# THE SYSTEMS ALUMINUM-LEAD-TIN
# AND
# ALUMINUM-TIN

by

Robert Kartzmark

A Thesis Presented to the
Faculty of Graduate Study and Research,
University of Manitoba,
In Partial Fulfilment of the Requirements
For the Degree of Master of Science.

Winnipeg,
May, 1956.

TO MY SISTER.

# ACKNOWLEDGMENTS

In particular, I wish to express my sincere thanks to Professor A.N. Campbell for his constant advice and encouragement in this, my first venture into the field of research.

I am much obliged to Professor C.M. Hovey of the Department of Civil Engineering, who instructed and assisted me in the microscopic examination of alloys.

Mr. Gordon Trider and Mr. Jack Atkinson were most helpful in building and maintaining the equipment used.

I would also like to express my appreciation to the Consolidated Mining and Smelting Company Limited of Trail, B. C. for their Fellowship grant and for their extra grant for the purchase of equipment.

# 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

METHODS AND TECHNIQUES

PREVIOUS INVESTIGATIONS

EXPERIMENTAL

# LIST OF TABLES AND PLATES

PLATES

# 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.

## PREVIOUS INVESTIGATIONS

It is proposed to review the literature with the object of presenting all pertinent information related to the problem under study.

In this section a brief description of the pure metals will be given, followed by an account of the phase diagrams of the three binary systems and finally a complete discussion of all previous work on the ternary system, from their first appearance in the literature to the present.

### The Three Metals

The freezing point of aluminum is 660.1°C and the density at 20°C is 2.70 grams per cc. Aluminum crystallizes in a face-centered cubic lattice with a cell edge of 4.05Å.

Lead also crystallizes with a face-centered cubic lattice but with a larger cell, the edge length being 4.94Å. Lead has a density of 11.34 grams per cc at 20°C, the highest density of the three metals used in this system. The freezing point is 327.3°C.

The freezing point of tin, the lowest freezing metal in this ternary system, is 231.9°C. Tin exists in two allotropic forms: ''white tin'', with a body-centered tetragonal lattice with cell constant $a = 5.83A$ and $c = 3.182A$ undergoes a transition to ''gray tin'', with the diamond structure and a cube edge of 6.46Å, at 13.2°C. The densities at 20°C are 7.31 grams per cc and 5.75 grams per cc for ''white'' and ''gray'' tin respectively.

The postulated existence of a so-called rhombic, brittle or gamma tin which is sometimes mentioned in technical literature (Handbook of Chemistry and Physics) and texts (Moeller's ''Inorganic Chemistry'') has been definitely disproved (5). This modification was said to be the form stable between 161°C and the melting point. Careful investigations, based on Xray and physical properties, have failed to find any evidence for the existence of this modification. In 1931 Matuyama (6) investigated this alleged high temperature form. The tin used contained the following impurities: 0.01% zinc, 0.008% lead and a trace of cadmium. No breaks were found in the electrical resistance vs temperature curve, the differential dilatation-temperature curve, the differential thermal analysis curve and the thermoelectromotive force-temperature curve. Xray powder patterns taken at room temperature and at 220 to 223°C were identical. A small amount of cadmium was supposed to accelerate the transformation to gamma tin. Matuyama also found that Xray powder patterns of a 4% cadmium alloy taken at room temperature and at 152 to 163°C were identical.

## The System Al-Pb

Wright (7), who in 1890 was the first to study the liquidus region of these two metals, found that two liquid layers were formed. Analysis of these two layers, after they had been kept at a temperature between 750 and 850°C for about eight hours, showed that the aluminum-rich upper layer contained 1.91% lead and the lead-rich lower layer contained 0.07% aluminum.

Pecheux (8), about fourteen years later, claimed to have obtained three liquid layers for systems whose lead concentration was greater then 10%. He melted the metals together and after stirring poured them into a steel mould for quenching. Analysis of the middle layer gave from 3 - 10% lead. Alloys containing 2.5 and 7% lead were stated by him not to give two layers and their densities decreased with decreasing lead content. Their fusion points were near that of aluminum and rose as the amount of lead decreased. The existence of three layers was disproved by the results of later workers.

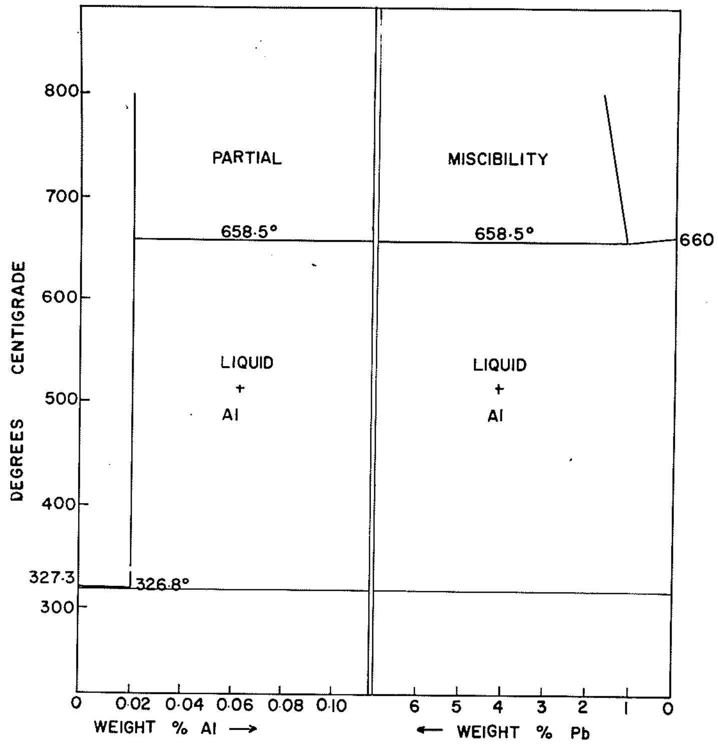
Gwyer (9) conducted a more systematic and thorough investigation which included a microscopic study of the solidified alloys. He found two halt points on the cooling curve, one at the freezing point of pure aluminum and the other at the freezing point of pure lead, corresponding to the formation of two almost completely insoluble liquid layers. He states that alloys with 1, 2, 3, and 5% lead showed primary crystals of aluminum surrounded by secondary lead. Two layers were found in the cold regulus in alloys containing from 5 - 99.5% lead; viz., a pure lead layer and an aluminum layer containing a small constant amount of lead detectable microscopically.

