tensive application to all the available data and a theoretical basis will be given in a later article.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE SOLID SOLUBILITY OF ANTIMONY IN LEAD AS DETERMINED BY CONDUCTIVITY MEASUREMENTS ON COLD-WORKED ALLOYS

BY EARLE E. SCHUMACHER AND GEORGE M. BOUTON

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Introduction

In 1923, Dean[1] showed the existence of an appreciable solid solubility of antimony in lead at the eutectic temperature. Shortly thereafter Dean, Hudson and Fogler[2] demonstrated that dispersion hardening takes place in these alloys. They found that a 2.5% antimony alloy, a homogeneous solid solution at 247°, precipitated more than half of its antimony from solution after being maintained at room temperature for a short time. A more detailed study of the solubility conditions, using the conductivity method to follow changes of solubility with temperature, was made by Dean, Zickrick and Nix.[3] Unfortunately, at the lower temperatures, they were unable to obtain equilibrium values due to the slow rate of precipitation of the solute.

Recent work indicates that the rate of precipitation of the excess of antimony is greatly accelerated if the alloys are first severely cold-worked. Presumably equilibrium would be reached much more quickly under these conditions. Therefore, it seemed desirable to determine the solid solubility values for antimony in lead on severely cold-worked alloys, hoping thereby to secure more accurate values than those previously obtained.

Photomicrographs Showing the Effect of Cold Work

Several photomicrographs, taken by Mr. F. F. Lucas[4] of these Laboratories, are given to show the structural effect of cold work in these alloys. A lead-antimony alloy containing 1% of antimony and 99% of lead was cast in the form of a rod, 0.5 inch (1.3 cm.) in diameter. This rod was heated at 230° for one hour to get most of the undissolved antimony into solution. The rod was then divided and one section was severely cold-worked by swaging. Both the worked and unworked sections were maintained at room temperature, 20° for five days and then photomicrographs were taken of each. The specimens photographed

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[1] Dean, THIS JOURNAL, **45**, 1683 (1923).

[2] Dean, Hudson and Fogler, *Ind. Eng. Chem.*, **17**, 1246 (1925).

[3] Dean, Zickrick and Nix, *Trans. Am. Inst. Mining Met. Eng.*, **73**, 505 (1926).

[4] Lucas, Preprint No. 1654 E, *Am. Inst. Mining Met. Eng.*, February, 1927.

were prepared by the microtome method[4] and etched[5] with acetic acid and hydrogen peroxide. Fig. 1 shows the structure of the annealed but unworked specimen and Fig. 2 shows the structure of the annealed and worked specimen. In the case of the unworked specimen the structure is essentially that of a solid solution, whereas the worked specimen shows the typical disturbed structure due to cold work and also a fine mottling of dark material which, when isolated by means of selective etching and spectroscopically analyzed, proved to be almost entirely antimony. From these photomicrographs it is apparent that cold work has a marked effect in causing the precipitation of the excess of material from the supersaturated solution. Fig. 3 is a photomicrograph of a representative piece of lead-antimony cable sheath, containing 1% of antimony and 99% of lead, which had aged in service for eight years. The structure here revealed, including the widened grain boundaries, is typical of specimens of sheath that are subjected to cycles of mechanical and thermal disturbances over a long period of time. A comparison of this photomicrograph with the one shown in Fig. 2 indicates that as much precipitation has taken place in the cold-worked

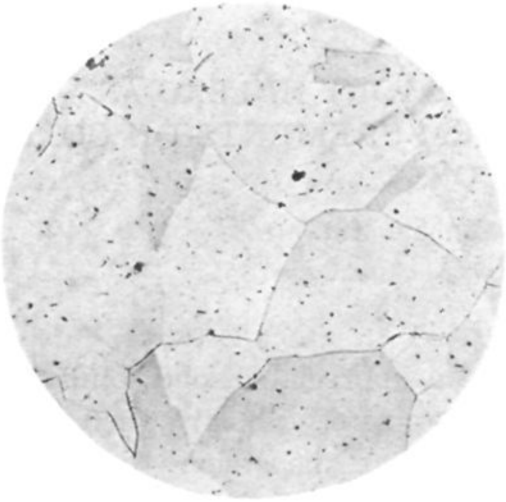

Fig. 1.—Lead-antimony alloy (99% Pb – 1% Sb) which had been annealed at 230°C. for 1 hour and aged at 20°C. for five days. Mag. × 200.

