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.

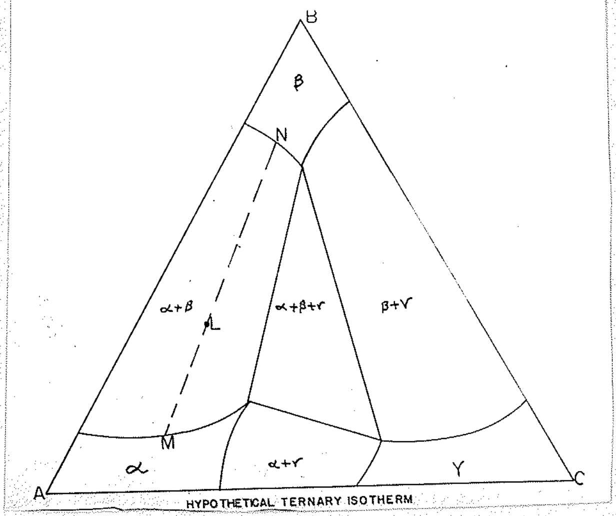


Plate 1.

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.

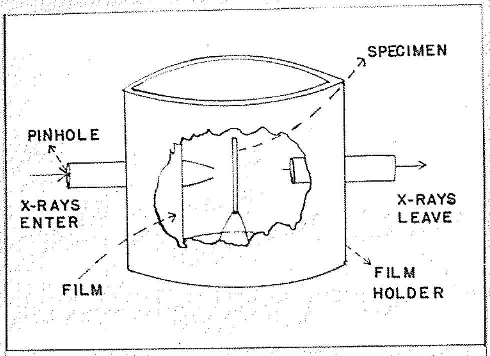
Before 1912 there was no known way of getting at these structures. Scientists had made shrewd guesses as to the causes of the external symmetry. Roule (1703 - 1770), teacher of Lavoisier (33), made the astute remark that

> "...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.

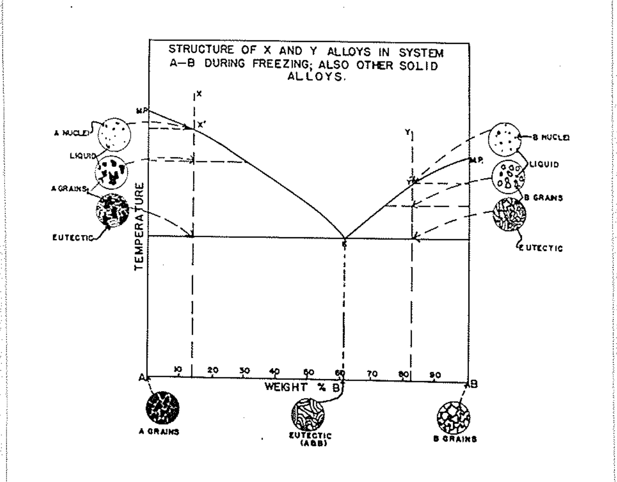


Plate 3.

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).

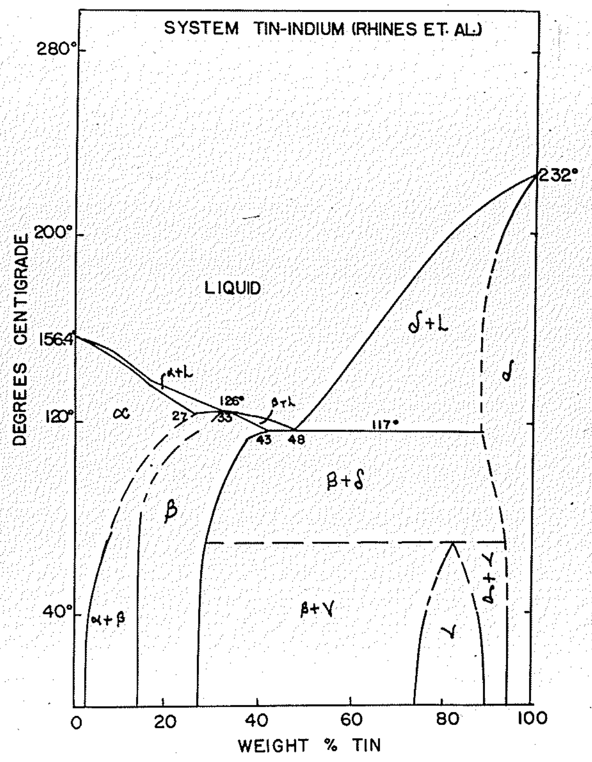

SYSTEM TIN-INDIUM (RHINES ET. AL.)
280°
232°
200°
DEGREES CENTIGRADE
LIQUID
156.4
δ+L
α+L
δ
126°
β+L
α
120°
27
33
43
48
117°
β+δ
β
β+γ
δ+γ
40°
α+β
γ
0
20
40
60
80
100
WEIGHT % TIN

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

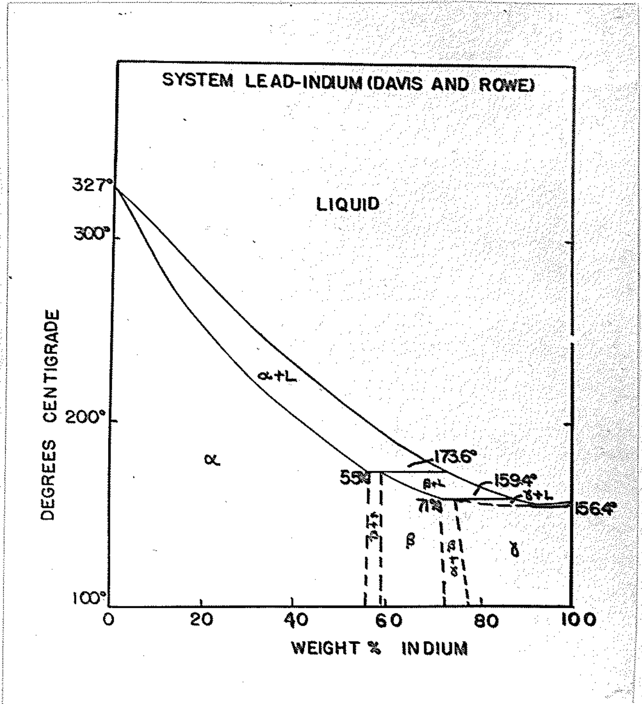


Plate 5.

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.

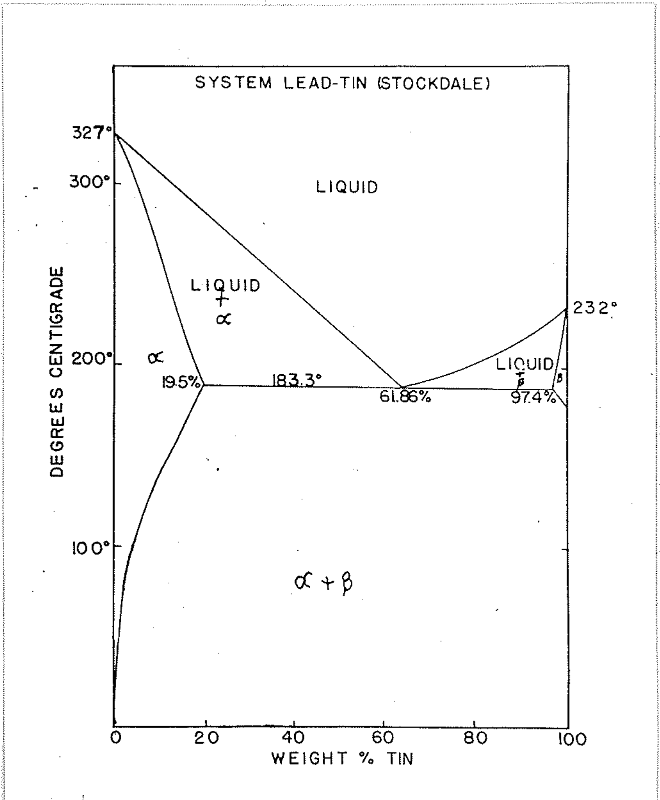
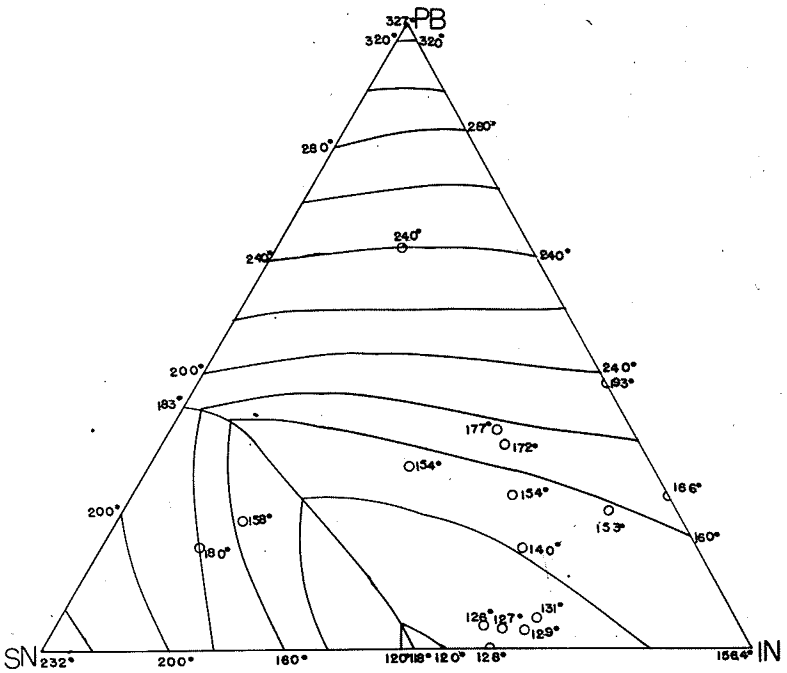


Plate 6.

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.

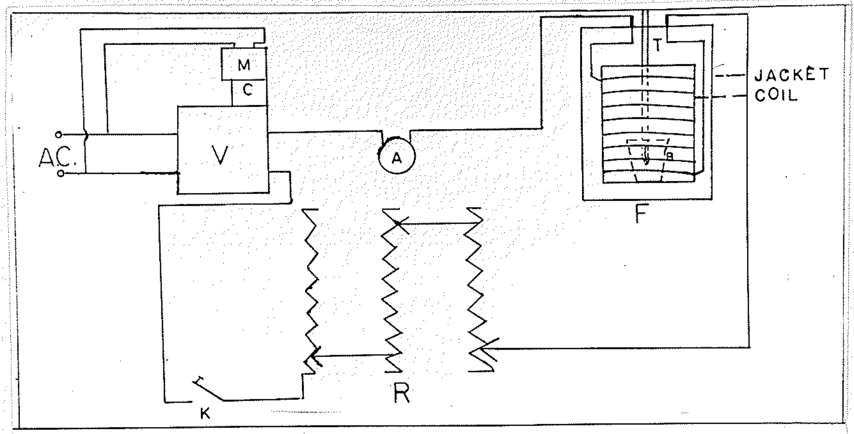
The second consideration in the experimental approach to the present problem was that of equilibrium conditions in the alloys under examination. Phase rule applies fully only to alloys in complete equilibrium, and such equilibrium is rarely strictly obtained (in terms of the second law of thermodynamics, 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 into a thin-walled (about 1/16 of an inch thick) crucible, about four cm. and two and one-half cm. in height and width, respectively. This charge was inserted in the furnace, preheated to about 60 degrees above the liquidus as read from plate 7. The indium metal, always placed over the other constituents of the charge, melted first and formed a supernatant, protective layer of molten metal. After fusion and repeated stirring with an alundum rod to ensure homogeneity, the melt was cooled to roughly three degrees above the temperature of the liquidus; the whole process taking about three hours. The continuous-cooling mechanism, now set in motion, assured the desired annealing treatment.