Hansen and Blumenthal (10), in 1931, started the most recent series of investigations of this sytem. They used the method of thermal analysis and reported a depression of 1.5° ± 0.5°C in the freezing point of aluminum produced in alloys with 3, 5, 7, and 24% lead. The aluminum used was 99.91% pure and was found to be practically insoluble in molten lead.

More recently Claus (11) has stated that aluminum and lead are slightly soluble in each other in the liquid state and also that as much as 5% lead is taken up by the aluminum in the form of colloidal suspension rather than true solution.

The work of Claus was followed by that due to L.W. Kempf and K.R. VanHorn (12) who investigated the solubility of lead in liquid aluminum, and determined it to be about 1.52% at the freezing point of aluminum; they found that it increased continuously with temperature to about 14.75% lead at 1038°C. The maximum depression in the freezing point of aluminum by the presence of lead was 1.5°C.

The most recent work was that carried out by A.N. Campbell and R.W. Ashley (13). The diagram shown in plate 1 is based on their results. They found that the system exhibits two invariant points; one is a eutectic at 326.8°C, corresponding to 0.021% alumimum; the other is the invariant point of the two liquid layers and solid aluminum which occurs at a temperature of 658.5°C and a composition of 98.8% aluminum. The mutual solubility of liquid lead and liquid aluminum is small below 800°. Like Claus, they, too, found that liquid aluminum can take up as much as 10% lead in the form of an emulsion which, however, was found to separate readily when the alloy was held at a fixed temperature for several hours. Aluminum and lead are mutually insoluble in the solid state but solid suspensions containing small amounts of lead were reported to be harder than pure aluminum.



SYSTEM ALUMINUM-LEAD. (Campbell and Ashley)

Plate 1.

## The System Pb-Sn

Since lead and tin are the major components of most common solders it is not surprising to find that this system has been the object of many investigations. The first systematic research on the lead-tin system was carried out by Roberts-Austen in 1897 (14). He reported the eutectic temperature as 180°C, corresponding to 69 weight per cent tin. From his examinations of the solidified alloys he concluded that lead and tin were completely insoluble in each other in the solid state.

The work of Roberts-Austen was followed by Rosenhain and Tucker (15). They obtained their results by the use of thermal analysis, differential thermal analysis, and microscopic analysis. They found the eutectic temperature to be the same as that of Roberts-Austen but they reported a eutectic composition of 62.93 weight per cent tin. They found that lead could dissolve up to 16 weight per cent tin at 182.5°C and 18 weight per cent at 149°C. An evolution of heat was reported at 149°C for alloys containing 18 - 63 weight per cent tin and at a slightly lower temperature for those containing 8 - 18 weight per cent tin. They attributed the heat effect to an allotropic transformation of an $\alpha$ solid solution to a $\beta$ solid solution. The $\beta$ form was thought to contain less tin and hence the heat effect was due to precipitation of that metal. Hence their equilibrium diagram contains a transition line at 149°C.

Degens in 1909 (16) published his work on this system which showed that lead and tin were completely miscible in the liquid state but only partially miscible in the solid state.

The eutectic temperature was reported as 181°C, and the eutectic composition as 36.7 weight per cent lead. The solid solubility of lead in tin extended to 0.37 weight per cent lead, and of tin in lead to 7.6 weight per cent tin at room temperature.

The thermal effect noted by Rosenhain and Tucker was observed by Degens to occur at 146°C. This thermal effect was of maximum duration at 57 weight per cent lead which corresponds to a composition of $Pb_4Sn_3$. In trying to determine the cause of the transformation Degens noted that on cooling large masses of tin a break in the cooling curve occured between 160 - 164°C. Pure tin also showed a decided volume change at 161°C, as shown by use of an air dilatometer. The presence of the change in Pb-Sn was also found dilatometrically to occur at 146°C. Degens claimed that the cause of the heat effect was compound formation. Thus the experimental results of Rosenhain and Tucker were to a large extent confirmed but the heat effect was attributed to a different cause.

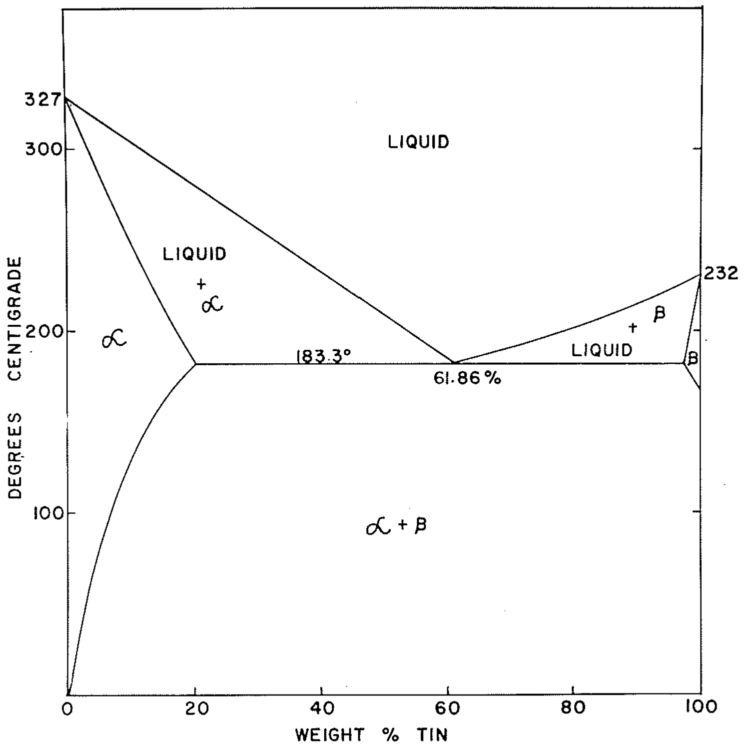
In 1920 Parravano and Scortecci (17) determined the solubility of tin in lead. Their results showed that the solubility decreased from 14.5 weight per cent at 175°C to 1.5 weight per cent at 25°C. They claimed that the heat effect was due to supersaturation resulting from metastability during cooling.