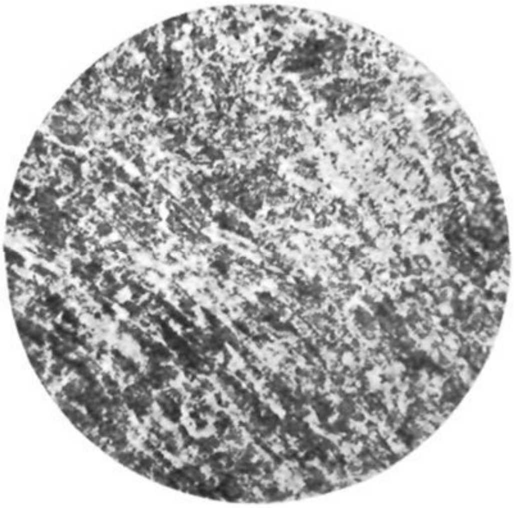

Fig. 2.—Lead-antimony alloy (99% Pb – 1% Sb) which had been annealed at 230°C. for one hour, cold worked and then aged at 20°C. for five days.

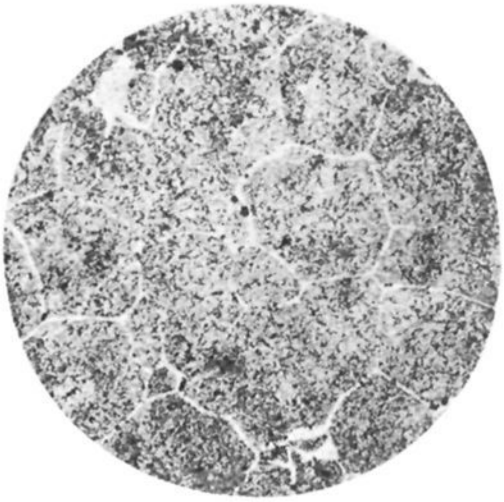

Fig. 3.—Lead-antimony cable sheath (99% Pb – 1% Sb) which had aged naturally in service for eight years.

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[5] Rutherford, *Proc. Am. Soc. Testing Materials*, **24,** 739 (1924).

sample as in the specimen aged in service. In other words, an equilibrium[6] which normally takes years to reach appears to be established in a few hours by cold-working the alloy.

Apparatus and Method Used in Determining the Solid Solubility of Antimony in Lead at Various Temperatures

Following established practice, conductivity measurements were found useful for determining the solid solubility limit. Measurements were made on a series of alloys in wire form in which the percentage of antimony ranged from 0.10 to 3.02. The change in conductivity with time was followed for each alloy and the equilibrium values of the conductivity were thus obtained. By plotting these equilibrium values against antimony content the solid solubility for the temperature at which the experiment was conducted was readily determined, since at the limit of the solid solution range there is a marked change in the slope of the conductivity-composition curve.

The measurements were made by a standard potentiometric method. An electromotive force was impressed on a standard resistance in series with the alloy wire. The drop in each was measured with a Leeds and Northrup Type K precision potentiometer and a d'Arsonval type galvanometer.

Throughout the experiment, the alloys being tested were kept in thermostats maintained constant to within ±0.02° of the temperature desired. For temperatures below 75° an air thermostat was used, consisting of an asbestos-lined box containing a heating element, a fan and a temperature regulator. For temperatures above 75° oil-filled thermostats were used.

Experimental Procedure and Results

The alloys used in this investigation were prepared from Kahlbaum's antimony, which analyzed: arsenic, 0.01; tin, <0.01; sulfur, <0.01; antimony, 99.97+%. Bunker Hill lead was found to contain: silver, 0.0006; bismuth, 0.001; antimony, 0.003; iron, 0.001; tin, 0.001; lead, 99.99+%.