From the ingot so prepared the oxide film was removed with a lathe. The lathe also served to prepare a specimen, approximately 7 mm. in width and 4 mm. in height, for microscopic examination. Turnings for analysis were taken from the immediate vicinity of the prepared surface, thus ensuring the validity of the assay. No demarcation marks, denoting gross phase separations during cooling, could ever be detected by a vertical saw-cut. The general agreement between final analysis and original composition of the charge lends support to the assertion that no appreciable concentration gradients existed in the ingots. At any rate, the method of sampling for analysis vitiates any objections on this point.

By use of a keen-edged, thin-bladed knife a strip for X-ray examination was cut from the surface of the specimen. In this way a strip could be prepared which approached 0.2 mm. in diameter. A powder pattern was now taken of the fragment on a North American Phillips X-ray unit, using a simple Debye camera of 57.3 mm. diameter. Copper radiation and a nickel filter were used. The exposure time varied from one to three hours depending on the composition and size of the specimen.

Filings could not be prepared readily because of the "smearing" properties of the alloys. In two or three-phase samples the different hardnesses of the phases would also give different sizes of filings for each. It is very doubtful whether such a procedure will give a more accurate representation of the actual conditions. The small degree of cold-working by the knife edge would only cause a slightly preferred orientation of the grains and this effect was neutralized by rotation of the specimen during exposure to X-rays.

After chemical analysis and X-ray study came the microscopic observations. The process described here is the one finally developed after much trial and error. Preparatory to polishing the surface was lightly rubbed on a stationary fine mill-file, the teeth of the file being cleaned after each stroke. The final polish was given on a wheel-driven silk cloth (selvyt), using the "light" variety of powdered magnesium oxide as polishing agent. If the sample contained large amounts of lead tarnishing was a problem. Soap was found efficacious in preventing this. Too much water on the cloth increased the tarnishing, while too heavy a tarnished layer could be removed by dabbing with glacial acetic acid. Otherwise polishing was carried on, close to the center of the wheel, until the surface had a lustrous appearance, as far as possible scratch-free.

An etching reagent consisting of seven parts of glycerol, two parts concentrated nitric acid, and one part of glacial acetic acid gave the best results over the whole concentration range. The HNO_3 content was varied with different samples to achieve the best effect. The same reagent, but with different proportions of the constituents, was used by Villela and Beregekoff (45) for lead alloys. Etching took place by immersion for 5-30 seconds at approximately 40°C. Electrolytic polishing as described in the "A.S.T.M. Standards" (50) was tried; but was not suitable for most of the alloys. Samples #5 and #6 were polished in this way.

A model CM-Bausch and Lomb microscope with a movable stage served in this investigation. In order to examine the polished and etched surface it was necessary to set the same accurately perpendicular to the optical axis. A simple device, consisting of a brass ring on a flat metal surface, did away with any need of tilting the stage. The specimen was laid, with the smooth surface downwards, on the metal surface within the circumference of the ring. A small quantity of modelling clay was placed on the specimen, and an ordinary glass micro-slip was pressed down very gently until it was in perfect contact with the ring. The slip, with the specimen now adhering to it, was lifted, turned over, and placed on the stage, and required no further levelling. Objective lenses magnifying to 48, 135, and 250 diameters were employed. To assure that the true structure of the sample did not remain latent, a process of alternate light polishing and etching was carried out. This, furthermore, decreased the danger of coldworking from overpolishing and deterioration of a delicate microstructure from overetching.

A photomicrograph of the desired magnification could conveniently be taken with a Bausch and Lomb press-type camera, which fitted this microscope. Positive prints were then "run-off" in the customary manner, while enlargements to X 1000, if desired, were obtained by a standard instrument.

The last tests to be undertaken were the Brinell Ball and Vickers Diamond Hardness tests. Extreme softness of the ingots prevented application of the available Brinell Hardness machine. Consequently a smaller one was constructed having the ratio of the load in kg. to the square of the diameter of the ball in mm. of 'one' as specified in the Metals Handbook (25). A lever system allowed the slow lowering of the load (5.5 kilos) on to the specimen, which was subjected to this load for 30 seconds. A sintered magnet, set in the load body, held a steel ball of 2.35 mm. diameter in position. Indentations, two to a sample, were made on the surface formerly polished and etched. The surface diameters of the indentations were read with a Zeiss ocular micrometer which, for this purpose, took the place of the eyepiece on the microscope. Two diameters were read on each indentation and the readings averaged. The Brinell Hardness Numbers (Bhn) were calculated from the formula

$$\text{Bhn} = \frac{P}{\frac{D}{2}\left(D - \sqrt{D-d^2}\right)}$$

where P = test load in kilos, D = diameter of the ball in mm., d = diameter of impression in mm. The resulting Bhn values, which agreed reasonably well, were averaged.

On the same surface two indentations were made using a Vickers-Armstrong hardness tester with a 5 kilo load. The indenter consisted of a square-based, pyramid-shaped diamond having an included angle of 136° between faces. As before, two indentations were made, the diagonals of each read with the attached microscope (fitted with an ocular micrometer that contained movable knife edges), and the Diamond Pyramid Hardness (DPH) ascertained by substitution in the formula

$$\mathrm{DPH} = \frac{1.8544L}{d^2}$$

where L = load in kilos, d = length of diagonal of impression in mm. Again, the two DPH values were averaged. Initially it had been intended to obtain the hardness of the different phases co-present by this latter method. Unfortunately the indentations were a little too large for this purpose.

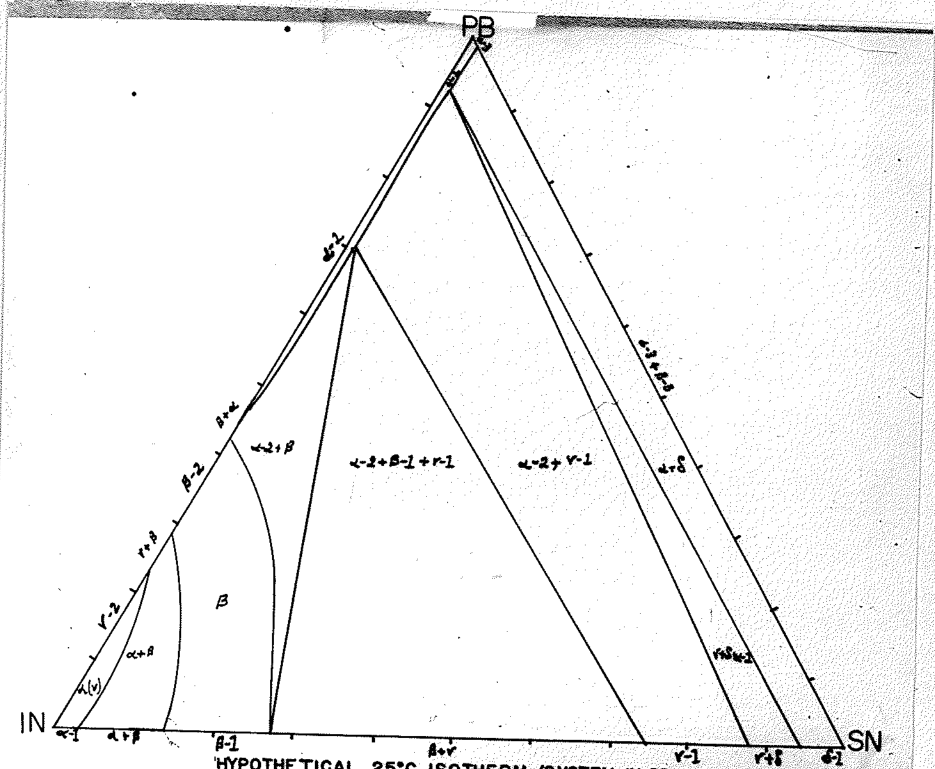
e. General Procedure.

Obviously, the first general step in the investigation had to be the determination of the powder pattern and the microstructure for each of the binary single-phase regions, and, preferably, for the two-phase regions as well. This latter consideration was given weight by the possibility that some of the phases might not give identifiable powder patterns in the presence of another phase until relatively high concentrations (maybe 15%) of the first phase had been reached. Moreover, the etching characteristics of a phase might well change when it occurred together with a second phase.

Accordingly, alloys were prepared and examined for each of the regions in the binaries, fifteen in all. In two-phase regions the composition was so regulated as to place the alloy a convenient distance from the boundary line.

As a first step in the inquiry into the three-component system, the extent to which the γ-1 lattice could entertain lead atoms was determined. It was quickly found that it did not do so at all, within the limits of experimental accuracy.

A glance at the two binary systems In - Pb and In - Sn shows that the two β-phases occur at roughly equal concentration ratios of their respective components. The discussion of these systems in Section II gives the lattice structure of β-2 as face-centered tetragonal and that of β-1 as identical to it, except for a difference in cell dimensions. Quite possibly then, a single-phase region spreads out from the limits of β-1 to those of β-2. With this view in mind a hypothetical phase diagram for the ternary system at 25°C. was constructed and is shown in plate 9. The phases present in each region are designated in the usual way. Tie-lines are to be imagined, drawn across the two-phase regions. Considerations from the standpoint of the phase rule prove the construction to be theoretically sound. The diagram assumes the nonexistence of a ternary compound.



HYPOTHETICAL 25°C ISOTHERM (SYSTEM IN-PB-SN)

Plate 9.

All that was now needed was an experimental check of the diagram and the resolution of the course of the phase boundaries. The ensueing study formed the last and main part of the investigation. A number of alloys, discreetly placed, checked the existence of the postulated single-phase region with the β-1 and β-2 structure. A determination of one point on one of the boundaries of each of the three-phase regions necessarily fixed their areas, as well as the area of the interjacent two-phase region. Greatest care was taken with the limits of the one-phase region extending across the ternary plot. A few later points were used to control further the soundness of the results (see section IV, alloys 36 -38).

Hardness determinations served as a rough test of the conclusions arrived at by the two principal methods.

IV. Experimental Results.

a. Direct Results.

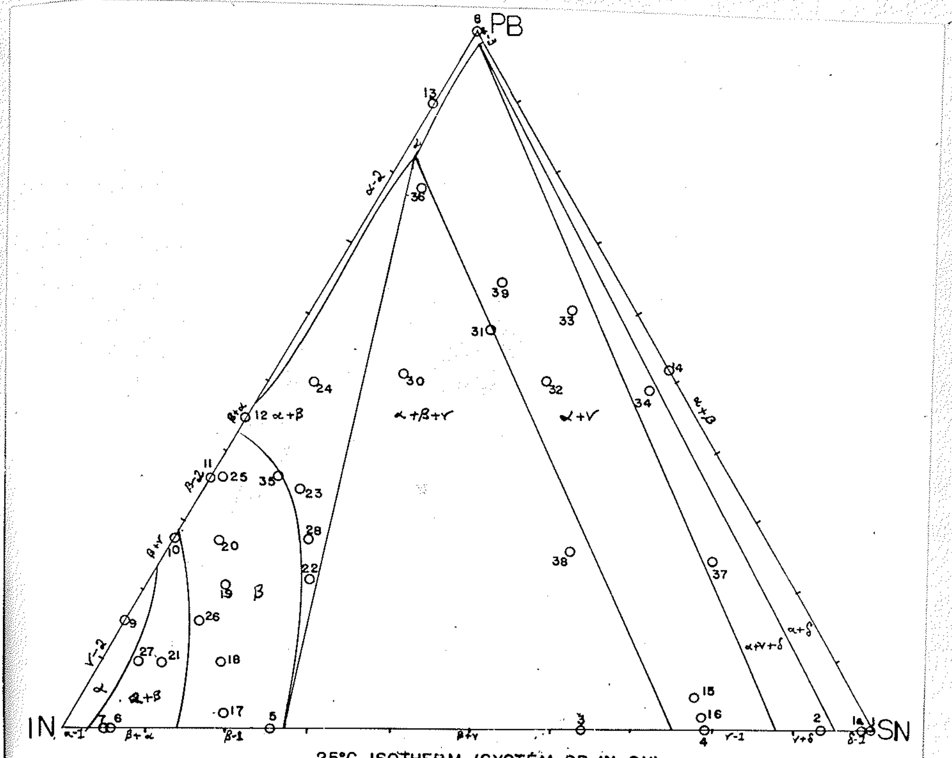
The experimental results can conveniently be given in the order now described. Table I relates the composition of the various alloys studied, as well as the Brinell hardness numbers (Bhn) and the Diamond Pyramid Hardnesses (DPH) of each. Then follows the final isothermal section at room temperature for the system Pb - In - Sn, Plate 10, as determined from the microscopic and X-ray evidence about the ingots. The photomicrographs and a few typical X-ray powder patterns are then presented. These series of plates are not intended as a myriorama; instead, they compose the evidence on which the diagram of Plate 10 was constructed and will be discussed seriatim. Finally, plates 63 and 64 represent, respectively, a plot of hardness against composition for the two binary systems Pb - In and In - Sn at room temperatures, and a rough plot of hardness contours for the ternary system as deduced from Table I.

