THE ROOM TEMPERATURE ISOTHERM OF THE SYSTEM
LEAD - INDIUM - TIN

by

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To my Father.

"The decomposition of three metals ..., is too long to inquire of."

-Sir Francis Bacon (1).

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ABSTRACT.

An investigation by X-ray and microscopic methods of the room temperature isotherm of the system lead - indium - tin has been made. A one-phase region extends across the ternary diagram from the intermediate phase occurring in the region of high indium concentration in the indium-tin system to the intermediate phase present in the lead-tin system. These phases are of closely similar crystal structure. There are also present two triangular three-phase areas, which account for a large part of the diagram.

Polishing of microsections was done on a selvyt cloth with "light" magnesia for an abrasive. An etching reagent consisting of varied proportions of nitric acid, glycerol and acetic acid served to distinguish between all phases. X-ray powder patterns were obtained for all alloy samples. Brinell ball hardness numbers and diamond pyramid hardnesses were determined for each alloy; values of these varied from about one for indium to about eleven for the hardest samples.

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INTRODUCTION

In 1952, Campbell and Screaton (34) undertook an investigation of the system: lead - indium - tin. The purpose was, of course, the determination of the regions of stable existence of the various phases present as the three determinative variables, temperature, pressure, and composition change, i.e., the characterization of each particular state of heterogeneous equilibrium by the number and identity of the phases present (the equilibrium diagram).

The study of this ternary system at constant pressure (atmospheric) was made using the thermal analysis technique. The liquidus only was determined and it was found that no true ternary eutectic appeared in the system. Because of the small heat effects accompanying the phase transformations, the positions of the peritectics could not be found in the ternary system by thermal analysis alone.

To complete the work a study of the nature of the solid regions, by means of X-ray and microscopic methods, was desirable. An examination of the room temperature isotherm of the above system was therefore engaged in. The regions of stability of the various pure phases, as well as the regions of coexistence of the several phases, were to be fixed.

A discussion of the methods (and a subsidiary aid) recommended by Campbell and Screaton, their application to the problem in hand; and the experimental results obtained thereby, together with their interpretation, form the subject matter of the present thesis.

I. Considerations of Methods and Techniques.

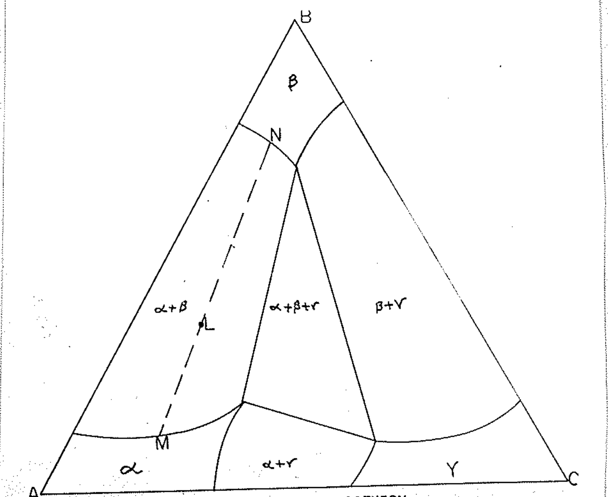
A comprehensive discussion of the phase rule, of the theory and applications of X-rays, and of microscopy and its metallographic uses would not only be impossible but otiose as well. There are innumerable textbooks and advanced reference works on these subjects; various periodicals concern themselves with them. Here only a brief expose will be given. It will be confined to a nonmathematical description of those aspects of the methods which immediately concern this study.

a. The Phase Rule.

The phase rule states that, if the equilibrium between the phases is influenced only by temperature and pressure and not by gravitational, electrical, or magnetic forces or by surface conditions, then $F = C - P + 2$, where P is the number of stable phases present, F is the number of degrees of freedom, and C is the number of components. A phase may be defined as any physically distinct part of a system that is separated from the other parts of the system by definite bounding surfaces. The number of degrees of freedom of a system is the number of independently variable factors, taken to be temperature, pressure and composition of any phase, that must be specified completely to define the conditions in the system. The number of components of a system is the smallest number of independently variable substances by means of which the composition of any phase present can be expressed. In alloy systems this is the number of metals present.

The phase rule offers a guiding principle and greatly simplifies interpretation; excluding all sorts of possible explanations for uncertainties originating in lack of or slow approach to equilibrium. Roozeboom (29) derived the possible types of binary temperature - composition diagrams with which all systems, including metallic, must comply. We see in his work, or in any similar work (5,28), that there will be regions of single and two-phase equilibria alternating with each other across the diagram at any constant temperature.

As a logical extension one finds in a ternary equilibrium diagram that there are represented single, two, or three-phase equilibria, and this somewhat complicates matters. To plot the phases in a three component system, one usually uses an equilateral-triangle plot at constant temperature and pressure.



HYPOTHETICAL TERNARY ISOTHERM

Plate 1.

Plate 1 illustrates a possible location of phase fields in a ternary diagram, giving the equilibrium relations for one temperature below the liquidus. A, B, and C represent the pure metals, which all form solid solutions to some extent with each other. All the binary alloys of these metals will be represented by points along the boundaries of the triangle, and alloys containing all three components will lie within the triangle. Point L contains A, B, and C in proportion to the perpendicular distances from L to the opposite sides of the triangle, respectively.

Certain rules are to be observed. Three-phase fields (central portion in plate 1) are always triangular. Extension of the single-phase boundaries (corner areas) at corners should result in either two lines extending into the two-phase regions (quadrangular portions) or in two lines passing into the three-phase triangle.

