

THE ROOM TEMPERATURE ISOTHERM OF THE SYSTEM

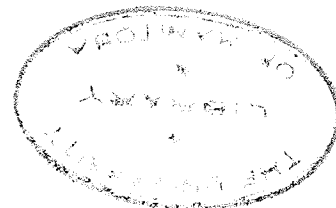
LEAD - INDIUM - TIN

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 Screamon (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 Screamon, 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.

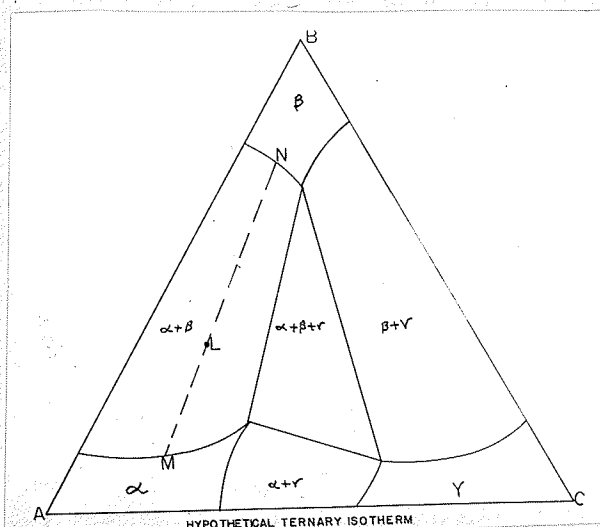


Plate 1.

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