TABLE I. COMPOSITION AND HARDNESS.

SAMPLE NO.	COMPOSITION By Weight Pb	Sn	In	Bhn; diameter of ball/load/time of application = 2.35 mm/5 kilos/30 secs.	DPH, Load of 5 kilos.
1		100		3.9	5.8
1a		98.6	1.4	8.4	7.9
2		93.7	6.3	10.0	12.8
3		64.7	35.3	3.8	7.1
4		79.1	20.9	10.1	11.4
5		25.5	74.5	1.01	1.04
6		5.6	94.4	1.3	1.9
7		5.1	94.9	0.89	1.7
8	100			2.6	4.3
9	15.1		84.9	3.5	4.4
10	27.4		72.6	5.5	7.7
11	35.9		64.1	8.1	10.2
12	44.7		55.3	8.4	11.4
13	89.7		10.3	7.3	7.8
14	51.4		48.6	9.2	13.4
15	4.6	75.3	20.1	10.1	13.8
16	1.8	77.8	20.4	8.5	11.0
17	2.0	18.2	79.8	1.8	2.1
18	9.5	14.8	75.7	2.3	3.1
19	20.2	9.9	69.9	4.2	5.2
20	27.0	5.4	67.6	5.9	6.9

TABLE I (cont'd)

SAMPLE NO.	COMPOSITION BY WEIGHT Pb	Sn	In	Bhn	DPH
21	9.9	7.1	83.0	2.7	3.3
22	21.3	19.1	59.6	4.3	5.1
23	34.8	11.2	54.0	8.4	9.7
24	49.8	5.1	45.1	10.9	13.3
25	35.8	1.0	63.2	7.9	9.4
26	15.9	8.8	75.3	3.7	4.4
27	9.9	4.1	86.0	2.9	3.5
28	27.1	16.6	56.3	6.0	7.7
30	51.5	15.8	32.7	9.0	12.4
31	57.8	23.3	18.9	10.9	13.6
32	50.2	34.1	15.7	10.0	13.0
33	60.9	32.3	6.8	10.4	13.2
34	49.8	47.6	2.6	10.5	14.5
35	36.0	8.1	55.9	7.1	8.2
36	77.9	4.4	17.7	10.1	11.6
37	24.2	66.3	9.5	7.4	11.4
38	24.9	49.8	25.3	10.0	12.8
39	64.3	21.5	14.2	10.8	13.4



25°C. ISOTHERM (SYSTEM PB-IN-SN)

Plate 10.

It will be noted on plate 10 that a single phase region extends across the isotherm from β -1 to β -2. This is by far the most interesting of the results and indicates, at the least, that the two phases are of closely similar structure. The invariant triangle in which γ -1, β -1 and α -2 (lead lattice) are coexistent occupies a large part of the isotherm. In the various two-phase regions, tie-lines may be drawn in the customary manner.

In the following photomicrographs the etching reagent, unless otherwise indicated, consisted of a mixture of glacial acetic acid, glycerol, and nitric acid in varying proportions.

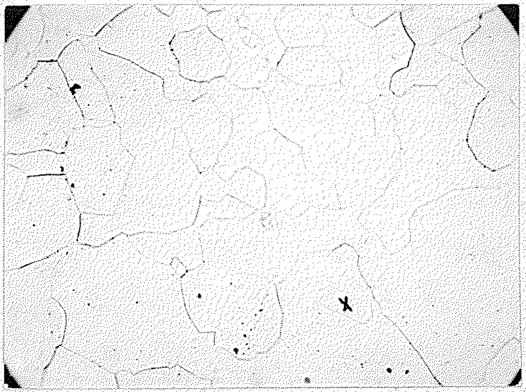


Plate 11. Alloy 1, X 135. Grain boundaries in pure tin. See text re grain marked with a cross.

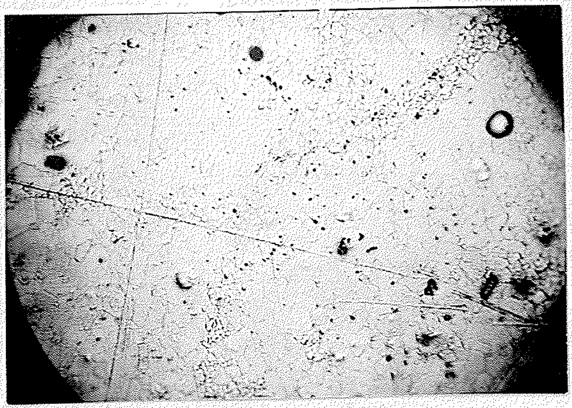


Plate 12. Alloy 2, X 250. H_2SO_4 etch, showing the grains of γ-1(small) growing from δ-1 phase.

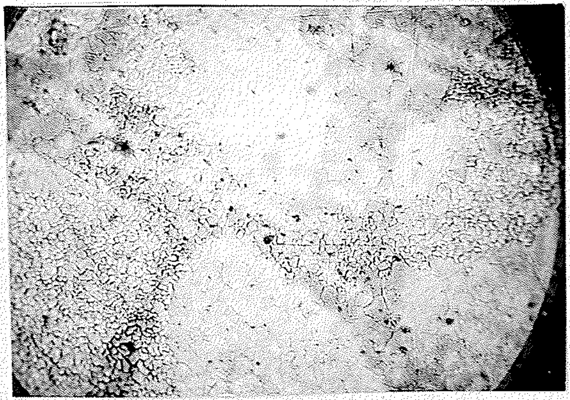


Plate 13. Alloy 2, X 250. H_2SO_4 etch; γ-1 and δ-1 present. Hardly any difference in etching characteristics.

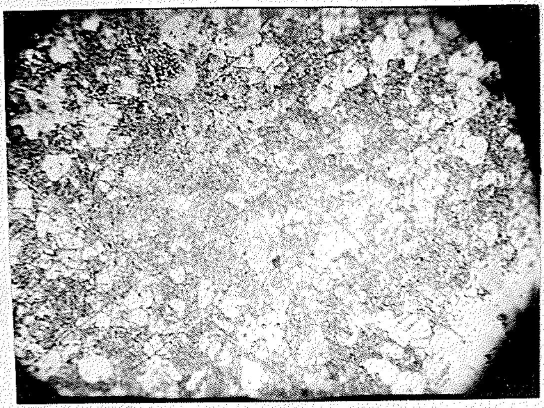


Plate 14. Alloy 2, X 250. Usual etch; note the difference in etching characteristics of γ-1 (light) and δ-1(dark).

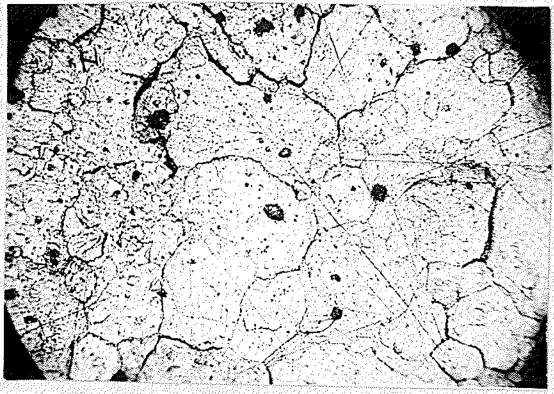


Plate 15. Alloy 4, X 135. Grain boundaries in γ-1; black spots are probably spurious, although some β-1 may be present.

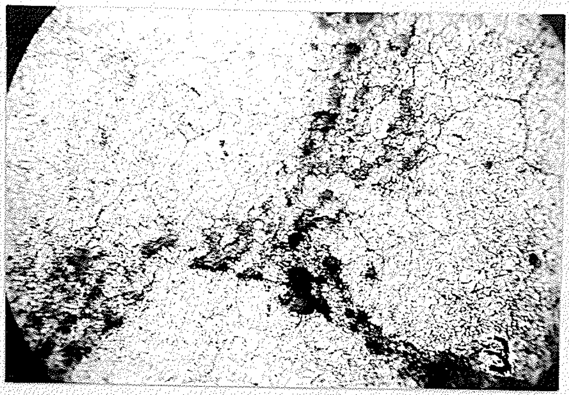


Plate 16. Alloy 3, X 250. β-1 (black) present at the former grain boundaries of δ-1, now converted to γ-1.

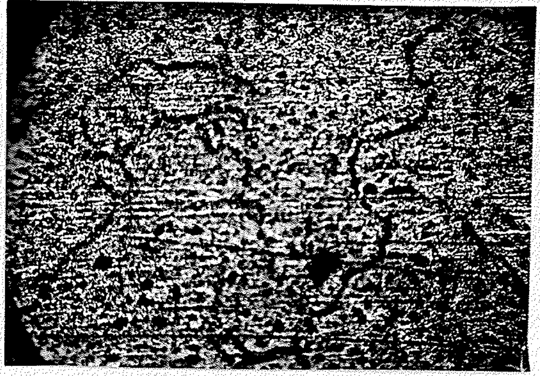


Plate 17. Alloy 5, X 135. Grain boundaries in β-1, exhibiting the characteristic pitted appearance of this phase.

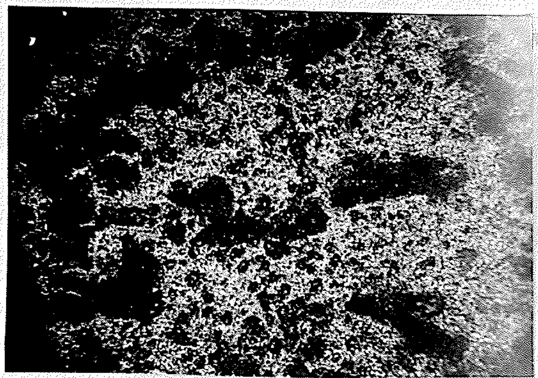


Plate 18. Alloy 6, X 135. β-1 (black) present in a background of α-1 which also tends to pit.

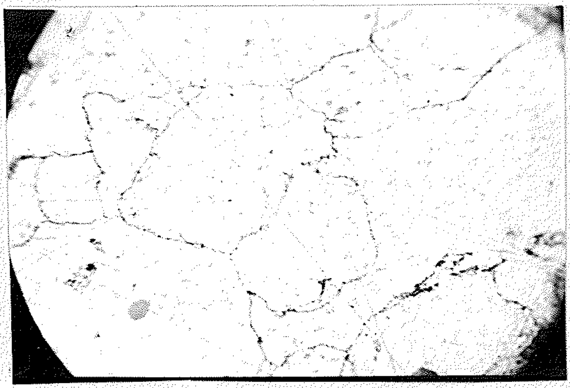


Plate 19. Alloy 9, X 250. Grain boundaries in γ -2, a solid solution of lead in indium.