The tie-lines in two-phase areas, giving the composition of the two coexisting phases, are straight lines. They never intersect and change direction slowly from one side of the area to the other. Relative proportions of two phases in equilibrium are given by the "inverse rule", as with binary alloys. Thus, in plate 1,

$$\frac{\text{quantity of } \alpha}{\text{quantity of } \beta} = \frac{\text{length of LN}}{\text{length of LM}} .$$

In the three-phase areas the relative proportions are given by a logical extension of these rules. A line is drawn through the point in question, cutting one corner of the triangular area. The ratio of the lengths of the segments formed by the intersection of the constructed line with the side opposite to the corner it cuts yields, by inverse proportion, the quantities of the two end phases.

By the phase rule we conclude, that at constant temperature and pressure, three-phase regions are invariant, i.e., the state of the system is completely defined thermodynamically. Similarly, two-phase regions are univariant and one-phase regions are bivariant. Here one and two variables, respectively, must be arbitrarily fixed before the state is defined.

This account has set forth the main principles of the phase rule used in this investigation. The meaning of various terms usually employed in phase rule discussions will become clear on examination of the diagrams given in section II. Campbell and Smith (5), as well as Ricci (28), present thorough treatments on the various systems encountered in practice. An enlightening theoretical discussion on heterogeneous equilibria can be found in Paul (26).

b. X-rays and Phase Diagrams.

Solids are classified as crystalline or amorphous. The fundamental property of the crystal is its atomic pattern, the external form being only one result of this pattern. Crystals which are closely related in their atomic grouping and bonding may differ widely in their external symmetry. The right basis for commencing the study of crystal structure is the conception of a pattern based upon a space lattice. This consists of points, representing identical groups of atoms, regularly arranged in space. It is only occasionally necessary to consider the external crystalline form in the treatment. These facts are very important in the study of metals, the crystals of which usually do not have well defined external faces.

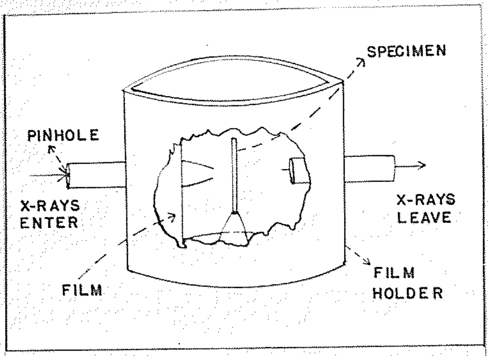
Before 1912 there was no known way of getting at these structures. Scientists had made shrewd guesses as to the causes of the external symmetry. Roule (1703 - 1770), teacher of Lavoisier (33), made the astute remark that

> "...minerals observe regular figures ... and their parts are united not by intussusception but by juxtaposition".

Today this regular internal structure of crystals is common knowledge.

As applied in this study X-rays were used, in a sense, as a super-microscope. The application depends upon the fact that all crystals act as diffraction gratings for X-rays, because the atoms lie on parallel planes with spacings of a few angstroms, compatible with the wave-length of X-rays. The well-known Bragg law governs this interaction between a regularly built lattice and X-rays. A pattern of spots or lines is photographed, which is just as characteristic of the inner ultimate structure of each crystalline substance as, say, a fingerprint is uniquely characteristic of each human being. This pattern is interpreted in terms of the unknown structure and nature of the specimen. The specimen may be in the form of a single crystal, in which case the so-called Laue pattern is obtained; or it may be a powder, with a line pattern.

The powder, or Debye, method was the one used in this investigation. A diagrammatic sketch of a camera is shown in plate 2 (2). It consists of a pinhole, a wire-shaped specimen and a cylindrical film. A tube conducts the undiffracted beam out of the camera. Diffracted rays leave the specimen along cones concentric with the primary ray, each cone having an apex angle of 4θ, where 2θ is the angle of the diffracted or reflected beam from the set of planes in question. When the film is developed and laid flat it has the appearance shown in plates 52 to 63.



POWDER CAMERA

Plate 2.

It is best to choose the target so that the K_α emission has a longer wave length than the K absorption limit of the principal chemical elements in the specimen. Otherwise the specimen will emit fluorescent radiation, which will fog the film, e.g., Fe targets will cause As to fluoresce. A properly chosen filter is placed in front of the pinhole to eliminate K_β radiation.

An important practical use of this method is the identification of phases by their powder patterns. This may be done without solving the crystal structure, simply by comparing the patterns of the unknown material with patterns of known substances. The films are laid side by side, and the similarities are directly observed. Every individual line must be accounted for. Identification is often possible when the specimen contains as many as three different substances, provided that each substance represents an appreciable fraction (five per cent or sometimes more) of the mass of the specimen. Each substance produces its pattern independently and the result is a superposition of the lines with relative intensities dependent on the relative amounts of the different phases present. Difficulties may be encountered if lines from different patterns coincide, or nearly so, on the film. If a series of alloys is prepared, spaced across a ternary diagram, the powder patterns will follow the different one, two, and three-phase areas. These latter considerations form the basis for the use of X-rays in the determination of the isotherm in question.

Some substances will produce a pattern in a mixture if they represent one per cent or so of the material (lead with lighter metals). Many will not show at less than ten and sometimes twenty per cent. Elements present in solid solution may not be detected by the method as described. A limitation is thus imposed on the simple method outlined above. Boundary lines will evidently not be more closely ascertainable than about five per cent.

When special back-reflection cameras are available, accurate determinations of such boundary lines is no insuperable problem. Two approaches, the disappearing phase method and the parametric method, are then used. An article by Hume - Rothery and Raynor (17) gives an excellent discussion of the average technique used in the investigation of an alloy diagram. Bradley (4) has published many papers on such investigations. A very recent publication is that of Straumani (39).

c. Microscopy and Phase Diagrams.