To ensure against supersaturation, Jeffery, in 1921 (18) cooled his alloys very slowly and obtained the phase diagram by electrical conductance measurements. The eutectic temperature occurred at 183 ± .3°C, at a composition of 66 weight per cent tin. The solid solubility of lead in tin was reported as 3 weight per cent at 183°C and of tin in lead to be 16.5 weight per cent at the same temperature.

To determine the phase diagram of an alloy by the electrical conductance method the change in resistance with temperature is measured. When the resistance is plotted as a function of temperature the curves are straight lines showing a sharp change in slope as the solid begins to melt and a similar sharp change in slope at the liquidus. The composition of the alloy is determined in the usual way and the temperature of the solidus and liquidus are those corresponding to the changes in slope of the resistance vs temperature curve.

K. Honda and H. Abe (19) using a differential thermal analysis method concluded that the heat effect (which occurred, according to them at about 160°C.) was due to a rapid decrease in solubility of tin-rich phase in the lead-rich solid solution with decreasing temperature. Therefore the horizontal phase boundary found on many diagrams at 160°C should be omitted and a sudden inflection should occur in the $\alpha$ phase boundary at this temperature at a composition of 18 weight per cent tin. They reported the eutectic composition to be 66 weight per cent tin.

The diagram presently accepted is that determined by Stockdale in 1932 (20). Plate 2 represents his results. Using thermal analysis, differential thermal analysis, micrographic analysis, and an electrical conductance method, he determined the eutectic to be at 183.3°C, at a composition of 61.86 weight per cent tin. The solubility of lead in tin was found to be 2.6 weight per cent at 183°C while tin is soluble in lead up to 19.5 weight per cent. At room temperature the mutual solubilities of the two metals are small (about 1.5 weight per cent tin in lead). Like other workers, Stockdale noticed an evolution of heat at 150°C in lead-rich alloys, which varied with the previous history of the specimen. He suggested that this may be due to separation of tin in some form other than white tin, which is subsequently converted to white tin with evolution of heat. Honda and Abe's point of inflection on the lead-rich solid solubility boundary, and consequently their explanation of the evolution of heat, was discounted by Stockdale.



SYSTEM LEAD-TIN (Stockdale)

Plate 2.

## The System Al-Sn

In 1890 Heycock and Neville (21) were the first to study the effects of the addition of aluminum on the freezing point of tin. They observed a regular lowering of the freezing point and determined the eutectic temperature to be 228.8° corresponding to 0.48 weight per cent aluminum.

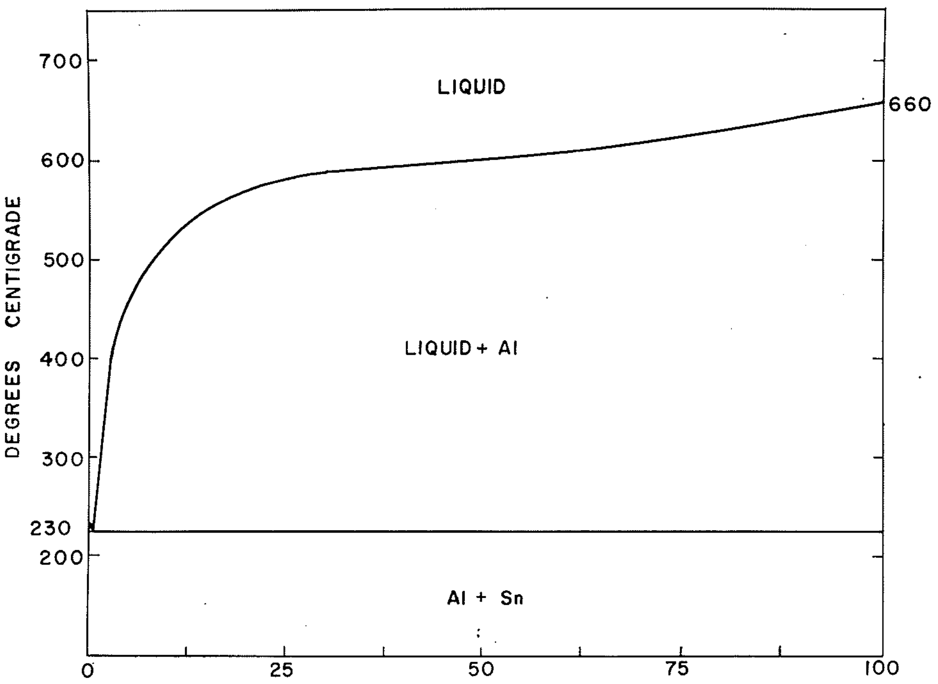
Gautier (22) in 1896, published the first freezing point diagram of this system. His curve exhibits a maximum at 81% tin, indicating a compound of the composition AlSn, and a minimum at 78% tin but Gwyer (23) in 1900, was the earliest worker to show that the liquidus was a smooth curve with no irregularities and it ran continuously from the melting point of aluminum to the eutectic. This proved that the compound AlSn did not exist. The eutectic arrest on the cooling curve was found with as little as 5.1 weight per cent tin.

The argument for the existence of the compound AlSn was renewed two years later (in 1902) by Campell and Matthews (24), who obtained results similar to Gautier. Their plot showed a gradual lowering of the freezing point of aluminum to 74 weight per cent tin at 570°C, then a sudden drop to 490°C and 80 weight per cent tin followed by a rise to 85 weight per cent at 550°C, then a regular decrease with addition of tin to the eutectic at 99.52 weight per cent tin and 229°C. These authors reported that the eutectic mixture appeared microscopically to be a single solid solution of Al in Sn.

In 1913 R. Lorenz and D. Plumbridge (25) placed the eutectic at 98 weight per cent tin and 229°C but they found no compound AlSn. Their investigations agreed well with those of Gwyer. Photomicrographs showed, in agreement with the indications of the thermal method, that alloys up to 98 weight per cent Sn contain crystals of pure aluminum deposited primarily. i.e., the alloys are heterogeneous.

The last of the early work on this system was carried out by Losana and Carozzi in 1923 (26). They placed the eutectic at 0.58 weight per cent aluminum and 229°C.

The most recent determination of the Al-Sn liquidus is due to Sully, Hardy and Heal in 1949 (27). Plate 3 represents their liquidus determination. They reported a



SYSTEM ALUMINUM-TIN (Sully, Hardy and Heal).