Plate 20. Alloy 10, X 48. Lineage type structure due probably to the effect of dendritic and branching growth of the β -2 phase.

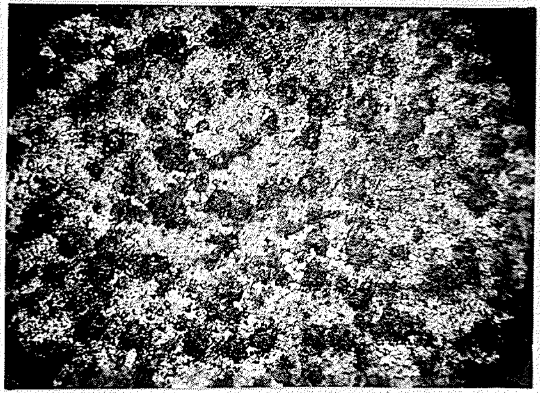


Plate 21. Alloy 10, X 250. Repolished and reetched after 3 months at room temperature; β -2 in a background of γ -2.

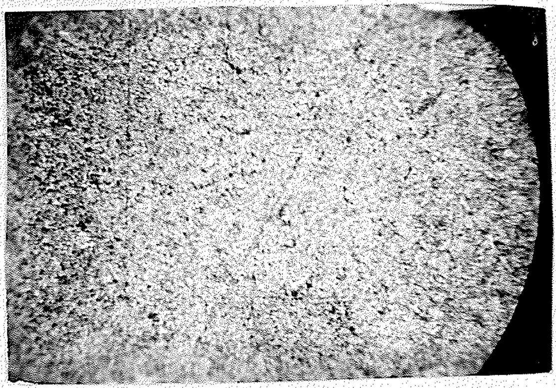


Plate 22. Alloy 11, X 250. Pitted appearance of β -2, but no grain boundaries easily seen.

Plate 23. Alloy 11, X 135. Repolished and reetched after 3 months at room temperature; grain boundaries in β -2.

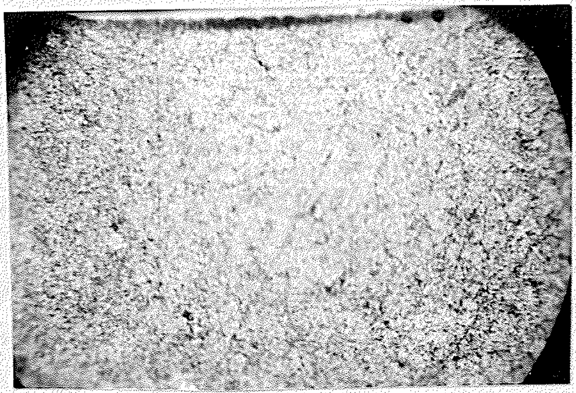


Plate 24. Alloy 12, X 250. No evidence present of heterogeneity of the sample; same appearance as alloy 11, plate 22.

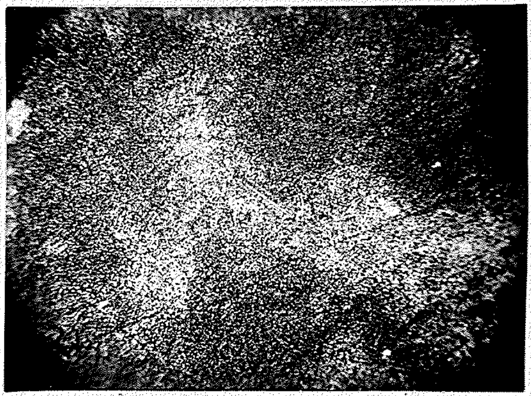


Plate 25. Alloy 12, X 135. Repolished and reetched after 3 months at room temperature; α -2 (light) with β -2, heterogeneity now being evident.

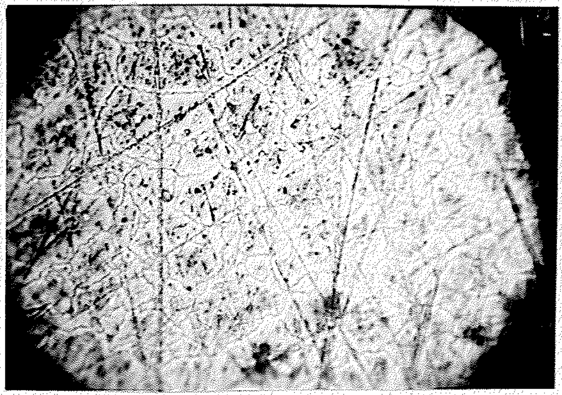


Plate 26. Alloy 13, X 250. Grain boundaries in a solid solution of indium in lead; coring, due to too rapid cooling, evinced by black spots.

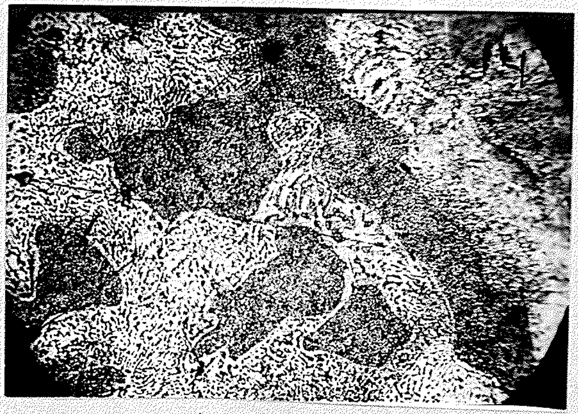


Plate 27. Alloy 14, X 250.
Lead grains (dark) in the
Pb-Sn eutectic.

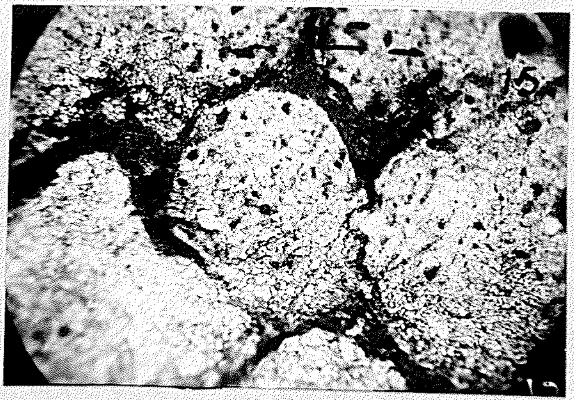


Plate 28. Alloy 15, X 135.
γ-1 (light) together with
a second phase, which must
be α-2 (lead lattice).

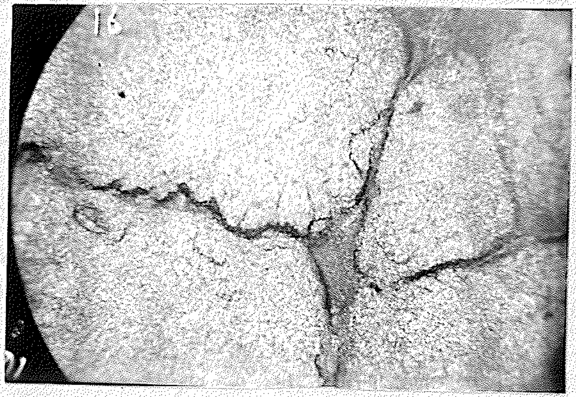


Plate 29. Alloy 16, X 135.
Same structure as alloy 15,
plate 28, with less of the
second phase.

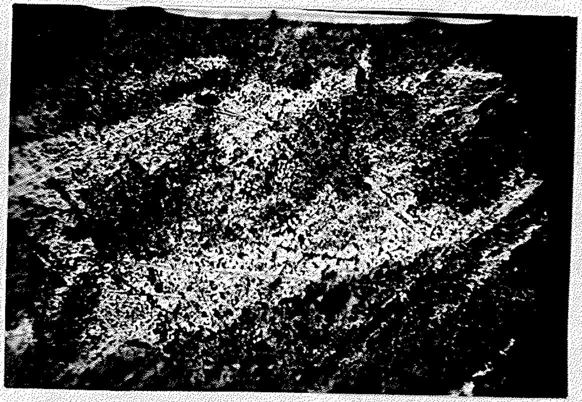


Plate 30. Alloy 21, X 135.
The β-phase together with
α-1 (γ-2) which is
light in appearance.

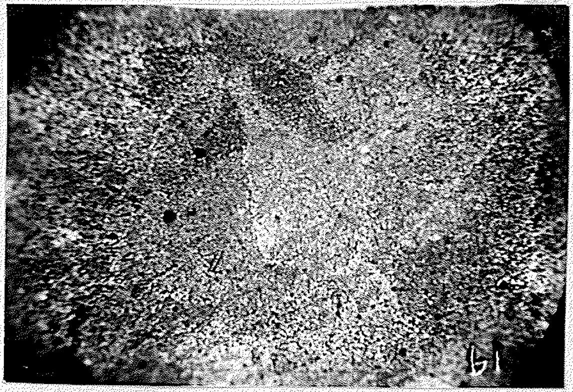


Plate 31. Alloy 19, X 135. Grain boundaries just visible in the β -phase extending across the ternary isotherm.

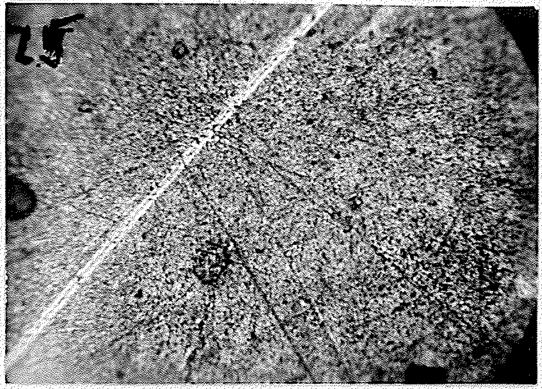


Plate 32. Alloy 25, X 135. Indefinite appearance of β -phase, similar to alloy 11, before solid diffusion, plate 22.

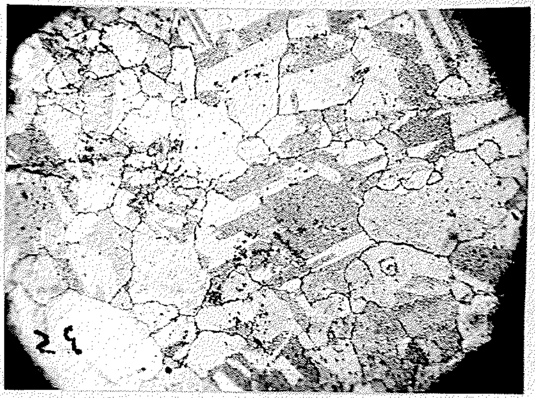


Plate 33. Alloy 25, X 250. Repolished and reetched after 1 month at room temperature; grains of β with bands very like twinning bands.

Plate 34. Alloy 25, X 1000. Upper center of plate 33, indicating that the dark spots are particles of β showing the pitted features met before for this phase.

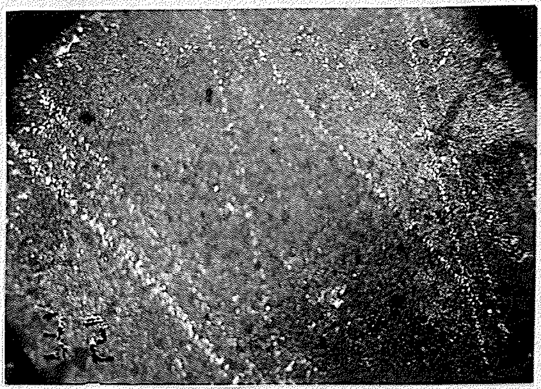


Plate 35. Alloy 35, X 135. β -phase with no grain boundaries; long white streaks are scratches.