Physical chemistry concerns itself in general only with the nature and relative quantity of the phases in a system, and the energy changes which accompany chemical changes; while metallography, as defined by Desch (9), takes into account also the arrangement of component particles in space.

The examination of metals by means of the microscope is not new. Robert Hooke (ca. 1665), Reaumur, and others carried out some brief experiments by this technique. H. C. Sorby, the father of metallography, devised a suitable technique for the preparation and examination of microscopic sections (ca. 1850). Martens and Stein in Germany, Wedding in England, and Osmond in France, carried out numerous investigations on the microstructure of iron and steel.

A short delineation of the nature of this method of study will now be given. Metals and alloys, opaque substances, must necessarily be examined by means of reflected light; a perfectly flat surface must therefore be prepared. If the metal is soft the specimen is prepared with a hack-saw or lathe. Care is necessary to prevent heating and distortion of the metal. When there is doubt about the homogeneity of the ingot, sections are cut from the inner and outer surfaces. The cut surface may now be made fairly flat by rubbing it on a stationary file, the teeth of which are cleaned after every stroke. The specimen may be mounted for convenience in plastic or wax moulds.

A smooth surface is obtained by rubbing on emery papers of increasing fineness, after which it is polished on a cloth-covered, rotating wheel with magnesia or some similar powder for abrasive. Water is used to prevent heating. According to Beilby (3) the polishing consists in a formation of flowed metal, the irregularities of the scratched surface being partly rubbed away and partly filled up. The final polish should present a mirror-like surface under the microscope; with soft metals, which present formidable difficulties in polishing, this condition is rarely reached.

At this stage the structure is latent and must be brought out in a suitable way. Carrying the fingerprint analogy a step further, one finds the process of etching a metal to bring out its microstructure similar to the insufflation method used to make latent fingerprints visible on an object. Etching usually consists in attacking the surface of the specimen with a chemical reagent which acts preferentially on one or more of the constituents, or which acts along certain directions in a homogeneous metal. The number of etching reagents is large. Books on metallography (8, 16, 30) cite numerous reagents in use, one constituent of which normally is an acid. With the increasing number of possible phases in a ternary system (three can be in equilibrium in a single ternary alloy) the identification of the etching characteristics of each phase, alone and in the presence of others becomes more difficult. This requires a preliminary study.

While awaiting examination the etched specimen may be stored in a dessicator or coated with a thin layer of thick varnish to form a transparent layer.

The fundamental difference between the ordinary microscope and one for the examination of opaque objects is in the method of illuminating the object. Vertical illumination is principally used in the study of the structure. Nowadays the source of illumination is a filament lamp placed perpendicularly to the microscope tube in a housing which connects to a prism. This prism refracts the light towards the objective, which here acts as a condensing lens and brings the light to a focus on the specimen. It is evident that areas on the surface which have not been attacked by the etchant will reflect the light back through the tube and thus appear bright to the observer; conversely, corroded areas will disperse the rays outside the tube and appear dark at the eyepiece.

If a permanent record of the microstructure is desired, the microscopical image is reproduced photographically. A special camera is brought into position to make a light tight connection with the microscope. The intensity of the light is reduced suitably and filtered through a greenish-yellow filter. The eyepiece, aided by another prism, throws the image on a ground glass plate parallel to the microscope tube, while at the same time focussing it on a filmholder at right angles to the tube. When the image is properly focussed on the glass plate, a negative of low contrast is properly exposed. The magnification of the image is determined by means of a stage micrometer, ruled in hundredths and tenths of a millimeter.

What are the etch patterns obtained for typical alloys? Some idea of what different structures look like must be reached before one can come to any conclusions about unknown samples. A short discussion of the following diagram, similar to that given by Doan and Mahla (10), will bring out the characteristics to be looked for in an etched surface.

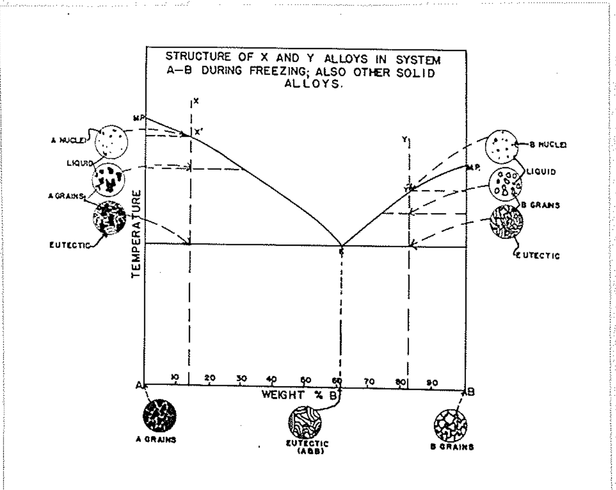


Plate 3.

Plate 3 illustrates a fictional phase diagram for two metals, A and B, completely insoluble in one another in the solid state. The phase relations at different temperatures are really self-explanatory. Thus a melt of composition X, when cooled, will at X' begin to crystallize out A, the composition of the melt altering along X'K as the temperature drops. At K solid B will also separate out to form with the last of A a eutectic structure of composition K. Since here the system is isobarically invariant (two components, three phases, constant pressure) the temperature remains constant until the whole is solid. A melt of composition Y will go through an analagous process of solidification.

The microstructure of alloy X is now simple to predict. It will show crystals of pure A which have come out in the earlier stages of freezing, prior to reaching the eutectic point, and grown to considerable size, so-called primary crystals of A, surrounded by alternate, smaller crystals (since each has had less time to grow) of A and B in a finely divided eutectic matrix (shown diagrammatically in the center of the bottom row of structures in plate 3). The primary A resembles the pebbles in concrete. Both the large and the small A crystallites as well as the small B crystallites will be pure in accordance with our assumption of complete insolubility in the solid state. A structure containing two crystalline varieties is called a duplex structure.

