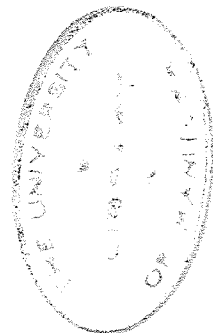


THE SYSTEMS ALUMINUM-LEAD-TIN  
AND  
ALUMINUM-TIN

by  
Robert Kartzmark

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TO MY SISTER.

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## ABSTRACT

A Phase Study of the Systems Al-Pb-Sn and Al-Sn

by: Robert Kartzmark

An isothermal method was used to investigate the Al-Pb-Sn system at 500 and 600°C, thermal analysis was used to determine the ternary eutectic temperature, and microscopic analysis to determine the phases present in the completely solidified alloy. The phase diagrams for the 500 and 600°C isotherms are continuous curves, which extend across the ternary diagram from the Al-Pb binary system to the Al-Sn binary system. The absence of two liquid phases is remarkable, in view of the work of Davies (30) and others at temperatures above 650°C. The ternary eutectic temperature for the Al-Pb-Sn system is 183.0°C and an eutectic composition of 0.08 weight per cent aluminum, 38.1 weight per cent lead, and 61.7 weight per cent tin. The solid phases present in this system at room temperature are primary aluminum,  $\alpha$  lead and  $\beta$  tin. Brinell ball and Vickers Diamond Pyramid hardness tests show that the ternary eutectic alloy is the hardest of this system. When the alloys are used as solder the Al-Pb-Sn eutectic composition has the greatest shear strength.

An isothermal method was used to determine the solubility of aluminum in tin between 400 and 645°C.

## CONTENTS

	Page
<u>INTRODUCTION</u> .....	1
 <u>METHODS AND TECHNIQUES</u>	
Isothermal analysis.....	2
Thermal Analysis.....	5
Microscopic Analysis.....	7
 <u>PREVIOUS INVESTIGATIONS</u>	
The Three Metals.....	11
The System Al-Pb.....	12
The System Pb-Sn.....	15
The System Al-Sn.....	20
The System Al-Pb-Sn.....	22
 <u>CONSIDERATION OF THE PROBLEM</u> .....	 25
 <u>EXPERIMENTAL</u>	
Purity of Materials.....	27
Methods of Chemical Analyses.....	28
Isothermal Analysis.....	30
Procedure.....	39
Thermal Analysis.....	41
Microscopic Analysis.....	43
Hardness Tests and Tensile Strength.....	45
 <u>Experimental Results</u> .....	 48
 <u>General Discussion</u> .....	 61
 <u>SUMMARY</u> .....	 67
 <u>BIBLIOGRAPHY</u> .....	 68

LIST OF TABLES AND PLATES

	Page
TABLE I	Composition of the Liquidus in the 500°C Isotherm of the System Al-Pb-Sn... 49
TABLE II	Composition of the Liquidus in the 600°C isotherm of the System Al-Pb-Sn..... 49
TABLE III	Solubility of Aluminum in Tin Between 400 and 645°C..... 50
TABLE IV	Comparison of the composition and Temper- ature in the Binary System Pb-Sn and the Ternary System Al-Pb-Sn..... 50
TABLE V	Some Mechanical Properties of the Pure Metals and Certain Alloys of the System Al-Pb-Sn..... 51
PLATES	
1.	Phase Diagram for Al-Pb..... 15
2.	Phase Diagram for Pb-Sn..... 19
3.	Phase Diagram for Al-Sn..... 21
4.	Phase Diagram for Al-Pb-Sn..... 24
5.	Temperature Control Circuit..... 32
6.	Photo Control..... 34
7.	Phase Diagram for Al-Pb-Sn at 500°C..... 53
8.	Phase Diagram for Al-Pb-Sn at 600°C..... 53
9.	Phase Diagram for Al-Sn Between 400 and 645°C..... 54
10-15	Photomicrographs of Alloys..... 56-58
16.	A Comparison of the Al-Sn Phase Diagrams 63a
17.	The 600 and 650°C Isotherms for Al-Pb-Sn 63a
18.	Temperature-Composition Diagram for Al-Pb- Sn. 66

## INTRODUCTION

The present investigation was undertaken to determine by isothermal sections, the liquidus surface of the Al-Pb-Sn system, and the composition and some metallurgical properties of the completely solidified alloy at room temperature. The determination of the equilibrium diagram gave results that were not in agreement with published data for the Al-Sn system; it was therefore decided that a part of the Al-Sn equilibrium diagram should be investigated.