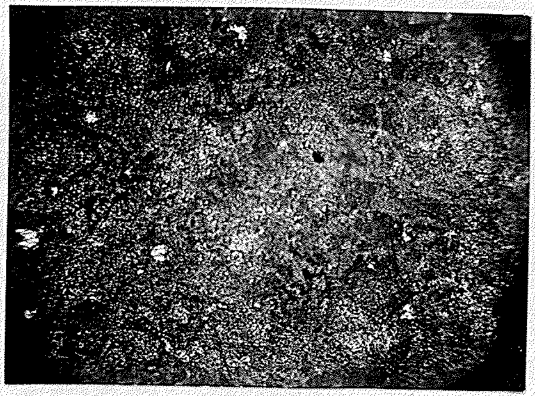


Plate 36. Alloy 35, X 135. β with a possible minute amount of α -2. The dendritic growth of β can be noticed.

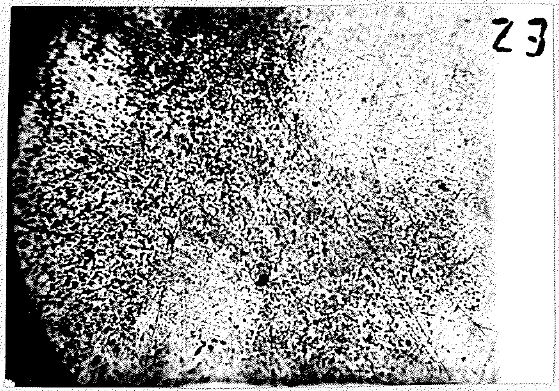


Plate 37. Alloy 23, X 135. β with light areas of α -2.

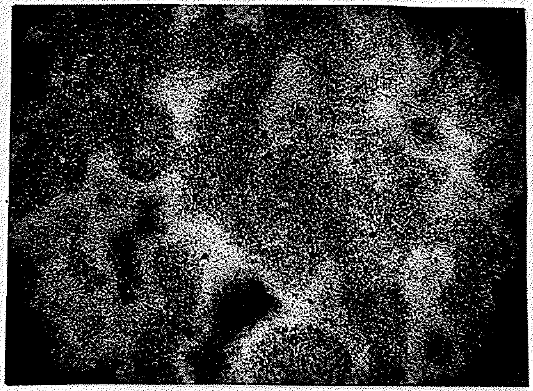


Plate 38. Alloy 23, X 135. Repolished and reetched after 1 month at room temperature; slightly overexposed, showing β and α -2.

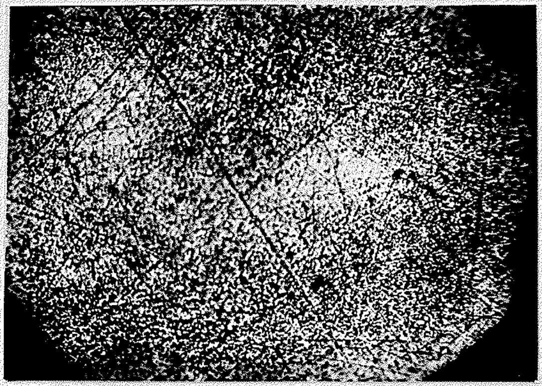


Plate 39. Alloy 28, X 135.
The β-phase with α-2 as light spots in two regions.

Plate 40. Alloy 22, X 135.
The β-phase with α-2 occurring as the light band across the photomicrograph.

Plate 41. Alloy 24, X 135.
α-2 now the dominant phase together with dark spots of β.

Plate 42. Alloy 30, X 250.
The dendritic growth of β is here well marked, α-2 and γ-1 are also present (light areas) as proved by X-ray photo.

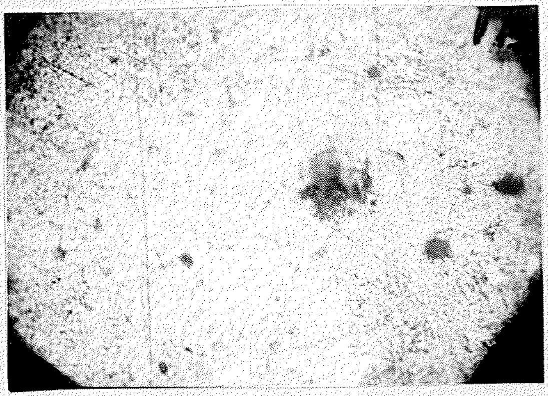


Plate 43. Alloy 31, X 250.
α-2 (very light) with
γ-1 (light grey) and a
little β.

Plate 44. Alloy 36, X 250.
α-2 and γ-1 (grayish)
as little nodules.

Plate 45. Alloy 36, X 250.
α-2 with γ-1 (grayish)
and a cluster of β; some
δ-1.

Plate 46. Alloy 32, X 250.
A region of the alloy where
α-2 is present with
eutectic of α-2 and δ-1;
now breaking up with the
disappearance of δ-1 and
appearance of γ-1.

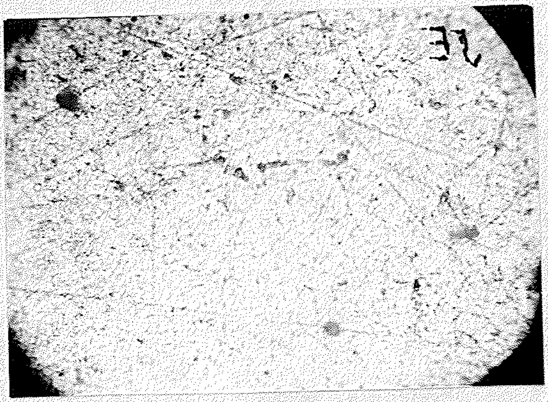


Plate 47. Alloy 32, X 250. The eutectic now broken up into α-2 and γ-1.

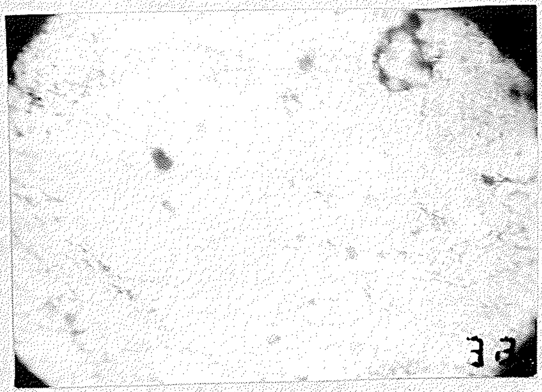


Plate 48. Alloy 33, X 250. Again, α-2 and γ-1 present together.

Plate 49. Alloy 39, X 250. As cast; α-2 (light) in a eutectic matrix of δ-1 and α-2. Note difference (re plate 27) in appearance of lead crystals when indium is present.

Plate 50. Alloy 34, X 250. α-2 (light) with δ-1 and very little γ-1; slightly underexposed.

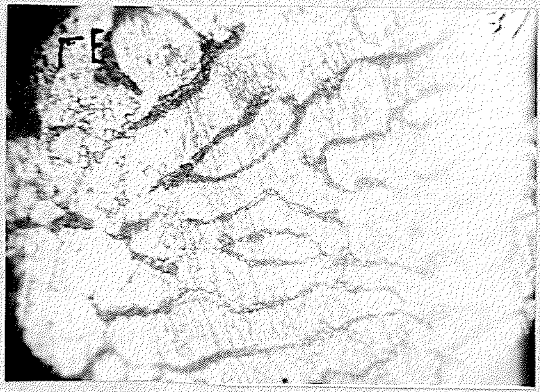


Plate 51. Alloy 37, X 250. α-2, δ-1, and γ-1 present; shows difference in appearance among the three phases: α-2 (lightest) and δ-1 (darkest).

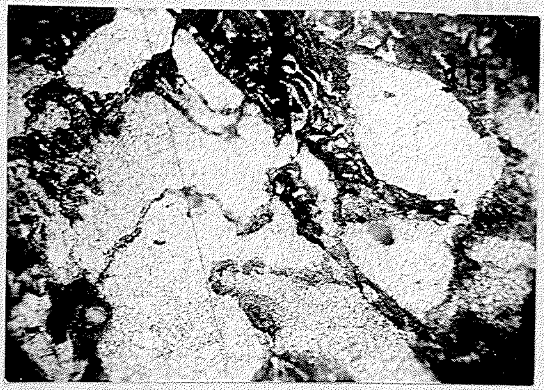


Plate 52. Alloy 38, X 250. α-2, β, and γ-1; some undecomposed δ-1 is probably present, although not indicated by X-rays.

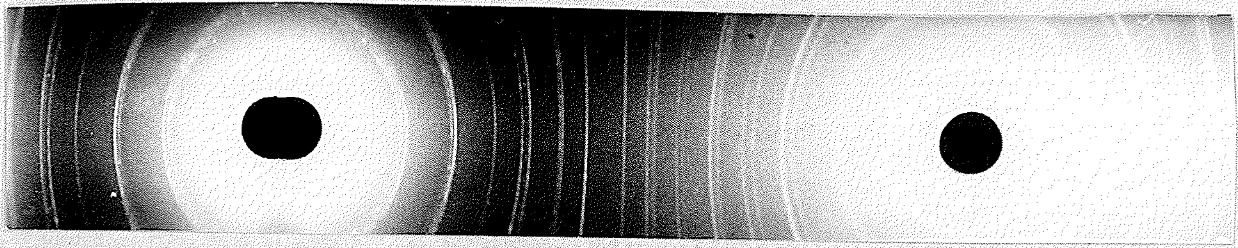


Plate 53. Alloy 1a - δ-1 phase with body-centered tetragonal lattice of tin.

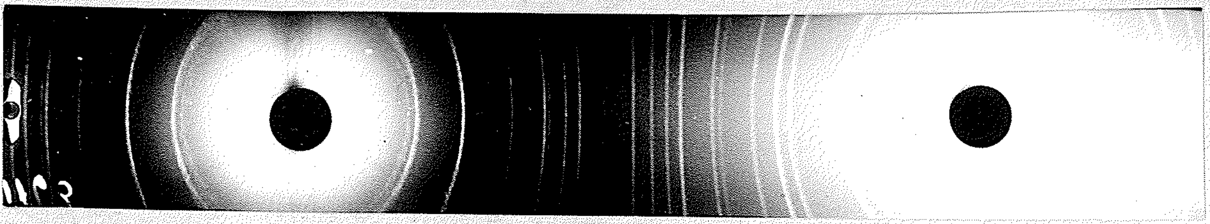


Plate 54. Alloy 4 - γ-1 phase with simple hexagonal lattice.

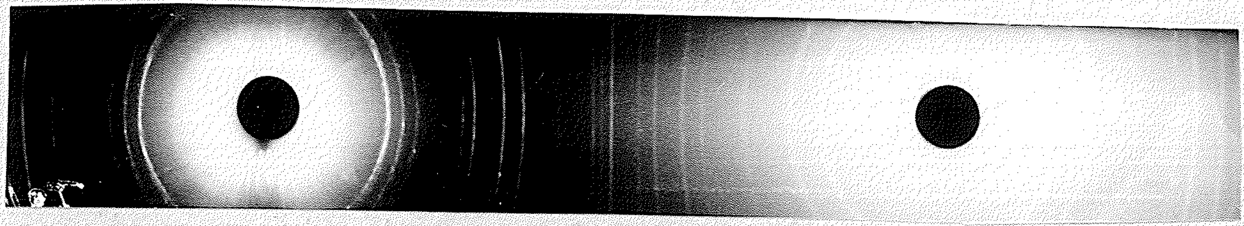


Plate 55. Alloy 5 - β-1 phase with proposed face-centered tetragonal lattice.