Plate 3.

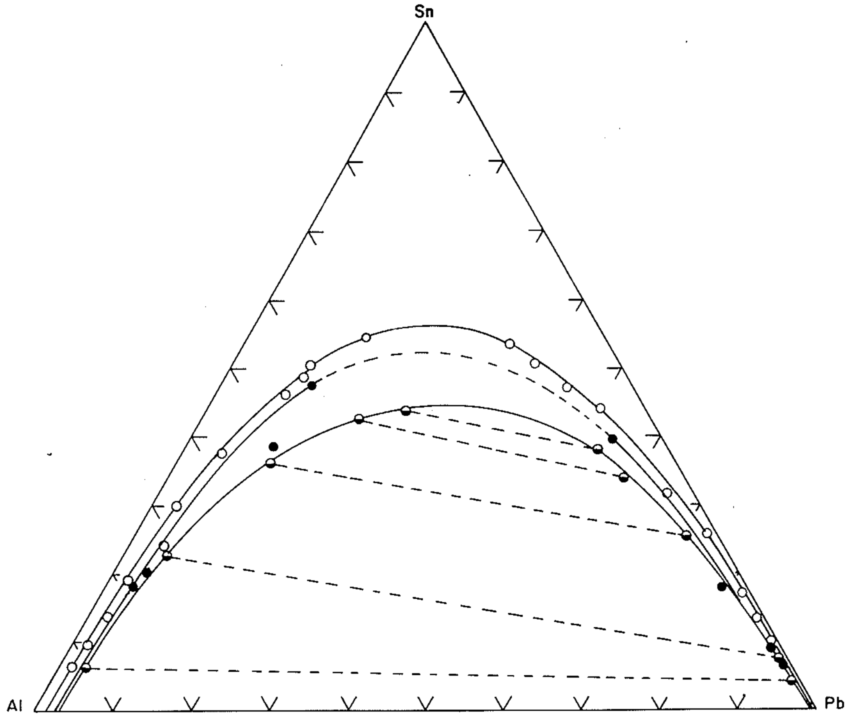
perfectly smooth curve which confirms the average curve of Gwyer although it is a few degrees higher between 50 - 80 weight per cent tin. No evidence was found of any liquid immiscibility. The eutectic concentration confirmed the findings of Losana and Carozzi as being about 0.5 weight per cent Al, but the authors reported the eutectic temperature as being 228.3°C the lowest temperature recorded to date for this system.

## The System Al-Pb-Sn

Unlike the binary systems, there has been very little examination of the ternary system. The first investigation was carried out by A. Wright (28) and consisted of an 'isothermal' treatment between 750 - 850°C. Wright had previously investigated the Al-Pb system and found that liquid lead retained on the average 0.07% aluminum, and aluminum 1.91% lead. He was therefore studying the effect of the addition of Sn to this partially miscible region. His data indicated a critical solution containing approximately 64% tin and 17% lead.

In 1929 Lorenz and Erbe (29) investigated the partially miscible region of the Al-Pb-Sn system at 750°C. They determined the composition of three alloys which had been shaken for an hour, allowed to stand for an hour, then quenched and samples removed from the solidified alloys. They reported that one of the alloys contained two congruent liquid layers, the aluminum-rich upper layer with 4.67 per cent lead, 39.01 per cent tin, the lead-rich lower layer with 69.39 per cent lead, 29.26 per cent tin. Of the two remaining alloys, one was in the region of homogeneous liquid and they considered the other to be in the partially miscible region although it did not show a definite boundary between the two layers in the solidified alloy.

A systematic investigation of the Al-Pb-Sn system was not undertaken until 1953 when Davies (30) studied the region of partial miscibility at 650, 730 and 800°C. Plate 4 represents a projection of these isotherms. For the sake of clarity the tie lines are included on the 800°C isotherm only. The materials used were Analar-grade lead (99.97 + %), super-purity aluminum (99.99%) and Chempur tin (99.99%). He used an isothermal method; the equilibrium times varied from 4 to 16 hours. Davies determined several pairs of points on each isotherm and obtained a smooth curve for the partially miscible region at each temperature. As shown by the diagrams plotted from his data the immiscibility region approaches the tin end of the phase diagram as the temperature is lowered. Unfortunately these data have never been published.



THE LIQUID IMMISCIBILITY REGION IN THE ALUMINUM-LEAD-TIN SYSTEM
AT 650° (○), 730° (●), AND 800° C. (◒). (Davies)

Plate 4.

## CONSIDERATION OF THE PROBLEM

The present study is an integral part of an investigation of the four component system Al-In-Pb-Sn of which the four three component systems are: Al-Pb-Sn, Al-In-Sn, Al-Pb-In, In-Pb-Sn. A review of the literature showed that the system Al-Pb-Sn had been investigated only at temperatures that were in excess of the melting point of aluminum which is the highest melting metal of this system. To complete the phase diagram of this system it was considered desirable to determine some isothermal phase diagrams below the melting point of aluminum, to establish the ternary eutectic composition and temperature, and subsequently to study some of the completely solidified alloys.

From the work of Campbell and Ashley (13) it was seen that the first solid to separate in the binary system Al-Pb, at temperatures below 660°C was primary aluminum. Likewise a study of the Al-Sn phase diagram, due to Sully, Hardy and Heal (27) reveals that primary aluminum is also the first metal to separate from this system at temperatures below the melting point of aluminum. Thus at any given temperature the compositions of the aluminum-lead liquid and the Al-Sn liquid in equilibrium with solid aluminum are known. Consequently, for any desired isotherm in the ternary system two points are known. All that remained was to determine the nature of the curve which joined these two known points. The determination of these curves formed the first consideration in the experimental approach to the problem.

When the phase diagram for the 600°C isotherm was completed it was found that the composition of the liquid at the Al-Sn end of the curve was 20% richer in Sn than any figure previously published. Owing to this very real difference it was considered desirable to investigate a part of the Al-Sn equilibrium diagram. An isothermal analysis of this system formed the second object of the present problem.

Finally the composition and temperature of the ternary eutectic were to be determined. The structure of the completely solidified alloy was to be studied in conjunction with hardness testing and tensile strength.