The phase diagrams obtained show the regions of stable existence of the various phases when the variables (temperature and composition) are altered.

In this investigation the methods of isothermal and thermal analysis were used. Photomicrography was used to study the structure of the completely solidified alloy and the usual mechanical tests were applied.

## METHODS AND TECHNIQUES

The object of the investigation of a system of alloys, such as is undertaken here, is the construction of the phase equilibrium diagram, which is a graphical representation of the dependence of the number and nature of the phases present on the composition and temperature. The pressure is not a variable since the system is open to the constant pressure of the atmosphere, and, in any case, the influence of pressure is negligible in the neighborhood of one atmosphere.

Of the methods used to determine phase diagrams the most outstanding are isothermal analysis, thermal analysis, microscopic analysis, and X-ray diffraction. Some of the methods of lesser importance are the determination of the electrical conductivity, the magnetic susceptibility, and the electrode potential. Generally, the first four methods are used in conjunction, the latter group being subsidiary aids. Isothermal analysis, thermal analysis, and microscopic analysis were used in this investigation and a brief discussion of these will be given.

### Isothermal Analysis

Isothermal analysis is the method most commonly used for an investigation of systems consisting of salts in water but not many workers have used this method to study alloy systems. There is theoretically no difference between a



freezing point curve and a solubility curve, therefore it should be possible to define the liquidus equilibrium curves of alloys by this method.

To determine the solubility curve, an alloy is prepared which has an excess of the solid phase present, the temperature is held constant until equilibrium is attained then a sample of the liquid is withdrawn and analyzed. The temperature is then altered and the process repeated. The solubility curve is obtained when the results are plotted as a function of the temperature. The difficulty lies in separating and determining the nature of the solid phase. If the solid phase is lighter or heavier than the liquid gravitational separation is possible but the nature of the solid phase must be determined by other means. When, however, the nature of the solid phase is known this method may be advantageously applied to determine the exact nature of the liquidus.

The isothermal method is also used to determine the composition of two congruent liquid layers. The composition of the original melt is made such that the two liquid layers will be present in nearly equal volumes at the temperature of investigation. When equilibrium between the two liquid layers is reached the top and bottom layers are sampled and analyzed. In a two component system the compositions of the two layers are constant at constant temperature; therefore only one determination is necessary. The temperature is then

altered and the process is repeated. The results show the variation in mutual solubility with temperature. For a system of three components which forms two congruent liquid layers the temperature is fixed and the composition altered. These results show in effect the increase in the mutual solubility of two partially miscible components by the addition of a third component.

To study alloys by the isothermal method it is important to obtain a solidified sample of the liquidus having the true composition, i.e., the composition must not alter during cooling. The solid samples may be obtained by one of two methods. In the first method the whole alloy is quenched by plunging into a cold bath such as a salt-ice-water mixture. Then samples are removed from the solid alloy as required for analysis. The quenching process must be rapid to eliminate any changes which tend to occur in the sample on cooling. These might include the separation into two liquid layers, or the separation of one or more solid phases. It is obvious that the more rapid the quenching process, the more successful it is in its aim. In the second method samples are removed by direct pipetting from the melt, the molten alloy solidifying in the pipette, which must be broken for recovery of the sample. This method can be used for determining the solubility curve when there is solid in equilibrium with liquid or when the melt consists of two liquid layers. But a slight error is introduced in the sampling of the lower layer since a small amount of the upper layer enters the pipette as

it is passed through.

A variation in the isothermal method was introduced by Alexejeff (1). A series of samples varying only slightly in composition are brought into equilibrium at the same temperature and quenched. If the composition range includes a transition from two liquid layers to one, or from a solid in equilibrium with a liquid to homogeneous liquid, an examination of the quenched samples should show within small limits of concentration where this change occurs. Thus, by varying the temperature and repeating the procedure a liquidus or miscibility gap may be determined. The disadvantage of course is the large amount of effort required to obtain a single point, and poor accuracy, that is, heterogeneity cannot always be detected.

### Thermal Analysis

Thermal analysis is the oldest and perhaps the most powerful method of determining the diagram of thermal equilibrium, which shows what phases may be expected to be present in an alloy of a given composition under given conditions of cooling. The principle of this method is found in the fact that a change in phase is accompanied by a heat effect, either the absorption of heat on heating or liberation of heat on cooling. These heat effects produce 'breaks' in the cooling curves (temperature vs time plots) in such a manner that the temperature of the phase change may be estimated.

