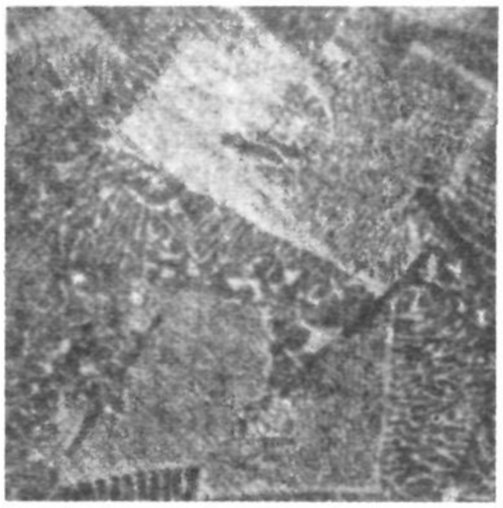


IX. Alloy No. 54 (× 150) showing two phases: (a) ternary eutectic (fine-grained patches), and (b) bismuth–lead binary eutectic (bold black and white patches).



X. Bismuth–lead eutectic (× 200).

XI. (× 150) etched in iodine and showing three phases: (a) ternary eutectic (almost white patches), (b) binary eutectic, and (c) zinc metal (dark lines).



XII. (× 150) etched in iodine and showing three phases: (a) ternary eutectic (fine-grained whitish patches), (b) binary eutectic, and (c) zinc metal (dark lines).

Fig. 11.—Photomicrographs of some of the alloys.

Figure 5 illustrates a section of Fig. 2 through 5% lead.

Effect of Bismuth on the Partial Miscibility of Lead and Zinc (Median through Bismuth).—Figure 6 illustrates the effect of adding increasing quantities of bismuth to a mixture of equal proportions of lead and zinc by weight. This is a section through the middle point of the lead–zinc base and Bi (Fig. 2). Up to 70% bismuth, zinc freezes out from these alloys at almost constant temperature. With higher percentages of bismuth, the freezing point rapidly falls to that of pure bismuth. Binary arrests show a minimum at 40% bismuth, 30% lead, 30% zinc. This composition lies at the Zn–TE line (Fig. 2).

Sections of the diagram (Fig. 2) at 5% bismuth and 10% bismuth are given in Figs. 7 and 8, respectively. The sharp fall in the binary arrests at high percentages of zinc or near the zinc corner of Fig. 2 is clearly noticeable.

Effect of Zinc on the Miscibility of Lead and Bismuth (Median through Zinc).—Figure 9 illustrates the effect of adding increasing quantities of zinc to a mixture of equal proportions of bismuth and lead by weight. There are three separate lines. The upper line represents the freezing points of the alloys. The middle one shows the binary arrests and the lowest line the freezing points of the ternary eutectic.

A section of the diagram (Fig. 2) at 5% zinc is illustrated in Fig. 10. The binary arrests show a minimum at 55% bismuth, 40% lead and 5% zinc. As this composition lies on the Zn–TE line the primary arrest is also low and is hardly distinguishable from the binary arrest.

Microscopic Investigation.—The conclusions drawn from the phase rule considerations (discussed above) are supported by microphotographs of some of the alloys as given in Fig. 11.

Summary

In this system a tertiary eutectic is formed with 55% bismuth, 43% lead and 2% zinc. Its freezing point is 124°.

By addition of 10–15% or more of zinc to the miscible binary alloys of bismuth and lead, the ternary alloys (thus formed) become immiscible.

LAHORE, INDIA RECEIVED AUGUST 9, 1943

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PERMUTIT COMPANY]

The Reaction Velocity of Ion Exchange

BY F. C. NACHOD AND W. WOOD

Many investigators have studied ion exchange phenomena and approached the subject from various directions. A great number of papers come from the soil chemist and, consequently, deal largely with ionic distribution in soils. Other investigators have described industrial uses and applications. Data on ionic equilibria between exchanger and solution have been collected.

However, surprisingly little information can be gathered if one wants to learn something about the rates of reaction taking place between the ions in solution and in the ion exchange material. One encounters qualitative statements that the reaction proceeds rapidly at first[1,2] and then slows down as the equilibrium is approached.

DuDomaine, Swain and Hougen[3] focussed their attention on cation exchange softening rates. Their technique consisted in passing hard water through thin layers of exchange material. The small dimension of the bed permitted disregarding concentration gradients and the authors arrived at differential rate equations. Certain limitations of the procedure are stated by the authors (p. 553 of ref. 3) and no rate constants were given, nor was the order of the reaction determined by these experiments. The data obtained by these authors are of value only for a particular cation exchange and a particular water composition. No net reaction rate could be obtained by their procedure.

Beaton and Furnas[4] obtained transfer coefficients by considering base exchange to be analogous to heat transfer. Their data on the hydrogen–copper exchange show again that the reaction is very rapid and about 90%[5] of it is completed in thirty minutes.

The difference between a good and a bad exchanger was shown graphically by Austerweil.[6] His experiments show that the exchange reaction is extremely rapid and completed after approximately fifteen minutes.

The writers have endeavored to measure the rate of reaction of ion exchange and their results are given below.

The ion exchange materials which were studied comprise two classes. In the first class are siliceous materials of natural origin, *e. g.*, the glauconite or greensand type exchanger as well as synthetic siliceous gel type exchangers which all are cation exchangers. The organic materials which form the second class embrace cation exchangers, characterized by the functional groups —SO_3H,

---

(1) J. R. Patton and J. B. Ferguson, *Can. J. Research*, **B15**, 103 (1937).

(2) H. F. Walton, *J. Franklin Inst.*, **232**, 318 (1941).

(3) J. duDomaine, R. L. Swain and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

(4) R. H. Beaton and C. C. Furnas, *ibid.*, **33**, 1500 (1941).

(5) Ref. 4, Fig. 1, p. 1503.

(6) G. Austerweil, *Bull. soc. chim.*, [5] **6**, 57 (1939).