The lead and antimony were melted together in graphite crucibles in an electric furnace under a vacuum of approximately 1×10^{-3} mm. of mercury. The molten mixtures were kept in agitation several minutes to effect homogenization, then the vacuum was broken and the alloys were chill-cast in the form of $^1/_2$ in. (1.3 cm.) rods. These rods were swaged to wires 100 mils (2.54 mm.) in diameter which were then cut into 16-inch (41 cm.) lengths. These specimens were annealed for 100 hours at approximately 230° in order to bring the alloys to a common structural

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[6] Equilibrium as used in this paper refers to a condition that will remain stable for a term of years.

condition before administering the final cold-working. The annealing was followed by a rapid quenching in water, after which the different specimens were severely cold-worked by swaging to approximately 60% of the initial diameter. Samples for chemical analysis were taken just before this final cold-working.

In the case of tests conducted below a temperature of 75°, the wires were immediately placed in a bakelite rack capable of holding 15 specimens. This rack was provided with heavy copper current terminal leads to which the ends of the wires were fastened. The voltage contacts were made of spring brass, sharpened to a knife edge to provide a good contact. When the rack was placed in the thermostat the proper voltage and current connections were made and the test was started. As the test progressed, resistance measurements were made at regular intervals. When the resistance of the wires remained constant for a period of from 200 to 300 hours, equilibrium was considered to have been reached. The wires were then removed from the thermostat and cut off at the knife marks made by the voltage contacts. Their length and weight were accurately determined and their conductivities calculated.

Above 75°, a similar procedure was used except that here the wires had to be protected from direct contact with the oil that filled the thermostat. This was found to be necessary as preliminary tests with several types of oil revealed a development of acidity at temperatures above 75°, which was sufficient to cause corrosion of the test wires. Satisfactory protection was secured by sealing the wires in glass tubes within which the current and voltage contacts were made.

Data typical of those obtained in these measurements are given in Tables I–III. Table I shows the increase in conductivity with time, of some of the wires that were maintained at 25°, and indicates that the conductivity becomes essentially constant before the completion of the test. The data given in Table II were used to prepare the conductivity

TABLE I

SOME CONDUCTIVITY DATA OF LEAD-ANTIMONY ALLOYS

(Conductivity in mhos per cm. cube $\times 10^{-4}$)

Antimony, % Time after swaging, hrs.	0.00	0.22	0.45	0.68	0.99	1.97	3.02
6	4.691	4.582	4.517	4.398	4.241	4.000	3.939
24	4.690	4.582	4.539	4.476	4.263	4.094	4.207
48	4.689	4.580	4.540	4.504	4.293	4.184	4.351
96	4.691	4.581	4.543	4.521	4.346	4.306	4.419
168	4.690	4.583	4.539	4.532	4.399	4.399	4.434
384	4.690	4.583	4.546	4.536	4.482	4.485	4.440
768	4.689	4.583	4.546	4.533	4.528	4.511	4.446
1104	4.690	4.584	4.548	4.533	4.543	4.515	4.447
1512	4.691	4.583	4.546	4.533	4.551	4.518	4.448

TABLE II

CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS AT EQUILIBRIUM

(Mhos per cm. cube × 10^{-4})

Antimony, %	146°	100°	70°	40°	25°
0.00	3.206	3.648	3.982	4.460	4.691
.10	3.180	3.621	3.963	4.409	4.653
.17	3.174	3.608	3.914	4.385	4.588
.22	3.150	3.596	3.915	4.333	4.583
.34	3.126	...	3.887	4.297	4.549
.45	3.102	3.540	3.861	...	4.547
.56	3.078	3.532	...	4.273	4.540
.68	3.048	3.500	3.841	4.270	4.532
.80	...	3.516	3.858	4.289	4.532
.86	3.042	3.515	3.879	4.281	4.545
.99	...	3.512	3.871	4.267	4.552
1.97	3.007	3.482	3.845	4.250	4.518
3.02	2.954	3.428	3.799	4.203	4.448

TABLE III

SOLID SOLUBILITY OF ANTIMONY IN LEAD

Temp., °C.	146	100	70	40	25
Antimony in soln., %	0.70	0.52	0.48	0.32	0.24

curves at various temperatures. Table III gives the determined values for the solid solubility of antimony in lead at the five different temperatures employed in these experiments.