When a pure substance cools without a change in state and the temperature of the surroundings is constant then a plot of temperature of the substance against the time elapsed is an exponential curve in accordance with Newton's Law of Cooling. When the substance being cooled is a pure liquid it commences to freeze at a characteristic temperature. The separation of the solid from the molten mass liberates a certain quantity of heat. Any further loss of heat causes the separation of more solid phase and this process continues, the temperature remaining constant, until the whole mass has solidified, after which the temperature again falls in a regular manner. This heat effect produces a horizontal in the cooling curve and the temperature of the phase change is determined. When a molten alloy is allowed to cool in this manner any separation of solid manifests itself on the cooling curve as a discontinuity. There is a discontinuity or a horizontal whenever a phase disappears or a new phase appears. By plotting the temperatures of these breaks for alloys of different compositions, one is able to construct some of the lines in the equilibrium diagram, e.g., liquidus, solidus, peritectic, eutectic horizontal, etc.

Obviously the break in the cooling curve is more easily detected if the cooling curve is linear rather than exponential. Plato (2) suggested a method whereby the surroundings are cooled progressively and regularly to obtain a rectilinear curve rather than an exponential one.

A differential method of thermal analysis was introduced by Roberts-Austin (3) in 1899. In this method the difference in temperature between the alloy and the furnace is measured. Since the temperature of the furnace is not so easily measured as a body enclosed in it, a neutral body is placed in the furnace near the alloy under examination and under the same conditions of temperature. A neutral body is one which gives a perfectly regular cooling curve; it must not, therefore, undergo any phase transformations over the range to be investigated. It must have the same heat capacity as the alloy and be similar in shape and size in order that both will cool at the same rate. Two thermocouples are used, one placed in a hole drilled in the neutral body and the other is placed in the alloy. These thermocouples are connected so that their E.M.F.'s oppose each other through a galvanometer. The alloy and the neutral body cool at the same rate and the temperature difference is zero, or at least constant. When the alloy undergoes a phase transformation a difference in temperature develops, the E.M.F.'s are no longer equal and the galvanometer is deflected indicating a phase change is taking place. The thermocouple in the alloy is then connected to the potentiometer to determine the temperature of this phase change.

#### Microscopic Analysis

Microscopic analysis has long been used in conjunction with the method of thermal analysis to construct phase

equilibrium diagrams of alloys. This method consists of examining prepared surfaces of alloys which have been annealed and quenched.

Since metals remain opaque in the thinnest slices it is necessary to examine the prepared surfaces by means of reflected light; therefore a perfectly flat surface must be prepared. If the metal is soft the specimen is cut to the required size with a hack-saw, care being taken to prevent the alloy becoming heated. The specimen must be selected carefully to ensure that the micro-section is representative of the metal under examination. If there is any doubt as to the alloy being homogeneous, sections should be cut from both the outer and the inner portions. The surface is now made approximately flat by means of a file. It is usually mounted in plastic or wax moulds for convenience in polishing.

The surface is prepared in a state suitable for polishing by rubbing it on emery papers of increasing fineness. The polishing is carried out on a cloth-covered rotating wheel using magnesia or some similar powder for abrasive. Water is used to prevent heating. According to Beilby (4) polishing results in the formation of a thin layer of flowed metal, the irregularities of the scratched surface being partly rubbed away and partly filled up. The finished specimen should present a uniform mirror-like surface under the microscope.

At this stage the structure is latent and must be brought out in a suitable way. This usually consists in attacking the surface of the specimen by an etching reagent which acts preferentially on one or more of the constituents, or which acts along certain directions in a homogeneous metal. The etching of the specimen is not entirely independent of polishing. Even well-prepared surfaces can have a film of cold-worked metal over the surface which must be eliminated in order to reveal the true structure of the specimen. This film cannot always be removed by etching alone and a process of light polishing and etching is followed as long as the structure improves in appearance. Since the specimen is examined under reflected light it is evident that the areas of the surface that have not been attacked by the etchant will reflect the light readily and appear light in color; conversely, corroded areas will disperse the light and appear dark.

While awaiting examination the etched specimen may be stored in a dessicator or coated with a thin layer of varnish to form a transparent layer. If a permanent record of the microstructure is desired, the microscopical image is reproduced photographically.

A prior knowledge of the appearance of the different phases possible in any one system is desirable before the system is studied microscopically. However, by studying alloys of the same composition quenched from different annealing

temperatures, it is possible to recognize the constituents common to a given phase region. Thus a series of determinations may set, quite closely, the various phase boundaries.

A necessary precaution, especially if the work is not being done simultaneously by another method, is to ensure that no segregation has occurred during quenching, and that the quenched sample does truly represent the conditions of the annealing temperature and not those of some lower temperature due to a very rapid transition.