[CONTRIBUTION FROM THE DEVELOPMENT LABORATORIES OF THE HAWTHORNE WORKS, WESTERN ELECTRIC COMPANY, INC.]

THE SYSTEM, LEAD-ANTIMONY

BY R. S. DEAN

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Introduction

The equilibrium in the system, lead-antimony, because of the commercial importance of this series of alloys, has been the subject of a very considerable number of investigations. The conclusion reached in most of them and generally accepted in all the recent handbooks and texts[1] is that neither solid solutions nor compounds are formed at least in the alloys rich in lead.

The earliest investigation of the system seems to have been made by Roland-Gosselin[2] who found by thermal investigations that the system was a simple eutectiferous one with the eutectic containing about 12.5% antimony and melting at 228°. This eutectic temperature was checked roughly by Ewen.[3] Stead,[4] however, in a thermal and microscopic examination of the system found a eutectic temperature of 247°, but his microscopic examinations confirmed the earlier conclusion that the system was simple eutectiferous. Campbell[5] with very little further data accepts Roland-Gosselin's results. In 1907 Gontermann[6] reviewed the conflicting data and made a very careful thermal investigation of the system. In general his results checked those of Stead. It is to be noted, however, that with alloys above 13% Gontermann obtained two arrests for the eutectic point. He explained this as a matter of crystal size, which explanation, however, has been questioned by Guertler who leaves the facts unexplained. Gontermann further found no detectable arrest in the cooling curve for 1% antimony alloy, but since his microscopic examination of the specimens showed dendrites he discarded the possibility of the formation of solid solution. The later investigations of Loebe[7] and of Leroux[8] have agreed quite closely with those of Gontermann.

A number of investigations of the physical properties of the lead-antimony alloys have been made from which conclusions have been drawn regarding the equilibrium. The potential of the lead-antimony series has been studied by Puschin[9] who found that all alloys had the same potential as lead which he interpreted to mean that neither solid solutions nor compounds were formed. The electrical conductivity of the series has been

[1] Guertler, "Metallographie," Bornträger, **1912**, Vol. 1, p. 792. Dessau, "Physikalische Eigenschaften der Legierungen," Vieweg, **1912**, p. 87. Bornemann, "Die Binaren Metallegierungen," Knapp, **1909**, p. 232. Reinglass, "Chemische Technologie der Legierungen," Spamer, **1919**, p. 13. Desch, "Metallography," Longmans, **1922**, p. 400. Tammann, "Lehrbuch der Metallographie," Voss, **1921**, p. 220. Hoyt, "Metallography," McGraw-Hill Book Co. **1921**, p. 52.

[2] Roland-Gosselin, *Bull. soc. encour. ind. nat.*, [5] 1, 1301 (1896).

[3] Ewen, *J. Inst. Metals*, **4**, 135 (1910).

[4] Stead, *J. Soc. Chem. Ind.*, **16**, 200 (1897).

[5] Campbell, *J. Franklin Inst.*, **154**, 205 (1902).

[6] Gontermann, *Z. anorg. Chem.*, **55**, 419 (1907).

[7] Loebe, *Metallurgie*, **8**, 7 (1911).

[8] Leroux, *Compt. rend.*, **156**, 1764 (1913).

[9] Puschin, Guertler, "Metallographie," Bornträger, **1921**, Vol. II. p. 322.

investigated by Mathiessen[10] who found a break in the curve at the composition corresponding to the formula PbSb. His figures near the lead end are too far apart to allow any conclusions to be drawn concerning the formation of solid solutions. The conductivity of liquid lead-antimony alloys has been investigated by P. Muller[11] and no evidence is found of a compound existing in the liquid state. The specific heat of the lead-antimony alloys has been determined by R. Durrer[12] who found that at constant temperature the specific heat was a linear function of the concentration, indicating no compound or solid solution formation. The hardness of lead-antimony alloys has been investigated by Saposhinkow and Kanewsky[13] who concluded that neither compounds nor solid solutions were formed.

In a recent investigation Ludwick[14] finds that the hardness of annealed alloys varies smoothly with the antimony concentration up to 8%, the highest concentration investigated. However, when the 2% alloy is annealed it increases sharply in hardness, but no great change is produced in the others by this treatment. Ludwick does not offer any explanation of this but it would appear to indicate the formation of a solid solution up to about 2% of antimony. The most recent investigation of these alloys is that of Gurevich and Hromatko[15] who find the maximum tensile strength in an alloy containing 10% of antimony.