The appearance of the two alloys, X and Y, at successive stages during the cooling of each is shown at the left and right in plate 3. It will be noticed that the proportion of primary A crystallites increases from zero at the eutectic composition toward 100% at pure A while that of primary B increases from zero for the eutectic alloy toward 100% for pure B.

The crystals of pure A or B do not exhibit the external symmetry compatible with their internal structure since the growth of each crystal is mutually obstructed by that of its neighbours and with this obstruction comes exhaustion of the liquid between the crystals. The final boundaries of the crystals are compromises between the abutting neighbours. The crystals are called grains and have multiangular outlines. In practice dendritic, pine-tree like, structures are frequently obtained and often obscure the grain boundaries (plate 42).

A discussion of inceptive crystallization (nucleation) and of the rate of crystallization with the appertaining theory, is given by Tammann

(40), Desch (8), and others. Modern ideas on such matters are found in Acta Crystallographica (7, 41, 1954), where Gay, Kirsch and Kelly revive the "foam structure" theory of Quincke in a different form. The "amorphous cement" theory of Rosenhain (31) will be mentioned and discussed in section V, in connection with certain photomicrographs.

The description in connection with plate 3 can be extended "mutatis mutandis" to partially soluble alloys, to completely soluble alloys, to alloys showing peritectics, to congruent compound formation (which melts unchanged in composition), and also to ternary alloys where the possibility of a third phase must be considered. In practice, ideal conditions are hardly obtained as will be seen in section V.

d. Comparison of the Two Methods; Hardness Testing.

The general consensus of opinion among workers in the field of metallography seems to be that the microscopical examination of alloys is the more generally useful method in phase boundary determinations. When suitable methods of polishing and etching are adopted the method is delicate, as quite small quantities of a new phase (one per cent easily) can be detected.

The method of X-ray examination comes next in importance. It has the limitation that small quantities of a new phase, distinguishable under the microscope, may be quite undetectable by the X-ray method. The X-ray method has also been widely used (Bradley et al.) for fixing the phase boundaries in a complex system at atmospheric temperatures. In such a case the information must be regarded as supplementing the evidence of the microscope, and not as taking precedence over it. It does identify the different phases and shows thereby what changes, if any, take place in the etching characteristics of these as the composition changes. The X-ray method is of special value in the examination of intermediate phases. When the intermediate phase differs only slightly in structure from an end phase it is easily overlooked when ordinary microscopical methods are used. Two cases in point will be met in section III. Since the introduction of the electronic rules by Hume-Rothery (18) and the application of quantum mechanics to these phases by Jones (19), this aspect of X-rays has become more important. In this study, however, there was no extrinsic concern about the internal structure of the phases.

It might be mentioned that recently (1953) Castaing and Guinier (6) have built a microanalyzer consisting of a metallographic optical microscope, an electron microscope and an X-ray spectrograph. The first is for the usual purpose of delineating surface structure; the second for collimating an extremely fine beam of electrons upon areas as small as one micron square; the third to analyze the characteristic X-rays emitted in these small dimensions. The result is a point by point analysis, both qualitative and quantitative, for a heterogeneous fine-grained specimen. The analysis of various phases of complicated ternary alloys is a difficult problem with ordinary methods, and it is likely that the electronic analyzer will be a useful tool in the field.

The mechanical properties of alloys are determined less for the study of the equilibrium diagrams than for the information obtained about their engineering properties. Nevertheless, these properties vary from phase to phase and with changing composition, and they do afford a check, somewhat crude no doubt, on information obtained in the wonted ways. Here only the testing of hardness, by the two methods employed in this study, will be considered.

The property of hardness is one which is difficult to define and equally difficult to measure. Our simplest conception of a hard substance is one which is not readily scratched. This is the use of the term as accepted by mineralogists and is the basis of the well-known scale of Mohs. For our purpose we may take hardness as the resistance of a material to penetration by another substance.

The usual method of testing hardness is that of the Brinell Ball Hardness Test. A ram or shaft forces a steel ball of a certain diameter into the prepared surface of the test specimen. Naturally, if the hardness of the surface approaches that of the ball, the results are inaccurate. The Brinell hardness number is expressed as the ratio of the load to the area of the surface of the impression (appropriate units being agreed on). A certain ratio of load to diameter of the ball must be maintained in order to get concordant results. A ball of ten mm. diameter is generally used and pressures of 500 - 3000 kg. for fairly hard metals (steel, copper, etc.). If a five mm. ball is employed, loads one-quarter of that given for the ten mm. ball would be appropriate. The hardness numbers remain more or less constant if the different loads for different balls are in the same ratio as the squares of the diameters of the respective spheres. The time of subjection to the load must be constant, usually 30 seconds.

The Vickers Hardness Test is similar in principle, but it uses a diamond indenter in the shape of an inverted, square-based pyramid. It is to be preferred for scientific purposes. The load is applied by means of levers, controlled by a cam. After the impinging of the diamond a microscope is swung into place, centering itself automatically. Two diagonals of the square impression are measured, aided by a calibrated dial, and the hardness, on the Brinell scale, read from a table. The Vickers principle has been applied to an attachment for the microscope, which makes it possible to determine the hardness of individual constituents (23).

The hardness of a metal may be very greatly altered by alloying with another metal. If the two metals are mutually nearly insoluble in the solid state the hardness is a linear function of the composition. Should the metals form a continuous series of solid solutions the variation of hardness is expressed by a smooth curve having a maximum at a composition not far from that corresponding with equal weights of the component metals. In the case of intermediate phase formation we find that these are, as a rule, harder than their constituents (11).