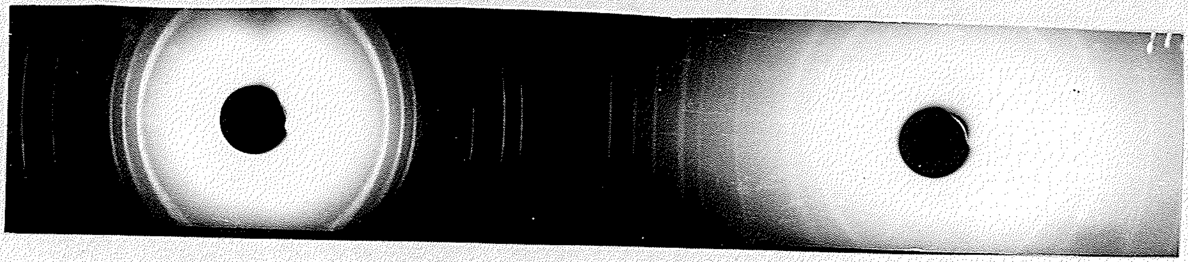


Plate 56. Alloy 11 - β-2 phase also with face-centered tetragonal lattice.

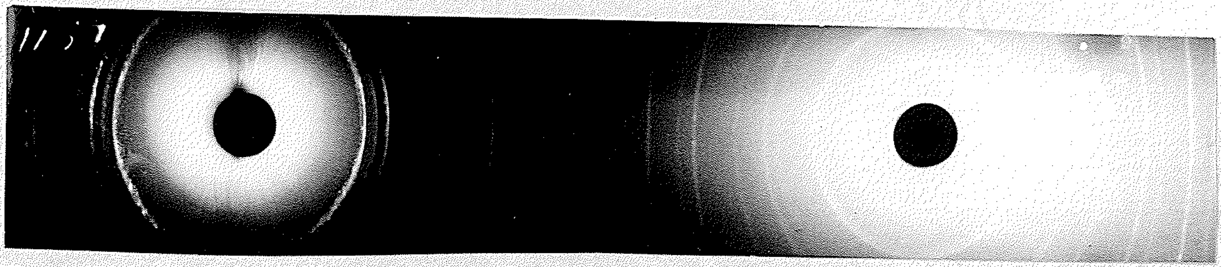


Plate 57. Alloy 9 - γ-2 phase with face-centered tetragonal lattice of indium.

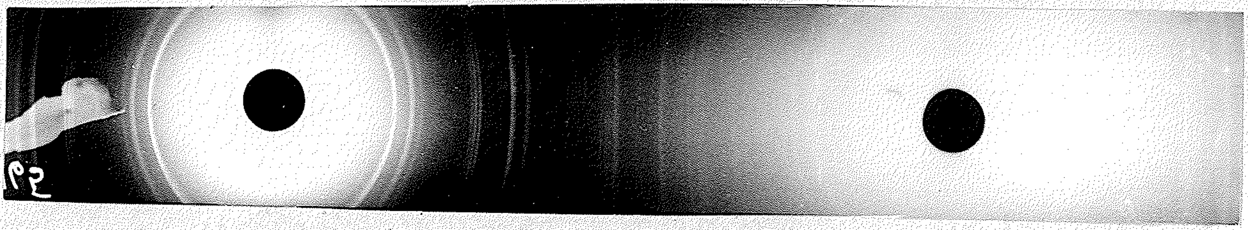


Plate 58. Alloy 12 - Showing lines for β-2 phase together with the strongest α-2 lines.

Plate 59. Alloy 13 - α-2 phase with face-centered cubic lattice of lead.

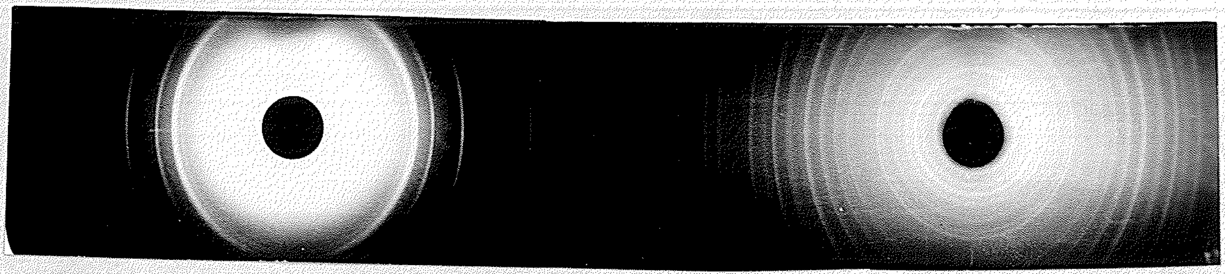


Plate 60. Alloy 37 - Showing lines for α-2, γ-1, and δ-1 lattices.

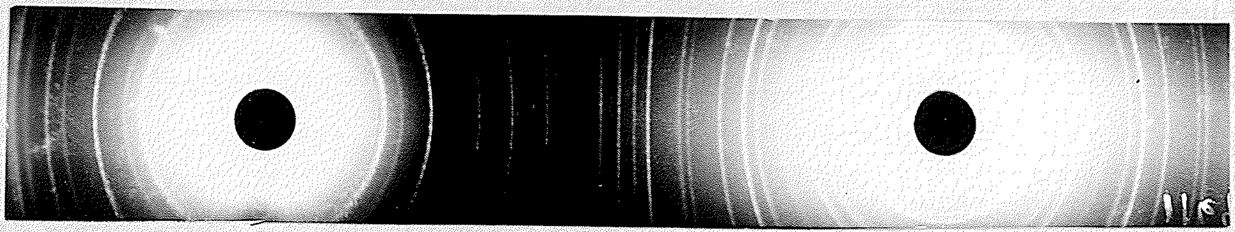


Plate 61. Alloy 15 - Showing lines for α-2 and γ-1 lattices.

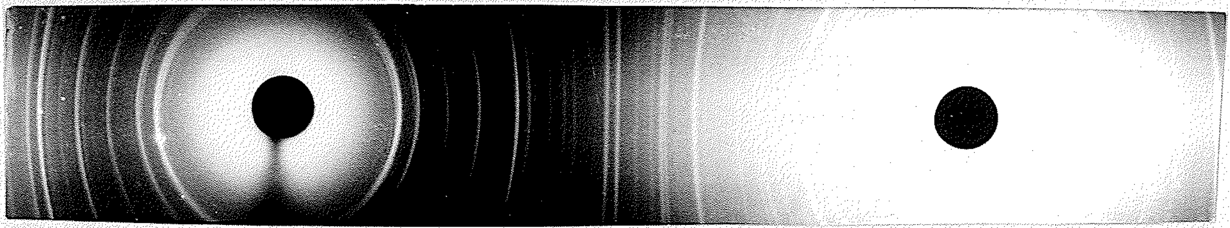


Plate 62. Alloy 39 - Showing lines for α-2 and δ-1 lattices in the cast alloy.

b. Interpretation of Photomicrographs and X-ray Patterns.

The photomicrographs and X-ray photos are arranged, not in order of alloy number, but so as to be conducive to a fairly systematic discussion of the room temperature isotherm.

Plates 11-27 are photomicrographs, as indicated in the captions, of the various binary alloys. The first one shows the furcated grain boundaries in pure tin, a result of the abutting of the differently oriented crystals at final solidification. The grain marked with a cross seems to be on a (001) crystallographic plane and is fairly well developed except for the corners (plate 53 is a powder photograph of the corresponding lattice). The next two plates (H_2SO_4 etch) show the γ-1 crystallites growing at the boundaries of δ-1 grains. They are small, in accordance with the fact that they grew in the solid phase (below 80°C.). Plate 14, where the normal etch was employed, shows the difference in etching characteristics between these two phases, the γ-1 being light, i.e., not attacked to the same extent as the δ-phase. The following plate shows the grain boundaries in γ-1 phase (the dark spots are probably spurious effects arising from polishing). That the γ-phase is the one actually present is proved by the powder photo (plate 56) of this sample, identical to the one obtained by Ferguson and Screaton (14), and showing the lines for the simple hexagonal lattice of γ-1.

Plate 16 illustrates the difference in etching properties of the β-1 phase (dark grey to black) and the γ-1 phase. The powder photograph indicated only the presence of γ-1; the β has to be present in large amounts (over 20%, as deduced from the composition of alloy 3) before it becomes detectable by X-rays. Furcular grain boundaries in the β-1 phase are evinced in plate 17 and were obtained by polishing in an electrolyte of equal parts of 70% $HClO_4$ and glacial acetic acid, the sample being made the anode with an aluminum plate serving as cathode (current density 0.3 amperes per cm.^{2}); followed by the usual etch. Note the pitted appearance of the surface. β-1 in a background of α-1 appears in the next plate, a photomicrograph of alloy 6.

Plate 19 exhibits the grain boundaries in the alloy of indium structure, face-centered tetragonal and host to lead atoms; plate 57 gives the powder photo. The following six plates demonstrate the microstructure of alloys 10, 11, and 12. The first exhibits a lineage structure, while the third and fifth do not present any evidence of grain boundaries or heterogeneity, respectively, although they should. The second of each pair, taken on repolishing and reetching after three months at room temperature, do unfold the required structures. Evidently solid diffusion has taken place. Plates 55 and 56 (X-ray photos) divulge the identical lattices of the two β-phases in alloys 5 and 11. No heterogeneity could be detected in alloy 10 by X-rays (β-phase recalcitrant in this respect) but plate 58 does show the strongest lines for the lead lattice present in some amount in alloy 12. Neither Klemm et al (20) nor Davis (27) could detect any heterogeneous areas in this binary system, using X-ray and microscopic means, respectively.

Plate 26 displays the divaricating grain boundaries in alloy 13, a solid solution having the face-centered cubic lead lattice. Coring, as indicated by the black spots having a different composition from the rest of the alloy, took place. An X-ray powder pattern of this alloy is given in plate 59. Blackish crystals of the lead structure in a eutectic matrix of lead and tin reveal themselves in plate 27. The eutectic has a lamellar structure; the lead etching darkly in the absence of indium.

With this knowledge of the etching characteristics of the various phases of the binary system and of the corresponding X-ray photos, the other photomicrographs may readily be interpreted. Plates 28 and 29 present the second phase, of lead structure, in the predominent γ-1-phase of alloys 15 and 16: this is proved by the X-ray photo, plate 61, showing the lines for these two phases. Plate 30, of alloy 21, displays the β -phase in a background of α -1 (γ -2). The next plate shows the seminal grain boundaries in the β -phase of alloy 19 and the three after that, photomicrographs of alloy 25. The first of these three contrasts with the second where, again, solid diffusion has taken place at room temperature. Bands, very like twinning bands, are to be seen in the grains. If they are such, they arose from the cold-working due to polishing.

In the six subsequent plates the microstructure of alloys defining the phase boundary between the one and two-phase regions, as seen on the isotherm, are exhibited. Plate 41 is of alloy 24 in the two-phase region. Their interpretation is obvious, when one notes that the α -2 phase, lead structure, etches very weakly (appearing light) in the presence of indium. This is so everywhere except in alloys 15 and 16. The X-ray photos substantiate this argument.