## EXPERIMENTAL

### Purity of Materials

Metals of the highest purity obtainable were used in this investigation. The metals were analyzed by the companies sypplying them and were as follows:

Aluminum (Supplied by the courtesy of
ALUMINUM COMPANY OF AMERICA)

| | |
|---|---|
| Copper | 0.0042% |
| Iron | 0.0010% |
| Silicon | 0.0014% |
| Magnesium | 0.0009% |
| Sodium | 0.0001% |

Lead (Merck Reagent Grade)

Maximum Impurities

| | |
|---|---|
| Antimony | 0.005% |
| Silicon | 0.002% |
| Total Foreign Metals | 0.05% |

Tin ('Vulcan Commercial Tin')

Batch No. 73

| | |
|---|---|
| Iron | 0.0020% |
| Antimony | 0.0023% |
| Lead | trace |
| Copper | trace |
| Tin | 99.9957 (by difference) |

## Methods of Chemical Analysis

During isothermal analysis the temperature is held constant and the alloy is allowed to come to equilibrium. If there is any preferential oxidation during fusion of the metals, or more than one phase is present at equilibrium, the composition of the phases cannot be determined from the weight of the metals used in the preparation of the sample. Therefore it is necessary to analyse each sample. The method of obtaining the sample for analysis will be described further on in this section.

Usually the samples weighed 0.5 - 1 grams. The sample was dissolved in 1:1 nitric acid, the solution concentrated to about 10 ml. then diluted to 50 ml. and digested at 80 to 90°C. This solution was filtered when hot and washed ten times with hot 1:20 nitric acid. The metastannic acid obtained was ignited in a porcelain crucible and weighed as stannic oxide. The filtrate was retained for estimation of aluminum and lead.

Initially it was thought that aluminum and possibly lead could be determined conductometrically, the aluminum by precipitation as the hydroxide and lead as the sulfate. If a method such as this could be adopted it would eliminate untold hours of tedious routine analysis. Owing, however, to the amphoteric nature of aluminum the conductance readings after the equivalence point were not consistent. The precipitation of lead sulfate did not produce sufficient change in the conductance to give accurate results. Therefore this method had to be abandoned in favour of gravimetric analysis.

The filtrate from the tin determination was diluted to a known volume. An aliquot was set aside for estimation of aluminum and the remainder used for the determination of lead as lead chromate in the following manner: The solution was heated, then sodium acetate was added to replace the nitric acid by acetic acid. Potassium chromate solution was added until the supernatent liquid was slightly coloured, the solution warmed for a few minutes, cooled, then filtered through a 'fine' sintered glass crucible. The precipitate was washed thoroughly with cold water and dried at 120°C.

Aluminum was precipitated and weighed as the hydroxyquinolate. Since lead was present in the filtrate it was necessary to prepare synthetic samples in order to determine the accuracy of the method. It was found that the presence of lead did not vitiate the results. The solution set aside for this determination was evaporated to dryness on a sand bath, care being taken that the residue did not become overheated, for this converts the aluminum hydroxide to the oxide and this is very difficult to dissolve even in an acid solution. The residue was dissolved in sufficient water that the concentration of aluminum was not greater than 0.05 grams per 100 ml. The solution was made slightly acid with hydrochloric acid and warmed to approximately 80°C, when a slight excess of a 5% solution of 8-hydroxyquinoline in 2N. acetic acid was added, allowing 1 ml. of reagent for each 3 mg. of aluminum present. Ammonium acetate solution (2N) was added slowly until a precipitate formed, followed by an excess (25 ml. for each 100 ml. of solution present), to ensure complete precipitation. The liquid was allowed to stand for an hour without further heating, and the precipitate was collected in a 'fine' sintered glass crucible. It was washed well with cold water and dried at 130°C.

When the alloy contained less than 2 per cent aluminum the hydroxyquinolate was reprecipitated in the following way: The crucible containing the hydroxyquinolate was placed in 0.2N hydrochloric acid and heated gently until the precipitate dissolved. The crucible was removed and 6N ammonium hydroxide added until a precipitate appeared. Approximately 3 ml. of 8-hydroxyquinoline were added, the solution was then buffered in the usual way.

## Isothermal Analysis

There are several important things that must be borne in mind when considering isothermal work at high temperature. The most important factors are the reproducibility of a given temperature with a high degree of accuracy and the maintainance of a chosen temperature within a very narrow range for a period of several days if necessary. Of lesser importance, but as an added convenience, the method should allow of the selection of any temperature without having to make major adjustments.

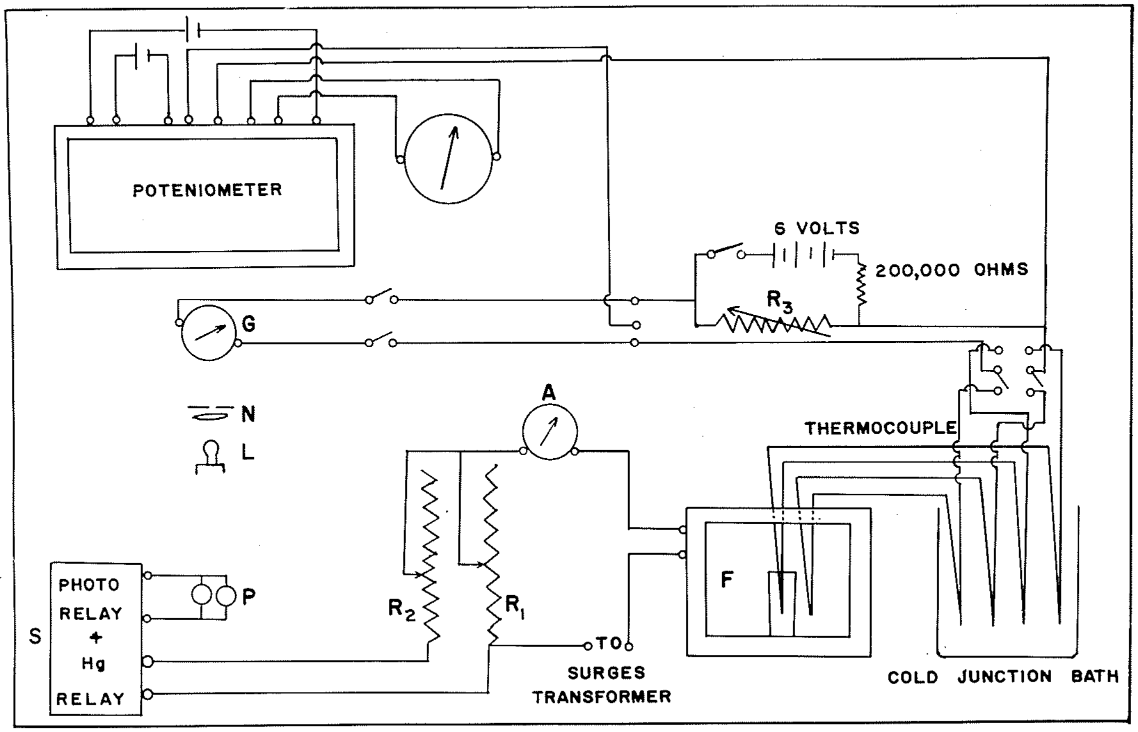
The method and apparatus used to maintain isothermal conditions for the present research have these features incorporated in them. The method is that of Lutz and Wood (31), with some modifications.