II. Previous Relevant Investigations.

In this section it is proposed to review briefly the literature relevant to the purpose in hand. A short description of the three pure metals is followed by an account of the phase diagrams for the three binary systems as they are accepted at present. Special note will be taken of the conditions existing at room temperature at the pressure of the atmosphere. The conditions above room temperature necessarily affect the latter. Finally, the apposite conclusions reached on the ternary system by Campbell and Screaton will be briefly given.

a. The Three Metals.

Lead crystallizes with a face-centered cubic lattice with a cell edge of 4.94 A. The interatomic distance in the structure is 3.49 A, an abnormally large value (49). Goldschmidt (49) gives a metallic radius of 1.75 A. This is calculated on the basis of twelve nearest neighbours; quantum mechanics, postulating the existence of the metallic atoms as ions in a sea of electrons, considers that lead is only partially ionized in the solid metal.

Indium is considered to exist structurally with a body-centered tetragonal lattice with cell-dimensions a = 3.248 A and c = 4.951 A. This can be thought of as a slightly distorted form of a face-centered cubic structure. Goldschmidt's metallic radius is 1.67 A, while the interatomic distance in the element is 3.24 A. Again, quantum mechanics considers it probable that indium is only partially ionized in the solid state.

Structurally, tin exists as "white tin" with a body-centered tetragonal lattice with the cell constants a = 5.83 A and c = 3.182 A. Below 13.2° C. it exists as "gray tin" with the diamond structure and a cube edge of 6.46 A. The metallic radius, for 12-coordination, is 1.58 A with an interatomic distance in the element of 3.016 A for white tin. Again, it is probably only partially ionized in the solid state, according to quantum mechanics.

A comparison of interatomic distances for the metals grouped around lead, tin and indium in the periodic table discloses that these three have exceptionally large values of such distances (about 10% larger than the others). This is supposedly due to the partial ionization in the solid state. This property of the metals has been stressed because of the use which will be made of it in section V.

b. The System In - Sn.

The equilibrium diagram best so far for this system is the one determined by Rhines et al. (27). Precision thermal and metallographic methods served to confirm that there is an eutectic at about 48 weight per cent tin and 117° C, and that there are two intermediate solid phases in the system, γ and β . A peritectic decomposition of the γ-phase (15) is not confirmed; in its place a peritectoid decomposition above about 80° C is suggested. Uncertain features have been indicated by dashed lines in plate 4. The range of stability of the phases is, at room temperature: α (0 to 3 weight per cent tin), β (14 to 27 weight per cent tin), γ (75 to 88 weight per cent tin), and δ (94 to 100 weight per cent tin).

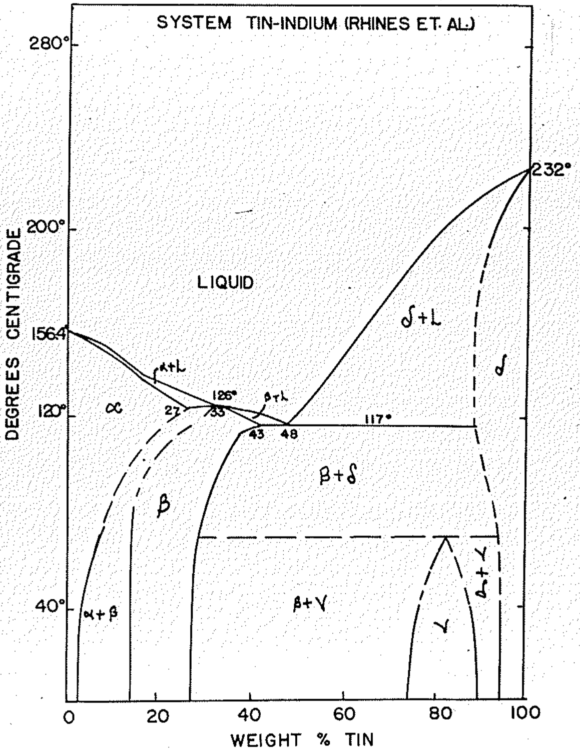

SYSTEM TIN-INDIUM (RHINES ET. AL.)
DEGREES CENTIGRADE
280°
200°
156.4°
120°
40°
232°
LIQUID
δ+L
δ
α+L
α
27
126°
33
β+L
43
48
117°
β
β+δ
β+γ
γ
δ+γ
α+β
0
20
40
60
80
100
WEIGHT % TIN

Plate 4.

Rhines et al. were able to distinguish the various phases under the microscope using an etching reagent of a mixture of water, potassium chromate, sulfuric acid, sodium chloride, hydrogen fluoride, and nitric acid. The β-phase always exhibited an uneven dark contour, which tended to obscure the presence of fine particles of the α-phase. It was found very easy to distinguish the β from the tin-rich phases. The γ and δ-phases could not be positively distinguished except when the two occurred together in fairly large masses; γ was light and β grey to black, depending on the grain orientation.

The γ-phase, according to Fink et al. (15), has a simple hexagonal lattice. This was confirmed by Ferguson and Screaton (14). Valentiner (41), Fink et al. and E. Orlamunder (20) found a tetragonal face-centered lattice for the β-phase, which is equivalent to a body-centered tetragonal lattice with a larger cell *. Ferguson and Screaton, who took into account the intensities of the observed reflections, do not agree with this result. The bearing these structures had on the experimental procedure will become evident later.

c. The System Pb - In.

Valentiner and Habestroh, who published a series of papers on this system (42, 43, 44), found that lead and indium do not form an unbroken series of solid solutions. This they determined by thermal and X-ray analysis. Their work indicates that lead dissolves indium (without change in lattice type) until a content of 30 atomic per cent lead is reached. Then a face-

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* By rotation of 45° in the plane of the 'a' axis a face-centered tetragonal lattice is converted into a body-centered tetragonal lattice, so that the new 'a' axis increases by a factor $\sqrt{2}$. The 'c' axis remains unchanged.

centered tetragonal structure with 18.75 atomic per cent lead appears. Below 20 atomic per cent lead the stable structure is also face-centered tetragonal with a smaller unit cell.