With alloy 30, plate 42, we enter the invariant triangle. The dendritic growth of the β -phase here manifests itself clearly, and explains the difficulty in distinguishing it from certain other phases in the binaries as found by Davis and Rhines. Such a growth can apparently produce interfluence between the phases. The γ -1 (gray) and α-2 (light) phases are also present, corroborated by the X-ray photo. Alloy 31, plate 43, happened to fall on the phase boundary; no β is present, only γ -1 and α -2. This trouvaille saved considerable labor. Alloy 36, which was given a better heat treatment than the others (24 hours at 180°, 20 hours at 70°) has still a little γ-1 and small amounts of β-1 present, as indicated by plates 44 and 45.

As we leave the invariant triangle and enter the adjacent two-phase region where γ-1 and α-2 are stable, the microstructures take on the appearance of plates 46-48. Plate 46 depicts a region of alloy 32 in which the eutectic (δ-1 and α-2) is in the process of breaking up into α-2 and γ-1. The next plate demonstrates the completion of the process, and the one after that the same condition in alloy 33. The structure of a cast alloy in this region is portrayed in the next plate, alloy 39 (X-ray photo, plate 62, shows lines for α-2 and δ-1). Note that the lead phase appears light, delineated by the dark structure of the eutectic.

Alloy 34 falls into the three-phase region containing α-2, γ-1 and δ-1 as the stable, solid forms. From plate 50 we see that there is present α-2, δ-1 and some γ-1, but very little (X-ray photo did not show γ-1). Plate 51, limning alloy 37, differentiates nicely among the etching characteristics of the three phases present in this region; the lightest is α-2, the darkest δ-1. Plate 60, X-ray photo for alloy 37, has lines on it of all three phases. On plate 52, of alloy 38, there occur the three phases β-1 (black), γ-1 (light gray) and α-2 (light) with possibly some δ-1 still unconverted.

Some ternary alloys, viz., 18, 20, 26, 27, were not examined microscopically. Here X-ray photographs sufficed to place them in the correct regions.

c. Results of Hardness Tests.

In plate 63 there are plotted the hardness numbers, both DPH and Bhn, for the two indicated binaries. For the Pb-In system there is no indication of the formation of the intermediate phase, β-2. Instead, the curve would support the original idea of Kurnakow and Ruschin (21) of a complete series of solid solutions for this system. Better agreement is

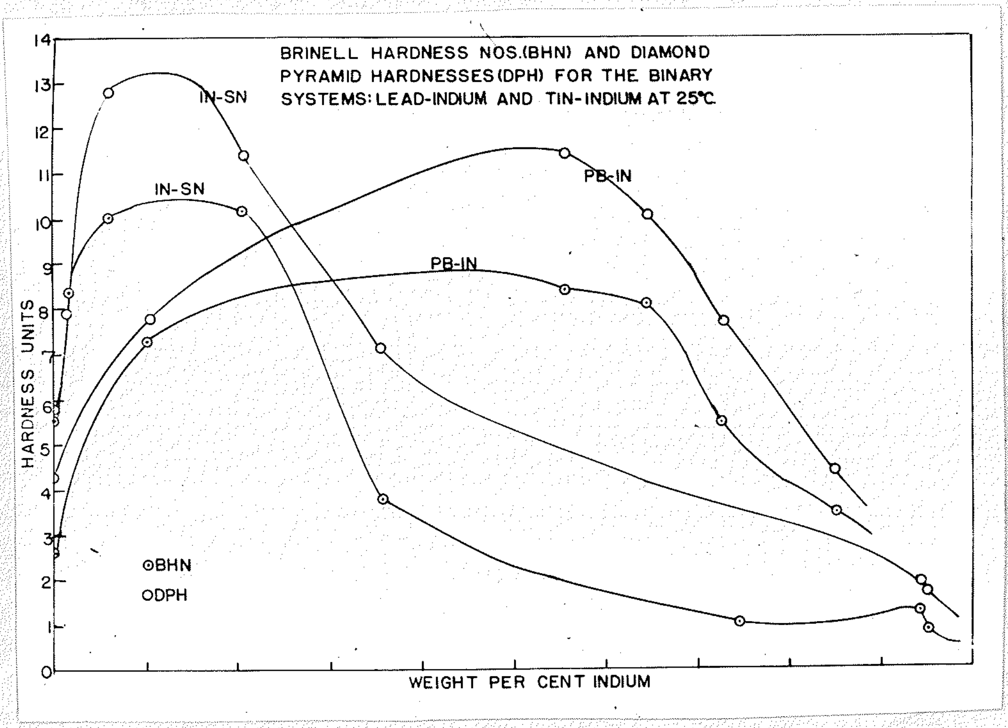
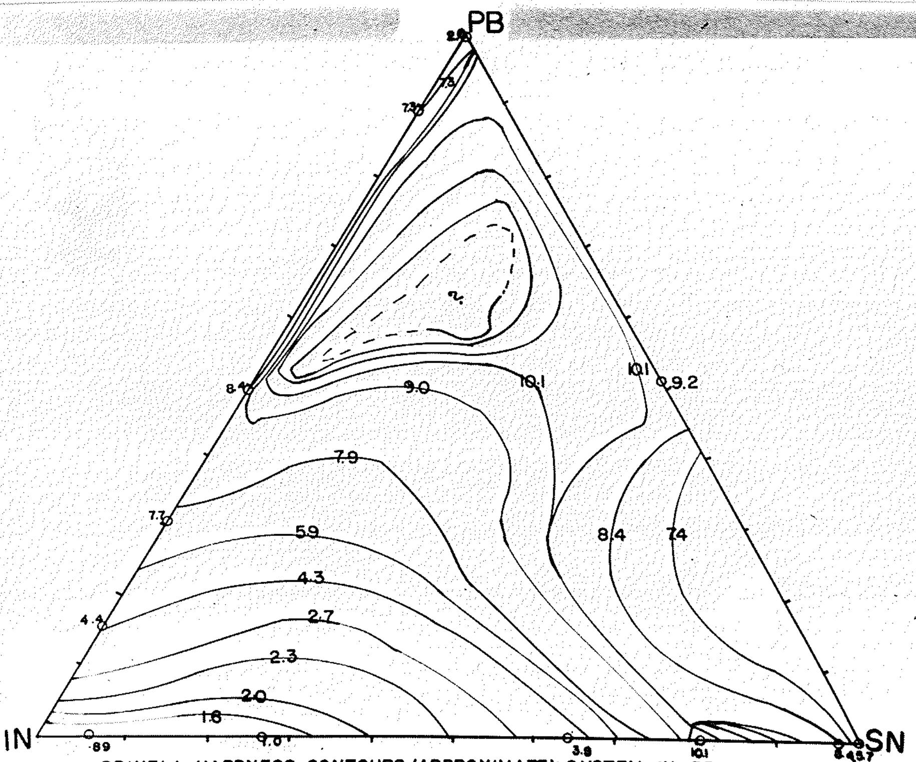


Plate 63.

apparent in plots for the In-Sn alloys. A maximum appears at the composition corresponding to the γ-1 phase; not so for the β-phase, which is softer than the alloys corresponding to the limit of solubility of In in Sn.

Finally, in plate 64, an indicative plot of hardness contours for the ternary system is given. No difficulty should be found in construing this graph; while, in doing so, it should be remembered that it was drawn up from limited data.

One might add, parenthetically, that all alloys containing appreciable amounts of γ-1 phase could not be dissolved in nitric acid or other acids without the aid of platinum strips.



BRINELL HARDNESS CONTOURS (APPROXIMATE): SYSTEM IN–PB–SN, 25°C.

Plate 64.

V. General Discussion.

a. Critical Points in Experimental Procedure.

The heat-treatment to which the alloys were subjected in this investigation was, as the photomicrographs verify, generally sufficient. Some criticism could be made in connection with alloy 38, but here the composition fell so close to the eutectic trough that almost the whole structure was, at one stage in the treatment, eutectic; and did not, perhaps reach practical equilibrium.

Further criticism of the samples used for X-ray analysis is anticipated, since filings were not employed. However, this was impossible in most alloys owing to their extreme softness. Moreover, W. Hume-Rothery calls attention to the fallacy of the assumption that filings have the same structure as the solid piece from which they derive. Suppose the original sample has a coarse-grained, two-phase structure. Fine filings from this might either be a particle of phase one, a particle of phase two or a duplex. Some alloys are so sensitive to transformation by cold-work that obviously filings do not represent the solid metal.

b. The Ternary Isotherm.

An examination of plate 10 shows that the boundary line most accurately determined is the one separating the β -phase from the two-phase region containing the α -2 and β phases; apart from the boundaries of three-phase regions where accuracy is easily obtained, boundaries being straight lines. The two lines defining the coexistence of α-1 (γ-2) and β could vary within obvious limits, although one sees from plate 30 that the longer of these is in all probability fairly accurate (±1%). It will be noticed that no definitive points occur for the α-2 region. Since the lead lattice will not play host to more than about 1½ wt. per cent of tin atoms at room temperature (less, according to Stockdale), there is no reason why it should do so in the presence of indium. At any rate, alloy 36, thoroughly heat-treated, contains appreciable amounts of γ-1; this would be impossible if the boundary of α-2 fell within one or two per cent of this point. Small changes in the construction will no doubt be made in the future.

Screaton and Ferguson (14) do not agree on the structure of β-1 with Valentiner who proposed a body-centered tetragonal lattice with 2 atoms per unit cell. They proved by consideration of the intensities of the lines of the powder pattern that Valentiner's structure is impossible, but did not establish the actual structure. It is suggested by Ferguson that it probably is a rhombohedral structure.

c. Solid Diffusion in Alloys 10, 11, 12, and 25.

As already noted, heterogeneous solids had not been obtained by previous workers in the Pb-In system at room temperature. True, plate 58 shows only the strongest lead lines; nevertheless, that is sufficient evidence for heterogeneity in alloy 12 substantiated by the photomicrograph. Alloy 10 also is indisputably heterogeneous, as proved by plate 21 (notice the similarity between plates 21 and 18).

What etching reagent was used by Davis and Rowe is not known. As both γ-2 and β-2 have face-centered tetragonal lattices they would be hard to distinguish. The acetic acid present in the etching reagent used by us was probably the differentiating factor (it tends to remove tarnished films).

Of interest is the solid diffusion that evidently took place in these alloys at room temperature, in which the dendritic structure (see plate 42) changed to a more compatible one. The migration of atoms through a solid metallic lattice is known as diffusion. Studies in this region by quenching techniques are thereby called into doubt.

The question of why the solid diffusion took place so easily in these alloys contrary to usual experience, is hard to answer with certainty. Fick's formula for diffusion, given in any book on colloids (46), immediately comes to mind but offers no obvious explanation. Now, the lattice points in a crystalline substance must be regarded as centers of oscillation of the atoms themselves, the amplitude of the oscillations depending on the temperature. The possibility of an actual interchange of atoms on the lattice points thus arises and presents a mechanism by which diffusion can take place. In our case we had first a solid solution formed, after which phase separation took place by diffusion (Kurnakow and Kuschin announced that indium and lead form a continuous series of solid solutions). This phase separation must have taken place by participation of the extraneous atoms in the normal interchange of atoms at the lattice points.

Kineticists would now bring in the idea of a potential barrier and this is precisely what Langmuir does (22). He assumes that an atom must possess a minimum energy E before it can surmount the normal potential barriers of the lattice and participate in the interchange, and derived the following formula:

$$D = \frac{Q}{Nh} \cdot d^2 \cdot e^{-Q/RT},$$

where D is the diffusion coefficient for a given metal, R is the gas constant, Q is the activation heat of diffusion, N is Avogadro's number, h is Planck's constant and d is the interatomic distance. If this value for D is substituted into Fick's formula one obtains

$$dS = \frac{Q}{Nh} \cdot d^2 \cdot e^{-Q/RT} \cdot q \cdot \frac{dc}{dx} \cdot dt$$

where dS is the quantity of substance that passes in time dt through cross section q under a concentration gradient dc/dx (appropriate units must be employed).