The temperature was measured with a chromel-alumel thermocouple which had been calibrated by means of the freezing points of four pure metals which are recognized as calibration standards, viz., tin, lead, zinc and aluminum, the temperatures being fairly evenly distributed over the range that was to be used in this research.

The method of control of a given temperature consisted of the calibrated thermocouple, placed in the alloy in the furnace, connected in series with a galvanometer and opposed to an E.M.F. which was equal to that produced by the chromel-alumel thermocouple at the desired temperature. A beam of light was reflected from the mirror on the galvanometer suspension. This reflected light operated a photo-electric relay which regulated the heating current in the furnace so that the desired temperature was maintained.

Plate 5 shows a schematic diagram of the apparatus as it was used for all the isothermal work in this research.

A Hoskins electric furnace was used in conjunction with a Surges transformer. The furnace drew thirty amperes at a maximum of fifty volts. The oven was a vertical cylinder



TEMPERATURE CONTROL CIRCUIT

Plate 5

fifteen inches long, open at both ends. It was filled with powdered asbestos packed firmly to a height of five inches. A half-inch layer of magnesium oxide powder was placed on top of the asbestos. This loose powder enabled the operator to move the crucible around until it was in the center of the furnace where it would be heated equally from all sides. The furnace was then fitted with a cover made of half-inch transite, which had holes drilled in it for entrance of the hot junctions of the thermocouples and the pipette used for sampling.

The hot junction of the thermocouple was silver soldered, and the two leads from this junction were insulated from each other by a two-holed alundum tube. This two-holed tube was inserted in an outer thermocouple casing. The covering prevented the alloy from coming into contact with the junction. The cold junctions were connected to copper leads and each junction was inserted in a separate sealed pyrex tube which in turn was immersed in the cold bath.

The cold junction was maintained at a constant temperature of 30.6°C by means of a water thermostat heated by a one hundred watt heater controlled by a mercury regulator and mercury relay. The temperature of the thermostat was chosen higher than room temperature to avoid fluctuations.

The furnace F was connected in series with an ammeter A, that would register a maximum of thirty amperes and this, in turn was in series with a water-cooled resistance $R_1$ with a maximum of 10 ohms. A second resistance $R_2$ with the same specifications was connected in parallel with $R_1$ through a mercury switch relay S which was operated by the photo cells P and electronic control E. The purpose of $R_2$ was to supply the additional current required to maintain a given temperature in the furnace. It was found that the parallel arrangement of the resistances was necessary at high currents, since a difference of a few tenths of an ampere only between the heating and cooling currents was required for good temperature control.

The leads from the cold junctions were connected to a D.P.D.T. switch, the common terminals of which could be connected to the potentiometer used for measuring the temperature, or to the galvanometer and opposing E.M.F. which controlled the temperature. The potentiometer was a Leeds and Northrup type K with a wall galvanometer. The E.M.F. which opposed that of the thermocouple was the voltage across the variable resistance $R_3$, which was in a circuit containing a 6-volt storage battery and a 200,000 ohm resistance in series.

The galvanometer in the heat-controlling circuit was a Leeds and Northrup type 2400 with a sensitivity of 0.003 microamps per mm at one meter. Plate 6 shows a cut-away view of the temperature controlling mechanism.

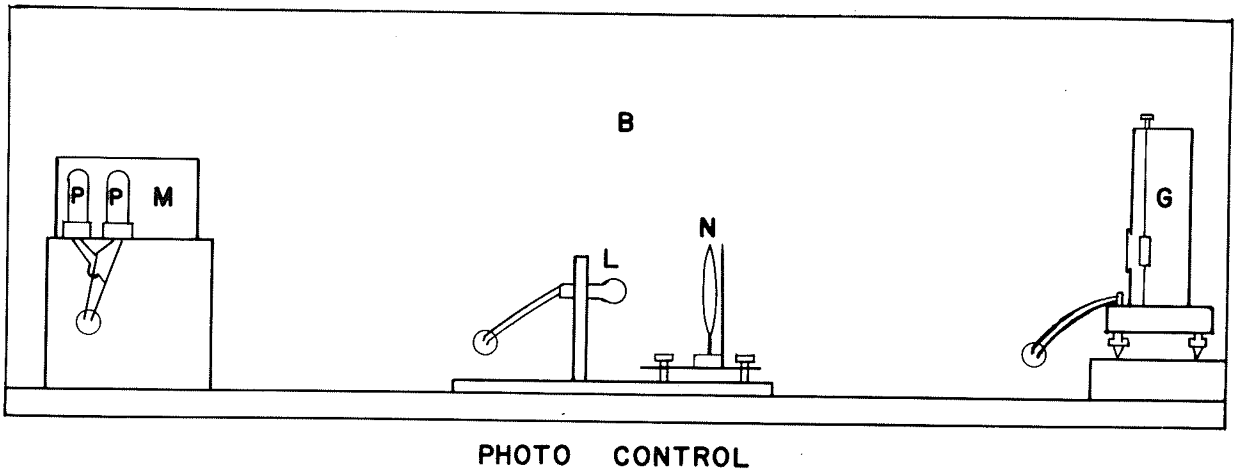


Plate 6.