Our interest in the lead-antimony system was from the standpoint of the manufacture of cable sheath and we were, therefore, particularly concerned with alloys containing up to 2% of antimony. It is obvious that in an extrusion process the temperature of working must not be above the melting point of any of the constituents of the alloy but on the other hand it is advantageous to use as high a temperature as possible, as the plasticity of metals approximately doubles for every 10° rise of temperature. Accordingly, the maximum extrusion temperature for lead-antimony cable sheath depends on the equilibrium near the lead end of the system. The present investigation was, therefore, made with a view to determining the equilibrium in the low-antimony alloys; however, in the course of the investigation it was found desirable to extend it less completely to alloys containing about 13% of antimony.

Investigation

The Solidus Curve of Lead-Antimony Alloys.—The method adopted for the study of the low-antimony alloys was based on the differential heating curve. A small cylinder of pure lead was used as the neutral body which was connected with a similar cylinder of the alloy under test by a copper-constantan thermocouple. The differential e.m.f. was measured on a high sensitivity galvanometer so arranged that its sensitivity was about 70 mm. of scale per microvolt. The actual temperature for the furnace was determined by means of a copper-constantan thermocouple and a

[10] Mathiessen, *Z. anorg. Chem.*, **51**, 415 (1860).

[11] Muller, *Metallurgie*, **7**, 730 (1910).

[12] Durrer, *Physik. Z.*, **19**, 86 (1918).

[13] Saposhinkow and Kanewsky, *J. Russ. Phys. Chem. Soc.*, **39**, 901 (1909).

[14] Ludwick, *Z. anorg. Chem.*, **94**, 161 (1916).

[15] Gurevich and Hromatko, *J. Chem. Met. Eng.*, **25**, 62 (1921).

small potentiometer and was accurate to 0.5°. This apparatus, although laborious to operate, probably gave as accurate results as could have been obtained with a recording instrument. The rate of heating was such that a temperature of 300° was reached in about 2 hours. Some of the results of these experiments are shown in Fig. 1, corrected for the calibration of the thermocouple made at the melting points of pure tin and lead. The unannealed alloys show a eutectic arrest at 258° even when only 0.5% of antimony is present, but a few hours' annealing causes the disappearance of this arrest in alloys containing up to 2%. The 2% alloy becomes free from thermal evidence of the presence of the eutectic only after 200 hours' heating at 235°, and in the 3% alloy the eutectic still persists after this time. The evidence from these heating curves would then indicate that