The latest paper, by Klemm et al. (20), is in agreement with these results except for the size of the first tetragonal lattice. They could not obtain any heterogeneous solids by X-rays and thermal analysis but placed the regions of heterogeneity as 8 to 12 atomic per cent lead, and 27 to 30 atomic per cent lead at room temperature.

The diagram shown in plate 5 is based on an unpublished work by H. M. Davis and C. H. Rowe and appears in the Metals Handbook (24). Substantially, these different workers agree in their results. From the

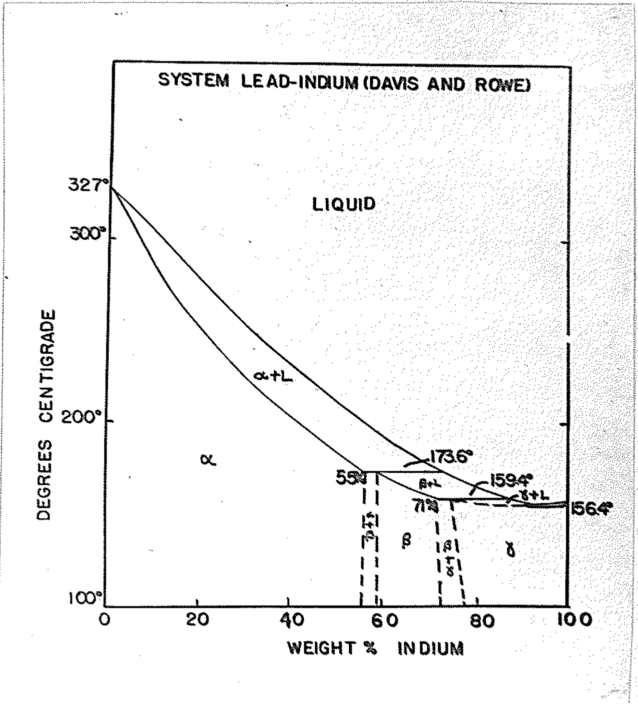


Plate 5.

written discussion following Rhines paper (27), we may conclude that Davis and Rowe used microscopic means in their investigation. They mention that they were unable to obtain any difference in etching characteristics between the γ and β phases. Since the γ and β phases both have face-centered tetragonal structures, this is not surprising. They draw dotted lines to indicate the regions of coexistence of the different phases in the solid state.

d. The System Pb - Sn.

Since lead and tin are the main constituents of most solders, much work has been done on this system. The diagram presently accepted is that of Stockdale (38); plate 6 represents his results.

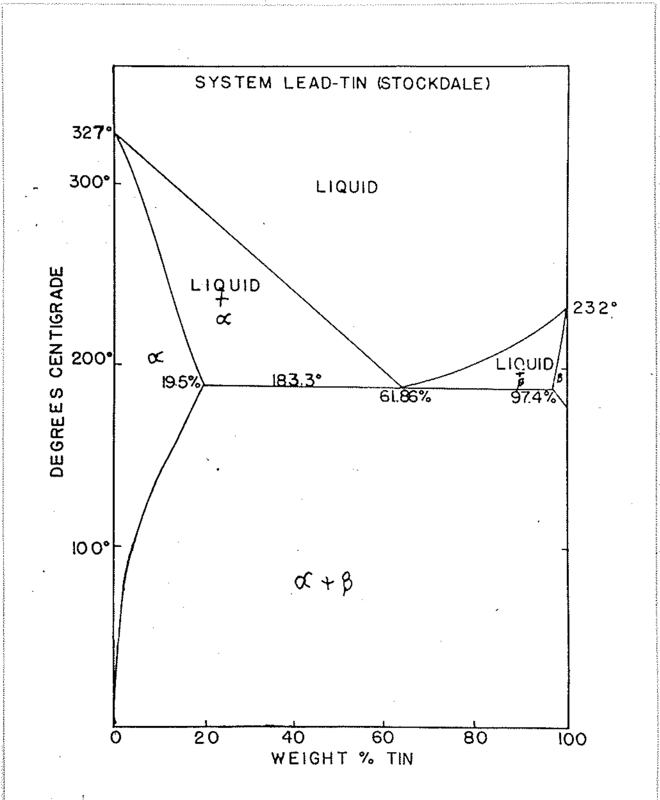
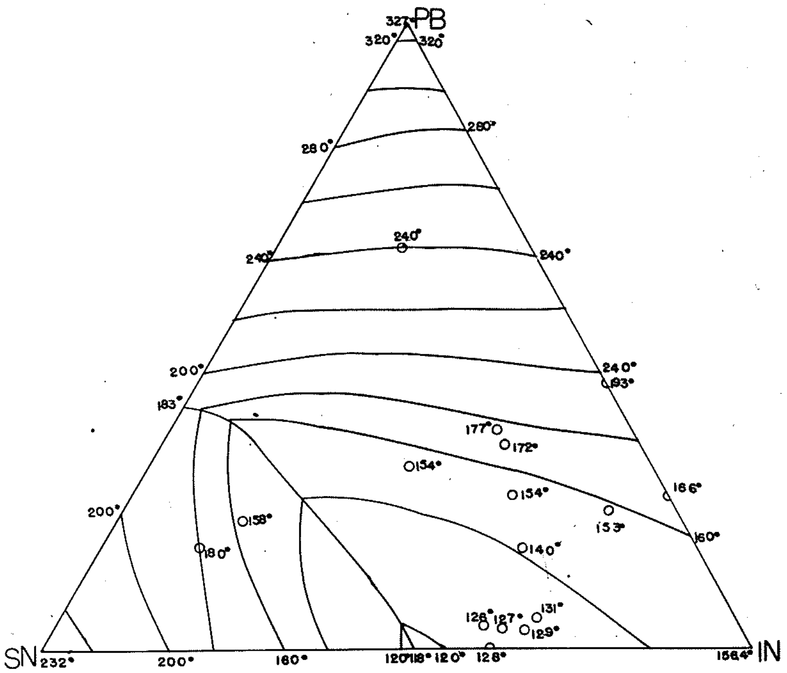


Plate 6.