The apparatus was enclosed in a box B six feet long, six inches wide, and one foot high fitted with a light-tight lid. The interior was painted black to cut down internal reflection. The galvanometer G was at one end of this box and at the other were two photo cells P, on a stand three inches high. These photo cells were connected in parallel with the electronic relay E which they activated. The photo cells faced the galvanometer and were staggered in such a manner that their sensitized filaments overlapped to form a continuous photo-sensitive band almost equal to the diameters of the cells. A polished steel surface M was placed at an angle at one side of the cells. When the beam of light happens to overshoot the cells this steel mirror reflects it back to the sensitized filament. At the center of the box was a point source of light L, a General electric No. 1083 automobile headlight bulb, supplied by a 6 volt A.C. transformer, which was shielded to prevent light from falling directly on the photo cells. There was a lens N in front of the bulb, with its focal point at the filament of the light. On the galvanometer side of the lens was a vertical adjustable slit. The light left the lens in a parallel beam the same size as the lens, and the slit allowed only a very narrow band of this transmitted light to fall on the mirror of the galvanometer. When the galvanometer was in the null position, i.e., no E.M.F. across its terminals, the mirror on the suspension was adjusted so that light from the slit was reflected over the top of the lens and slit assembly in the center of the box and fell on the outside edge of the sensitive filament of the photo cells.

The way in which this arrangement maintains a constant temperature is best explained by considering a temperature for which the E.M.F. is known. The resistances of the furnace are set to give heating and cooling currents that will maintain the furnace at a temperature a few degrees above or below that desired. The E.M.F. corresponding to the temperature required is placed across the variable resistance $R_3$ and opposed to the E.M.F. of the thermocouple. The galvanometer that operates the photo relay is then included in the circuit. If the temperature of the furnace is lower than that required, then the constant backing E.M.F. across $R_3$ is greater than that generated by the thermocouple in the furnace and current will flow through the galvanometer. Its mirror will turn slightly causing the light to fall away from the photo cells, in which case the electronic relay is activated, and current passes through the heating resistances inserted in the furnace circuit. As the furnace temperature rises the E.M.F. of the thermocouple approaches that across $R_3$ and the beam reflected from the galvanometer mirror approaches the photo cells. When the furnace has reached the desired temperature the E.M.F. of the thermocouple is equal to that across $R_3$ and no current flows through the galvanometer i.e., the galvanometer is at its null point. The beam of light from the slit is then on the photo cells and the relay is released. This release results in an increase in the external resistance and therefore the temperature decreases until the beam of light falls off the cells again then the cycle is repeated. This heating and cooling must be repeated for as long as the constant temperature, as determined by the setting of $R_3$, is required.

It was stated above that there were two photo cells and a reflecting mirror which effectively broadened the photo-sensitive region, but if by chance the light should jump both photo cells and mirror, it can be seen that the heating current would again be inserted, and the furnace would overheat. The original arrangement, as designed by Lutz and Wood, would return the beam even if it had passed both photo cells, but due to the complexity of the circuit, it was difficult to adjust or repair it.

At 600°C the temperature could be controlled to within ± 0.5°C. At lower temperatures the error could be decreased but no attempt was made to improve upon it. The variation in the voltage of the power source was the determining factor in the accuracy of the temperature control.

The chromel-alumel thermocouple used to measure the temperature of the alloy was calibrated using the following four metals which have the corresponding melting points

| | |
|---|---|
| Sn | 231.9°C |
| Pb | 327.3°C |
| Zn | 419.5°C |
| Al | 660.1°C |

The E.M.F.'s produced by the thermocouple at these temperatures were plotted on a large graph, so that the error in reading the graph at any temperature was negligible. A curve showing the variation of E.M.F. with temperature of a standard chromel-alumel thermocouple was plotted on the same graph using the data given in 'Temperature - Its Measurement and Control in Science and Industry' (32). This plot was used as a guide when joining the experimental points. The E.M.F. corresponding to any temperature between 230 and 660°C was obtained from this graph.

When a temperature was selected the E.M.F. corresponding to that temperature was placed on the potentiometer and the switches arranged so that this E.M.F. was opposed to the E.M.F. across $R_3$. The resistance $R_3$ was then varied until the E.M.F. across it was equal to that on the potentiometer as indicated by no deflection of the galvanometer. This E.M.F. corresponding to the desired temperature was then put in the temperature controlling circuit and, the heating and cooling currents having been set, the furnace would heat up to this desired temperature and then remain constant.

The method outlined provided a very simple and accurate means of controlling the temperature of the alloy, but some difficulty was encountered in sampling, especially if there were any solid phase present which, since it was essentially aluminum, was less dense than the liquid phase and rose to the top forming a layer that could not be penetrated with a pipette. During sampling it was necessary to remove the thermocouple from the alloy so an alternative method of control was introduced.

This method used a second thermocouple which was inserted between the crucible containing the alloy and the inside of the furnace oven. The cold leads were attached to the other side of the D.P.D.T. switch, as shown in the diagram. After the alloy had been maintained at the desired temperature for some time the thermocouple outside the crucible had also reached some fixed temperature, not necessarily the same as the alloy but some steady value. The E.M.F. corresponding to this temperature was placed across $R_3$ and the temperature of the alloy controlled by this second thermocouple. The thermocouple in the crucible was then used occasionally to check the temperature of the alloy but was removed to facilitate sampling. In this way the temperature of the alloy was maintained and the sample could be withdrawn through the hole in the upper crust left by the thermocouple casing.

## Procedure

Since the alloys were to be heated above the melting point of aluminum, pyrex glass apparatus (crucibles and pipettes) could not be used because the silica in the glass is reduced by aluminum at these high temperatures. Because of their inertness, alundum (aluminum oxide) crucibles and pipettes were used. The crucibles were three and three eighths inches high and had an outside diameter of one and three eighths inches.

As stated above the Al-Pb-Sn system was studied at temperatures below the melting point of aluminum, as was the

Al-Sn system when the solubility of aluminum in tin was determined at various temperatures. In order to establish equilibrium in a minimum of time the prepared sample was heated above the melting point of aluminum and mixed thoroughly before cooling to the desired temperature.