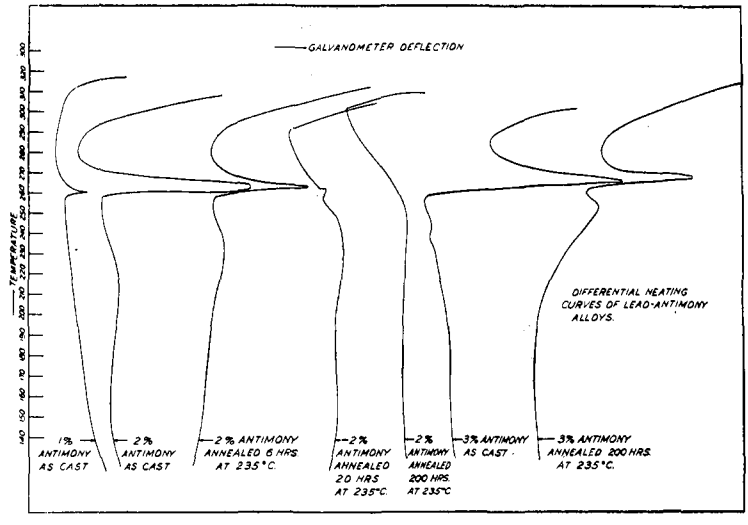


Fig. 1

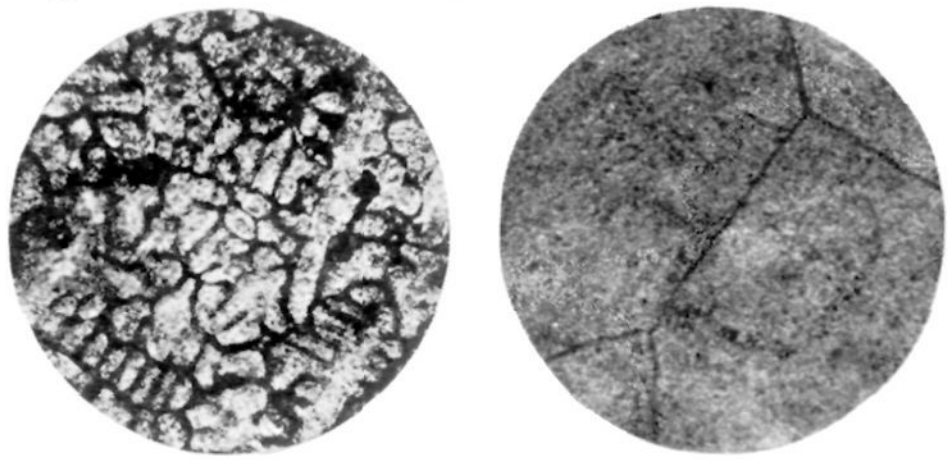
as much as 2 to 3% of antimony dissolves in lead when sufficient time is given. This slowness of attaining equilibrium is also characteristic of the lead-tin alloys as has been found by Rosenhain and Tucker.[16]

Microscopic Examination.—Microscopic examination confirms the findings of the thermal analysis in every respect. The eutectic which is present in the unannealed alloys disappears on annealing the alloys containing 2% of antimony or less. Fig. 2 shows micrographs of the 2% alloy before and after annealing. The etching is with silver nitrate and nitric acid. These microphotographs themselves would seem almost sufficient evidence for the formation of solid solutions in this system.

The Liquidus Curve of the Lead-Antimony Alloys and the Possibility of Compound Formation.—In order to have further data on the

[16] Rosenhain and Tucker, *Trans. Roy. Soc.*, **209**, 89 (1908).

freezing-point curve of lead-antimony alloys to supplement those of Gontermann, for the purpose of drawing the complete equilibrium diagram, several determinations were made. The apparatus consisted of an electric crucible furnace in which was placed a crucible of alloy, the temperature of which was determined by means of a mercury thermometer calibrated in freezing lead and tin, and compared with the thermocouple used in



× 100 × 50

Fig. 2.—2% Lead-antimony alloy polished with MgO; etched with silver nitrate and nitric acid

Left, as cast Right, annealed for 200 hours at 235°

the differential heating curves so that no discrepancies might arise in comparing the two results. The corrected results from these determinations and those from the previous heating curves are shown in the following table.

TABLE I

THERMAL ARRESTS IN LEAD-ANTIMONY ALLOYS

Composition % Sb	Cooling curve Liquidus	Cooling curve Solidus	Heating curve Solidus
Pure lead	327.1	...	...
0.5	326	none	...
0.75	...	...	above 315
1.0	321.5	none	309
1.3	...	...	305
1.8	...	...	300
2	313	245	292
3.0	305	245	258
4.0	301	247	...
10.4	255	247	...
11.0	...	...	258
12	...	...	258
12.5	...	247	...
13	252	245	253
16	272	245	...

There is a difference of several degrees between the positions of the solidus as determined by the cooling and heating curves, respectively.

The eutectic temperature from the cooling curves agrees well with that of Gontermann, namely, 245–246°, but the eutectic temperature on heating is 10° higher. In order to be certain of the reality of this hysteresis, both a heating and a cooling curve were obtained by use of the differential apparatus and a 3% antimony alloy. The resulting curves are shown in Fig. 3 and leave no doubt as to the existence of the hysteresis. Our work has not been carried far enough to offer a complete explanation of this phenomenon. The equilibrium diagram shown in Fig. 4 shows our tentative interpretation of the results. The diagram assumes the formation of a compound Pb_4Sb containing 12.6% of antimony which forms an eutectic with its solid solution in lead at 10% antimony. The data are not sufficient to fix these points accurately, however. This compound, forms very slowly and when the mixture is cooled is not formed from the liquid but from the solid eutectic between antimony and solid solution. As a result of the reluctance of this compound to form, the system as it cools behaves as if it were an antimony-solid-solution eutectic, and hence freezes at 247°. When this is heated the compound forms and the melting point is the eutectic point between compound and