When we attempt to apply this formula to the case in point we arrive at an impasse - Q is not known and an approximate value cannot be guessed readily. But we can say qualitatively that d is relatively much larger in these alloys than in those of other alloys (section II), that hence q is also larger and thus we can presumably account for the appreciable diffusion at room temperature.

From the equation it is obvious that as T increases the rate of diffusion also increases, an expected result in terms of increased amplitude of oscillation at increased temperature. Since these alloys melt at relatively low temperatures, the oscillations at room temperature are probably relatively large and thus facilitate diffusion. As seen above, this is not the only reason.

Polishing, if it distorted the metal at all would, by this distortion, raise the internal energy of the alloy and thereby contribute to Q or rather disrupt or lower the potential barrier, promoting diffusion. Possibly this was more important in the alloys under consideration than is suspected by us. In 1953, Eyring (13) developed the absolute rate theory for phase changes in solids which take place by diffusion. Its pertinence or rather extension to the problem in hand, was not clear.

In connection with the cold work produced by polishing, mention of the "amorphous-cement" theory of Ewen and Rosenhain (31) is requisite. According to them polishing produces an amorphous layer of metal on the surface of the metal. X-ray diffraction experiments have not borne them out. The theory postulates, moreover, that films of atoms in the amorphous state are left between each of the grains of an alloy after solidification is complete. These atoms are attracted equally by the two neighbouring lattices and therefore join neither of them. Like glass, this film is assumed to be hard at room temperature. It would be in a higher state of energy than the lattice atoms and hence would be readily attacked by an etching reagent (see plate 11). The postulated presence of considerable quantities of amorphous metal at a temperature so far below the melting point is difficult to accept. The theory has had a tempestuous life but seems to be in desuetude. The present trend is apparently towards the concept that the atoms at the grain boundaries may serve in more than one lattice (35) and are thus in a state of nonequilibrium or higher energy than the normally placed atoms. Attack by an etching reagent could be initiated at these points.

d. Heat Evolution in Pb-Sn System.

The heat evolution occurring on cooling in the Pb-Sn system at about 149°C. and, according to Rosenhain and Tucker (32), caused by the allotropic transformation of one form of solid solution of lead in tin to another form, has not been satisfactorily explained as yet. Various other proposals have not been accepted.

One which has not been put forward, and which seems quite reasonable, is that of superlattice formation. In an ordinary solid solution the different species of atoms are arranged at random on the atomic positions of the lattice. Sometimes, however, solid solutions that have a random distribution of atoms at high temperatures undergo an atomic rearrangement, at lower temperatures, and the foreign atoms (in this case lead) take up definite and periodic positions in the host lattice (tin). This periodic structure, or superlattice (Überstruktur), forms below a certain critical temperature with the evolution of heat. Energy must be supplied to interchange atoms from right to wrong positions; for the ordered state is one of lowest energy. Rather than regard these superlattices as definite compounds it is more correct to think of them as involving an atomic rearrangement that enables the atoms to fit together with a lower energy content and hence a greater stability (12). Such a formation could take place in the Pb-Sn system and would be more likely than compound formation, certainly easily detected by the usual methods.

A review of the literature concerning this system verifies the suspicion that no X-ray investigation of this system has been done. Such a study, systematic, using preferably a high-temperature camera would probably bring new facts to light.

Shockley (36, 37) gives a review of the theories concerning superlattice formation and presents one of his own. Specifically, his theory predicts a phase diagram for the Au-Cu system in which the ordered tetragonal phase, the ordered cubic phase, and the disordered solid solution are separated by two-phase regions. Both ordered structures have a maximum critical temperature at 50 at. %, and there is symmetry around this composition. Actually no such symmetry occurs in the Au-Cu system. Now, it is most interesting to see that tin has a tetragonal lattice, lead a cubic one and perhaps Shockley's theory could be applied. The mathematical technique is, however, quite involved.

e. Hardnesses and Corrosion of γ -1 phase.

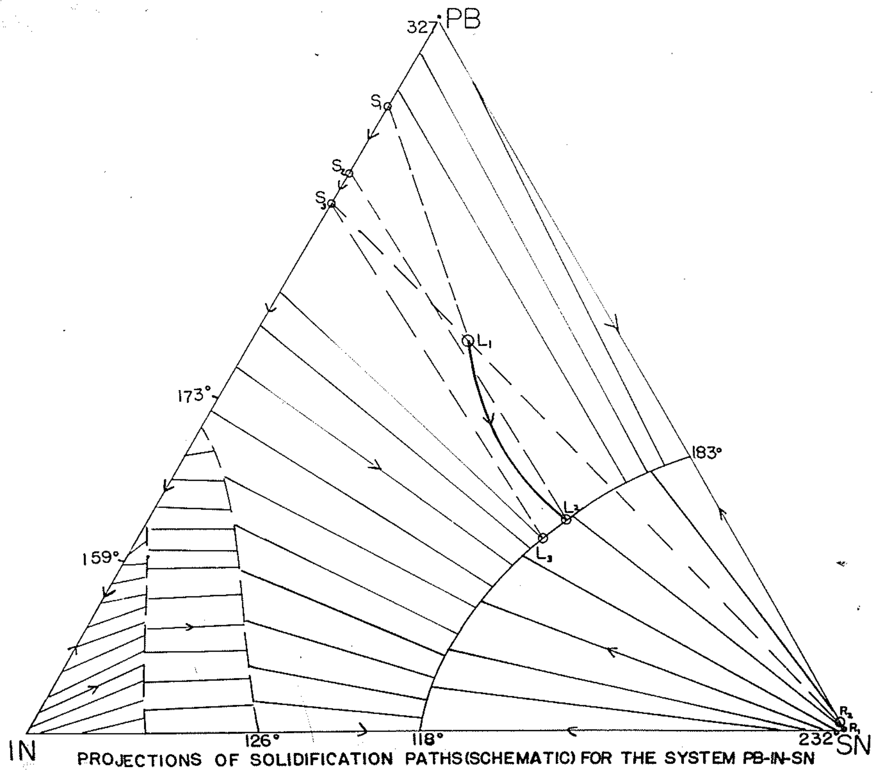
Plate 63 indicates, as mentioned, that a complete series of solid solutions occurs in the Pb-In system. It is quite likely, on further reflection, that not enough points had been determined. The nature of the effect of the solute atoms upon the hardness of a solid solution resolves itself into the effect of the solute atoms upon the solvent lattice and the nature of the lattice forces operative, owing to the interaction of different atomic species. One would expect that at 50 atomic % of each metal the lattice distortion would be a maximum and the consequent distorted periodicity of lattice forces would be least favorable for deformation. Since in alloy series (In-Sn, In-Pb) not exhibiting complete miscibility, solid solubility is limited by the capacity of the solvent lattice to undergo distortion in accomodating solute atoms, the solubility limit corresponds to the maximum distortion of which that lattice is capable. From the graph on plate 63 we note just this for the In-Sn system at both concentration ends.

For stable intermetallic phases in an alloy series the rule is that the intermetallic phase is usually harder than either of the combining elements. Again, we see this in the plot for In-Sn, where the peak on the curve lies in the γ -1 region. β -1 is softer than pure tin and just slightly harder than pure indium. In general, an intermetallic phase has some composition, within the boundaries of its stable existence, corresponding to a definite chemical formula. Such compounds, according to Hume-Rothery, correspond to definite valence electron-atom ratios and one can hence attribute much of their hardness to their tendency to form homopolar bonds. That this idea is indirectly supported by the present results can be seen as follows. The γ -1 phase, of simple hexagonal structure, is almost twice as hard as the body-centered tetragonal lattice of pure tin. Since the hexagonal lattice would have more planes for deformation slippage than the tetragonal some other forces must there be operative, e.g., homopolar bonding.

As noted above, alloys containing the γ-1 phase could not be dissolved completely in acids unless platinum was called to aid, causing galvanic action. It is possible that a layer of oxide (SnO_2 in case of HNO_3) was formed on the metal surface and this film was then impervious to the further ingress of reagent into the alloy. Resistance to solution may be due to passivity of the alloy, however produced, but passive metals dissolve in dilute acids, while the ones in point did not (within a few days). At any rate this property of the alloys containing γ-1 could be of interest to people concerned with corrosion. Admittedly, atmospheric corrosion differs from corrosion by acids.

f. Solidification Processes in the Ternary System.

An indicative solidification diagram wasconstructed for the ternary system and appears in plate 65. It is the result of a careful perusal of the liquidus contours in relation to the three binaries. Ends of lines in the plot intersecting the outer edges denote the primary phase. In the region of high indium content, the dashed lines indicate the defining boundaries of the β-phase at room temperature. The primary phase is γ-2 (α-1) followed by β at roughly the second dashed line, while the liquid composition continues on toward the eutectic trough. To the right of the



PROJECTIONS OF SOLIDIFICATION PATHS(SCHEMATIC) FOR THE SYSTEM PB-IN-SN

Plate 65.

eutectic trough δ-1 (β -3) constitutes the primary phase, and in the predominant region α -2 precipitates first.

Since the primary phases are solid solutions the path followed by the liquid during the crystallization of the pure phase is not really a straight line as shown, which it would be if only a pure solid crystallized (5). One illustrative case will be considered. As the melt L_1 on plate 65 cools, solid α-2 will first appear when the temperature is lowered to that of the point where the vertical dropped from L_1 in the solid model first strikes the surface for liquid saturated with solid solutions α-2. The solid will have some composition S_1. As the melt is further cooled L_1 will fall within the univariant region for liquids saturated with solid solution and, according to the generally altering direction of the tie-lines, the composition of the liquid will follow a curved path toward L_2 while the solid will follow S_1S_2 to S_2, L_2S_2 being the tie-line at the new temperature. At all times the line joining the two conjugate phases must pass through L_1, the total composition of the charge. At any instant during this stage all the solid phase must have a single composition on S_1S_2. When the liquid reaches L_2 solid δ-1 (β-3) of composition, say R_1, depending on the tie-line, begins to form for L_2 is on the eutectic trough. The liquid composition now follows the eutectic trough towards the binary eutectic at 118°C., depositing solid solution β-3 (δ-1) altering to R_2 and more solid solution α-2 of gradually altering composition towards S_3. By joining R_3, the limit of the solid solution of lead in tin at the temperature in question, to L_1 and producing the line to cut the outer edge of the ternary diagram at S_3 it becomes apparent that when L_1 is completely solidified to a mixture of β-3 and α-2, the composition of the latter can be no richer in pure lead than that represented by S_3. This must be the last solid solution to be formed, and the liquid L_3, on the tie-line L_3S_3, must be the last liquid. When the temperature is lowered further, other solid phases (e.g. γ-1) stable at lower temperatures, will make their appearance depending on where L_1 lies. Analogous processes take place anywhere in the ternary system. The composition of the last liquid depends on the original total composition.

SUMMARY

An investigation of the room temperature isotherm of the ternary system lead - tin - indium has been made, using X-ray and microscopic methods. This follows the investigation of the liquidus for this system by Campbell and Screaton (14) who find that no ternary eutectic exists and that, instead, a eutectic trough extends from the lead - tin eutectic to that of tin - indium. At room temperature the interesting result is that a one-phase regions extends across the ternary diagram from the β-phase (intermetallic) of the tin - indium system to the β-phase (intermetallic) of the lead - indium system. This supports strongly the opinion of Valentiner (41) that the two phases possess the same lattice, viz., face-centered tetragonal.

No heterogeneous areas in the solid phase of the lead - indium system have previously been detected by the above methods. The present study succeeds in doing this. Evidence for rapid solid diffusion in the solid state in a number of alloys is presented.

Hardness tests, Brinell Ball and Diamond Pyramid, have been carried out on all alloys examined, both binary and ternary. No abnormal values are found.

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