The eutectic is placed at 61.86 weight per cent tin at a temperature of 183.3°C. At room temperature the mutual solubilities of the two metals are small (about 1.5% for tin in lead). Like other workers, Stockdale noticed an evolution of heat occurring at about 150°C in lead-rich alloys, which varied with the previous history of the specimen. The nature of this heat evolution, for which as many reasons are suggested as there are debaters, is not understood. One more plausible reason for this phenomenon, and a method of testing this, will be suggested in section V.

e. The System Pb - In - Sn.

The only extensive work on this ternary system is that of Campbell and Screaton (34), who found that there is no true ternary eutectic in the system. The presence of two peritectics (one at 134°C, the other at 126°C) on the eutectic trough running from the Pb - Sn eutectic to that of In - Sn, is indicated. Weak halts in solidification were obtained at these temperatures; no definite conclusions could be drawn from them. In the Pb - In system the peritectic occurring at 173.6°C was checked; once more the evolution of heat at the peritectic transformation was small and prohibited any study of the path of the peritectic in the ternary system.



LIQUIDUS CONTOURS (SYSTEM PB-IN-SN)

Plate 7.

Plate 7 shows the projections of the liquidus isotherms for the system as determined by these workers. No irregular areas could be detected and the whole liquidus is fairly smooth. In section III reference will be made to this projection.

To facilitate subsequent discussions the phases, ordinarily designated by Greek letters, will be continued to be so designated; with the difference that the phases in the three binaries will be distinguished by the use of Arabic numerals, viz., 1 for In - Sn, 2 for Pb - In, and 3 for Pb - Sn.

A thorough discussion of this investigation is given by Screaton (34); as well as an extensive review of the literature on the three binary systems.

III. Experimental.

a. Preliminary.

The purpose of this investigation, as stated above, was the establishment of the phase rule diagram at room temperature for the system In - Pb - Sn. Practically, importance is attached to a knowledge of the phase structure of the cold alloys. Now, to locate the boundaries in such a diagram a judicious choice of the alloys used is imperative, or else the labour will be increased immensely; serendipity cannot be relied on. A good rule to follow is to choose the alloy as much as possible near the presumed boundaries of the single-phase regions, since X-ray and microscopic observations serve to show when one has crossed into a two-phase region. When two boundaries of a three-phase field have been determined that whole field has then been located since, by the phase rule, we have there an invariant triangle. From a survey of various three component systems it becomes apparent that the phases along the three binaries usually extend considerable distances into the interior of the triangle, and very seldom indeed are there single-phase regions that are entirely divorced from the boundaries. When similar structures occur at similar concentration ratios on two of the binaries, it might not be unlikely that a single-phase region will extend entirely across the ternary triangle from one to the other. Such rough generalizations formed the first consideration in the experimental approach to the problem.

Naturally, the more alloys that are studied the more precisely will the course of the boundaries be fixed. Here one must bear in mind the final object and say with Tammann that "... the goal will be reached the more rapidly the more the attention is concentrated on the principal point and the more it is possible to distinguish between the principal and the secondary consideration". To fix every boundary with the minutest accuracy (say ± .05% along the whole course) is unnecessary.

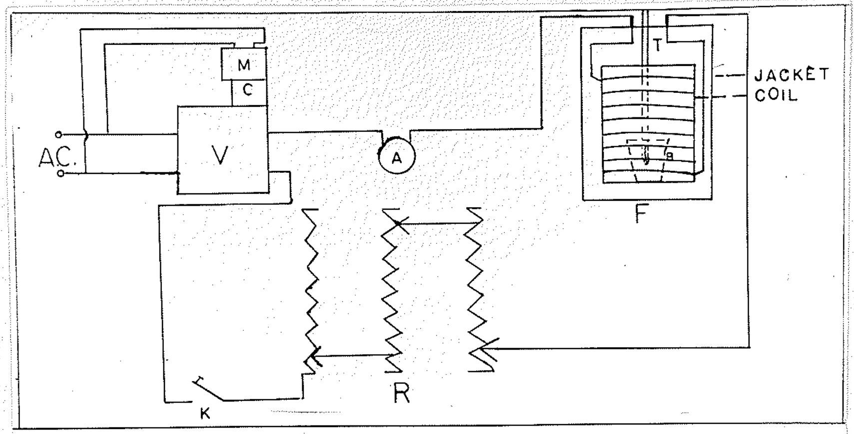
The second consideration in the experimental approach to the present problem was that of equilibrium conditions in the alloys under examination. Phase rule applies fully only to alloys in complete equilibrium, and such equilibrium is rarely strictly obtained (in terms of the second law of thermodynamics, a heterogeneous system is in equilibrium when the entropy of the system is at a maximum). Since only under circumstances of complete equilibrium is the constitution of an alloy fixed, this state is the one which a pure phase rule research must concern itself with. Infinitely slow rates of cooling during the preparation of specimens would in most cases be required in order to allow this state to be secured. However, the components in the present system melt, as indicated, all below 330°C. A look at the liquidus isotherms of plate 7 shows, moreover, that over the greater part of the system inceptive solidification occurs below 240°C; indeed, in the most interesting regions the liquidus lies under 170°C. Therefore it was thought that a cooling process of about 24 hours duration should be sufficient for practical, if not theoretically ultimate, equilibrium conditions to be obtained. Actual experiment would, of course, show whether this consideration was irrefragable or not.