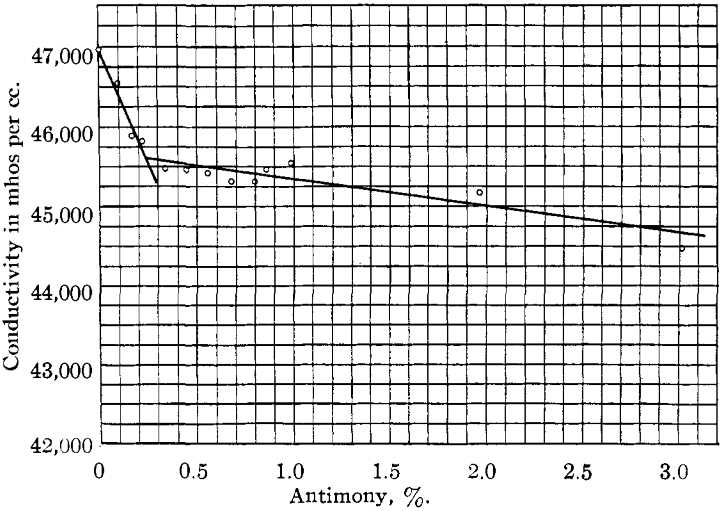

Fig. 4.—Conductivity of lead-antimony alloys at 25°.

Discussion

Since it is evident from the conductivity-time curves, Fig. 9, that at the end of the test the samples were changing very slowly, if at all, we may assume that the data shown in the conductivity-composition curves, Figs. 4–8, correspond to equilibrium conditions. This assumption is

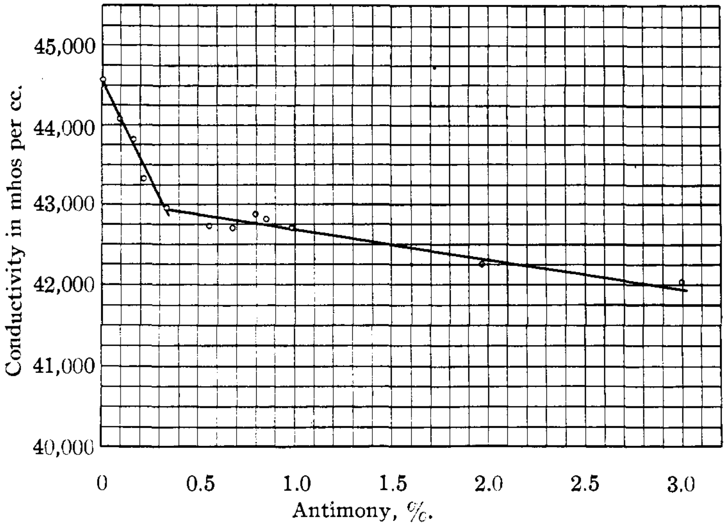

Fig. 5.—Conductivity of lead-antimony alloys at 40°.

also supported by the photomicrographic evidence presented in a preceding paragraph, which showed that shortly after severe cold-working,

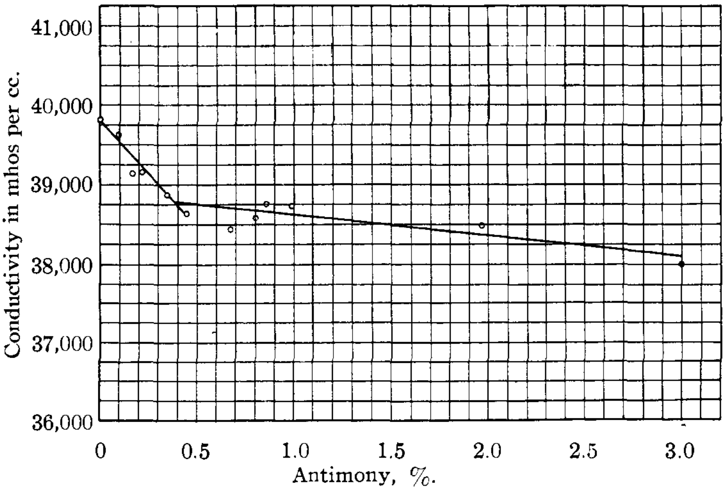

Fig. 6.—Conductivity of lead-antimony alloys at 70°.