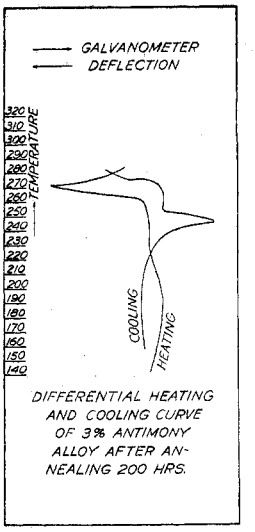


Fig. 3

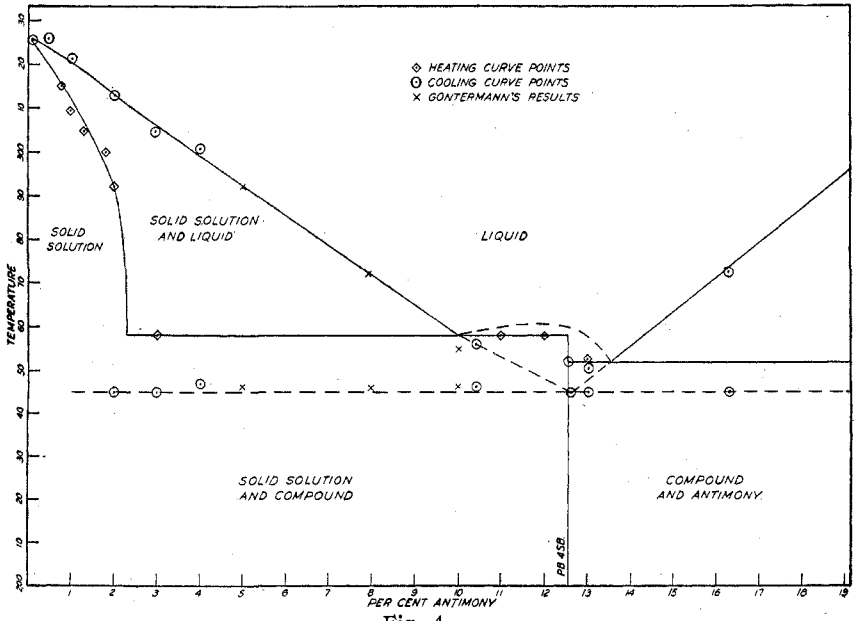


Fig. 4

solid solution at 258°. Mazzotto's explanation[17] of a similar hysteresis in the lead-tin eutectic is that the eutectic supercools with relation to the separation of tin. A similar supercooling with relation to antimony does not seem to be the explanation of our results, since the freezing point is not raised by seeding.

My thanks are due to Mr. G. S. Rutherford in charge of the Chemical Division for his interest and coöperation in this work.

Summary

Investigation by means of differential heating curves and microscopic examination has shown that antimony is soluble in solid lead up to between 2% and 3% of antimony at the eutectic temperature.

The alloys containing up to 13% show a higher eutectic temperature on heating than on cooling. A suggestion for the interpretation of this is made and a tentative equilibrium diagram drawn.

This investigation is being carried further to determine the solubility curve for antimony in lead at temperatures below the eutectic and to obtain further data on the possible existence of a compound in the system.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY, AND THE FIXED NITROGEN RESEARCH LABORATORY]

ANALYSIS OF HYDROGEN FOR TRACES OF NITROGEN[1]

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The usual method for the determination of hydrogen in a mixture of gases by combustion over copper oxide has been modified and applied to the determination of traces of nitrogen in hydrogen. The details of the modified procedure are described in this paper. This procedure was employed in the analysis of hydrogen used for some special tests on ammonia catalysts. It is also useful for the analysis of hydrogen which is to be liquefied, since traces of nitrogen interfere materially with the liquefaction.[2]

Briefly, the method consists in burning large amounts (12–20 liters) of hydrogen over heated copper oxide in an evacuated system, circulating the residual gases over copper oxide to insure complete removal of the hydrogen, collecting the residual unburned gases (designated as nitrogen), and measuring them by the usual gas volumetric method. The volume

[17] Mazzotto, *Intern. Z. Metallog.*, **2**, 269 (1911).

[1] The expenses of this investigation were in large part defrayed by the United States Fixed Nitrogen Research Laboratory.

[2] Dr. C. W. Kanolt of the Bureau of Standards, Washington, D. C., in connection with his study of the liquefaction of hydrogen, developed, subsequent to this work and independently of it, a similar procedure.