How this cooling process was carried out experimentally, what the methods of chemical analysis were, a description of the preparation and examination of a typical alloy; and an account, which will then be comprehensible, of the procedure followed in the mapping-out of the various regions, as dictated by the results already arrived at, form the content of this section.

b. Heat - Treatment Apparatus.

The essence of the heat-treatment given the samples was the gradual cooling over a suitable period of time. Since an electrical furnace was used, some device was needed which would automatically decrease the A.C. current through the furnace from the initial value to zero, during the crystallization. The instrument finally built consisted of an ordinary "Variac" on which was mounted a small electrical motor of low r.p.m. A set of gears, built in, reduced the revolutions per unit time considerably before connection by a worm gear to the coarse works of an alarm clock; which, in turn, took the place of the dial on the "Variac". In this way a slow decrease in current through the furnace, extending over about 23 hours, was achieved.

It is true that the voltage was thus decreased regularly but not the power input, since the power varies roughly as the square of the voltage. The resistance of the heating coil changes with temperature, introducing a corresponding variation in the power factor in which, since the coil forms an inductance, the impedance is not zero. But this does not vitiate the desired effect; a faster rate of cooling prevailed at the beginning of solidification and a slower rate afterwards and, in fact, this was desirable because of the slower rate of diffusion across concentration gradients in the solid state.



HEAT TREATING APPARATUS

Plate 8.

Plate 8 shows a schematic diagram of the experimental set up. Current from the A.C. mains flows through the modified "variac" V, thence through the ammeter A, passing on through the furnace F; from whence it flows through a bank of rheostats R. A key, K, completes the circuit. The furnace, slightly altered, was the one used and described by Screaton (34). It consisted in effect of a heating coil of nichrome wire wound on an alundum tube 16 cms and 5.5 cms in height and width, respectively. Suitable jackets and covers were of "Transite"; a hole in the removable top allowed the insertion of a thermometer T, into the furnace core. Because only approximate temperature readings were needed a thermometer reading to 360°C. sufficed. Convenient adjustment of the initial current was accomplished by means of the bank of rheostats and the ammeter. The motor M, and the clock C, were fastened to the "Variac" as described.

c. Purity of Materials and Chemical Analysis.

The metals used were analyzed by the respective supply houses and were marked as follows:

Lead	(Merck Reagent Grade)	
	Maximum Impurities	
	Antimony	0.005%
	Silver	0.002%
	Total Foreign Metals	0.05%
Indium	(Consolidated Mining and Smelting Company Limited)	
	Marked Tadanac 99.95 and Indium	
Tin	(Vulcan "Commercial" Tin)	
	Batch #73	
	Iron	0.0020%
	Antimony	0.0023%
	Lead	Trace
	Copper	Trace
	Tin	99.9957% (by difference)

Because the heat treatment of the specimens was carried out in the presence of air, each one had to be analyzed chemically; preferential oxidation and concentration gradients were taken into account by this means. How the sampling for analysis was done is described further on in this section.

Initially an attempt was made to analyze for all three components directly. Organic compounds often serve as convenient precipitating agents in the gravimetric determination of metals. A method is given by Welcher (47) for the determination of indium in the presence of lead ions in solution. The solution is to be buffered with acetic acid and sodium acetate and the indium is precipitated as the 8-hydroxy-quinolate with an alcoholic solution of the corresponding reagent. Tin is partially precipitated as the hydroxide at this pH; it was removed as stannic acid with HNO_3, followed by conversion of the HNO_3 to acetic acid with sodium acetate. The subsequent indium precipitate was then filtered off, dried and weighed, and the lead was precipitated at a higher pH in the filtrate, as described by Welcher (48). Reproducible results were not, however, obtained.

A few other procedures were also found unsuitable and finally it was decided to determine lead and tin by standard methods, indium being determined by difference. If accurate and precise results could be consistently obtained to within one or two per cent this would suffice, in view of the sensitivity of the X-ray and microscopic methods. Besides, indium is least oxidized at the temperatures in question, whereas a purple oxide film will form on lead in a short time even at 100°C. (by actual trial). Clearly then, if lead was known exactly the total accuracy should be controllable to the desired degree. A few "runs" on test samples, using the methods given below, confirmed this expectation; even for low indium concentrations. Those alloys which were attacked readily by nitric acid were assayed by a method given by Screaton (34). A sample weighing about one gram was dissolved in 1:5 HNO_3 and digested at 95 - 100°C. for a few hours. The metastannic acid was filtered off, washed ten times with hot 1: 10 HNO_3, and ignited to SnO_2 in a porcelain crucible. Lead was determined by the usual method of precipitation as $PbSO_4$, washing with ethyl alcohol and drying at 110°C. for one hour.

Those alloys, however, which did not readily dissolve in nitric acid were analyzed by the method, slightly modified, suggested by Cumming and Kay (7). About one gram of the alloy was dissolved in 20 cc. of concentrated HCl. Platinum scraps served as a second electrode in an internally shorted electrolytic cell, and thereby increased the rate of solution. To an aliquot of this solution 50 cc. of concentrated HCl and about one gram of antimony powder (free from sulfide) were added; the solution was diluted to 200 cc. After boiling for 15 minutes in a stream of carbon dioxide, the solution was titrated with standardized iodine solution, using starch as an indicator. Lead was determined as before.

d. Preparation and Examination of a Typical Alloy.

The treatment which each sample was subjected to will now be related.

A total weight of 40 grams of the desired composition was charged