samples possess a distribution of antimony similar to that found after prolonged aging in service. These curves accordingly reveal the limiting values of solid solubility at the respective temperatures. According to the general theory relating conductivity with constitution, alloys lying within the range of solid solubility should show a rapidly decreasing conductivity with increasing antimony content. Beyond the range of solid solubility the conductivity should change at a much slower rate with increasing antimony content. There should, therefore, be a definite

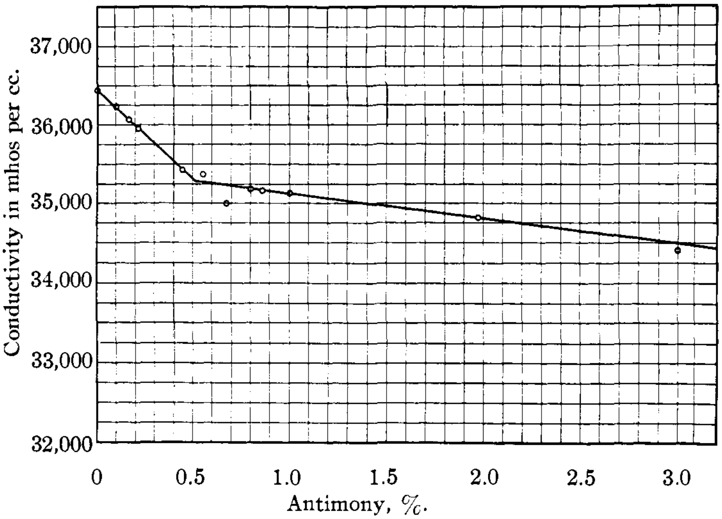

Fig. 7.—Conductivity of lead-antimony alloys at 100°.

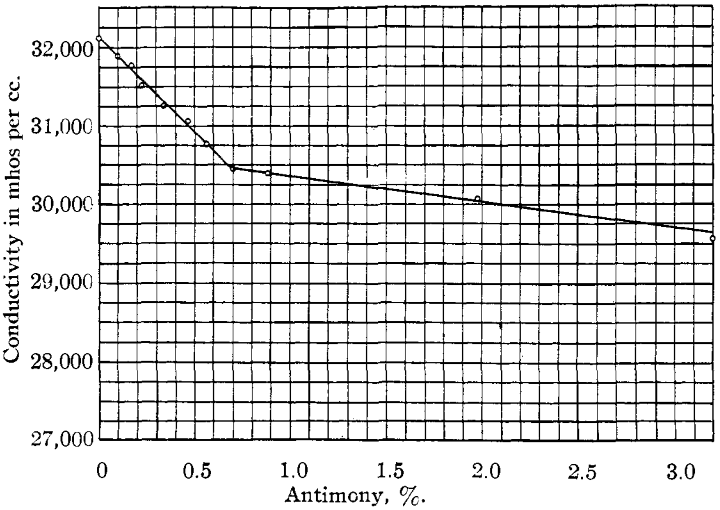

Fig. 8.—Conductivity of lead-antimony alloys at 146°.

break in the conductivity-composition curve at the limit of solid solubility. This appears clearly in Fig. 8, which represents conditions at 146°. The curve as drawn follows the points closely and consists of two straight lines of different slope meeting at 0.7% of antimony, which therefore is considered to be the limit of solid solubility at this temperature.

The curves obtained at other temperatures are similar, although not as sharply defined. The irregularities are presumably due to some of the samples having failed to attain perfect equilibrium. As stated above, the conductivity-time curves do not give positive evidence that all change had ceased by the end of the test, and for the lower temperatures true equilibrium values may not be reached for years, even after severe cold-working. In view of these considerations, the breaks in the curves have been approximately located by drawing in each case a straight line corresponding to each of the two sections of the curve, and taking the intersection of these lines as determining the break.

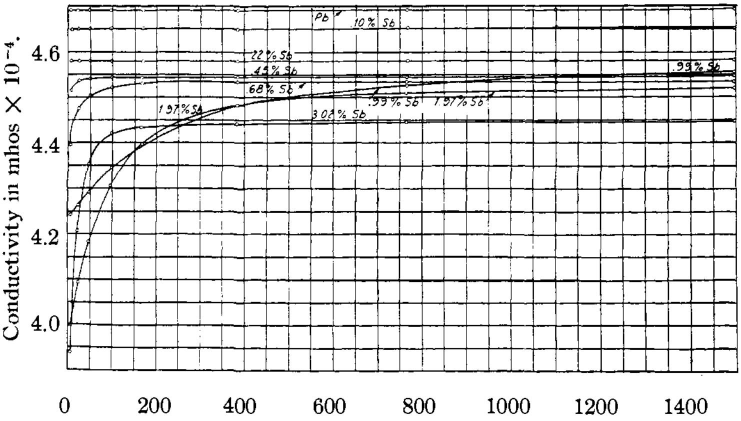

Fig. 9.—Conductivity of lead-antimony alloys at 25°, after being cold-worked.

In drawing the lines, consideration was given to the conductivity-time curves, since any definite increase in conductivity after cold-working a given sample clearly indicates the precipitation of antimony, and thus shows that it lies beyond the limit of solid solubility. Finally, it may be noted that however the lines determining the break are drawn, within the limits which the points will permit, no great change can be produced in the abscissa of the intersection which determines the composition of the limit of solid solubility with which we are primarily concerned. From these detailed considerations, it seems quite evident that no large errors are involved in the simple graphical method used to interpret these experiments.

The Revised Constitutional Diagram for the Lead End of the System Lead-Antimony

Since the liquidus[3] and solidus lines[7] at the lead end of the system lead-antimony have already been accurately determined and we have now contributed precise data defining the change of solid solubility with temperature, it is possible to construct a revised diagram for the lead end of this system. Such a diagram is shown in Fig. 10.[8]

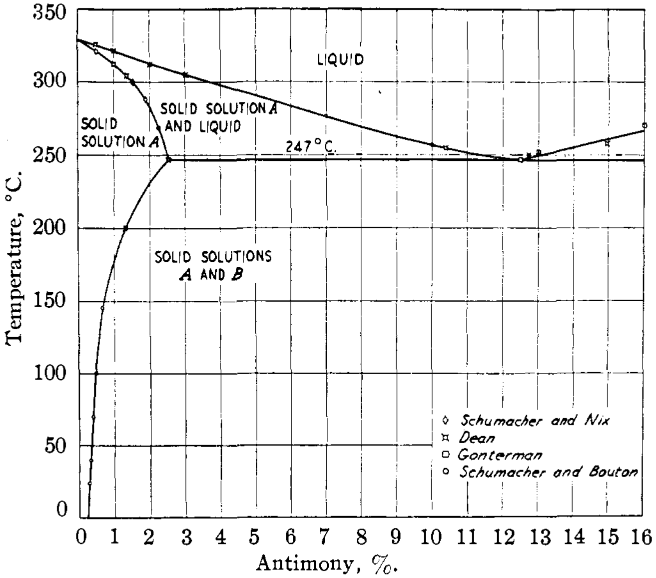

Fig. 10.—Partial equilibrium diagram of the system lead-antimony.

Summary and Conclusions

The solid solubility of antimony in lead has been determined for five different temperatures. The solubility changes from 2.45% at 247°, the eutectic temperature, to about 0.25% at 25°, room temperature. Cold work applied to lead-antimony alloys has been shown to decrease materially the time required to reduce the supersaturation of antimony in lead, and thus permits equilibrium values of the solubility to be more readily obtained. A revised constitutional diagram is given for the lead end of the system lead-antimony.

New York, N. Y.

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[7] Schumacher and Nix, Preprint No. 1636 E, *Am. Inst. Mining Met. Eng.*, February, 1927.

[8] Two points on the liquidus and one on the solidus line were determined during the course of this investigation in order to fix more precisely the location of these lines. The points on the liquidus were determined from cooling-curve data; the point on the solidus was determined by the quenching-test procedure developed by Heycock and Neville.