An Ajax high frequency converter type furnace was available which melted the alloy readily, with a minimum of oxidation. Because of the oscillating nature of the induced current it mixed the alloy thoroughly after melting it. Although this was found to be an ideal way to prepare a molten sample for isothermal study, it soon had to be abandoned because of the number of crucibles that cracked in the induction furnace. This method of fusion was used exclusively for melting the lead, which was in pellet form. The ingots obtained were cut and used in the resistance furnace, with a minimum of oxidation.

The alloy was placed in the Hoskins resistance furnace and heated to approximately 700°C, stirred thoroughly with an alundum rod, then allowed to cool to the temperature of the experiment. The equilibrium time was from 4 to 24 hours prior to withdrawing a sample.

Alundum tubes of 1/8 inch outside diameter and a 1/16 inch inside diameter, were used to withdraw the samples. A tube was lowered into the molten alloy, to any desired depth, then mild suction was applied. The alloy was drawn up into the cooler upper portion of the tube where it froze. The tube was broken to recover the sample and the entire sample was analyzed. This was done to minimize the error in case segregation had occurred.

The system Al-Sn was studied isothermally at 25° intervals between 400 and 645°C. The alloys were prepared by adding aluminum to the tin-rich liquids. The temperature of the furnace was raised until only molten alloy was present, stirred and cooled to the temperature of the experiment, care being taken that there was always solid present at equilibrium. The liquid was sampled in the usual way.

## Thermal Analysis

Thermal analysis was used to determine the Al-Pb-Sn eutectic temperature and composition.

The oven of the furnace used for thermal analysis was a sillimanite tube six inches long and two inches in diameter. One end was fitted with a disc of the same material as the cylinder, cemented into place. This cylinder was wrapped first with asbestos paper soaked in water glass, then wound with nichrome wire, the successive turns being as close together as possible without touching, and another layer of the treated asbestos paper wrapped over the wire. The oven completed as described was cemented to the center of a ten inch disc of half inch transite. The disc had a hole at the center equal to the diameter of the oven and two binding posts to which the nichrome leads were connected. This assembly was set on a sheet metal cylinder, nine inches in diameter and eight inches high, with a bottom that formed a dead air space to insulate the furnace.

Since the temperature of this investigation was less than 200°C a piece of board was used for the lid, having a hole for the thermometer, and a smaller one for a stirrer. The furnace was connected in series with an ammeter of 10 ampere capacity and a rheostat of 89 ohms resistance which could be shunted out of the circuit while heating the furnace. The alloy was heated to the desired temperature, when the rheostat was included in the circuit and the furnace allowed to cool with a small residual current. This was done to reduce the rate of cooling in order that a small phase change might be detected. The crucible used was of the same type as described previously (p. 39) and the stirrer was an alundum rod. A mercury in glass thermometer reading to 0.1°C, and which had previously been calibrated against a platinum resistance thermometer, was used to determine the temperature.

The Pb-Sn eutectic temperature was first determined, then alloys containing small amounts of aluminum were added to obtain the ternary eutectic temperature. It was found very difficult to dissolve a measurable quantity of aluminum in the Pb-Sn at eutectic temperatures. Therefore the desired amount of aluminum was melted in the crucible in the Hoskins furnace, and the tin then added followed by the lead. The molten alloy was thoroughly mixed, the crucible placed in the thermal analysis furnace, and a cooling curve determined, the alloy being stirred continuously. When the eutectic temperature was reached a sample was withdrawn in the same manner as previously described (p. 40), and analyzed.

## Microscopic Analysis

Microscopic analysis was used to study the completely solidified alloys in the region of the ternary eutectic. Samples of approximately one quarter inch cube, were cut from the ingots with a hacksaw. One face was filed smooth with a fine mill file, then the specimen was firmly imbedded in bakelite, using a standard instrument designed for this purpose, the prepared surface being level with the bakelite.

The mounted specimen was then ground on 2, 1, 0 and 00 abrasive papers successively; all were previously spread with a concentrated solution of paraffin in kerosene. The paraffin solution prevents the particles of lead from adhering to the paper and forming a glaze which drags and disorts the surface metal. Grinding on successive papers was continued until all scratches left by the preceding paper had disappeared. This was most easily accomplished by using a parallel motion and turning the specimen through 90° when changing from a coarser to a finer grade of paper. Since the paraffin solution retained the abrasive in suspension it was also necessary to wash the specimen before proceeding to a finer paper. When the specimen was removed from the last paper no scratches were visible to the unaided eye.

The final polishing was carried out on a revolving wheel over which was stretched a silk velvet (selvyt) polishing cloth. A paste consisting of medium weight magnesium oxide, liquid soap and water was applied to the wheel. Water in the form of a fine stream was directed on to the wheel as the polishing proceeded and a liberal use of the oxide abrasive was found necessary to prevent scratching as the polishing approached completion. The specimen was washed with hot water and dried by spraying with alcohol.

The etching reagent was that used by Villela and Beregekoff (33) for lead alloys. It consists of one part glacial acetic acid, one part nitric acid and four parts glycerol. The polished specimen was etched from 5 - 15 seconds at room temperature. The polishing and etching procedures were alternated, the specimen being examined under the microscope after each etching. This routine was repeated as long as the appearance of the structure showed improvement.

The microscope used for the analysis was a C.M. Bausch and Lomb with a moveable stage. In order to examine the polished and etched surface under the microscope it was necessary to have it perpendicular to the optical axis. This was accomplished in a very simple manner which did not require tilting of the microscope stage. The specimen was laid with polished surface downward on a glass tile, within the circumference of a brass ring with parallel ends. A small piece of plasticine was placed on top of the specimen and pressed down gently with a microscope slide until the slide rested squarely on the ring. The slide was then removed with the specimen adhering to it and placed on the microscope stage, no further leveling being required.

Objective lenses magnifying to 250 diameters were employed. Photomicrographs of the specimens were taken with a Bausch and Lomb press type camera which fitted the microscope. Positive prints (x500) were made with a photo enlarger.

## Hardness Tests and Tensile Strength

The hardness of the alloys and of the pure components was determined on the Brinell hardness number scale and also on the diamond pyramid hardness scale. The tensile strength of the alloys used as solders was determined using an Olsen tester.

Owing to the extreme softness of the specimens it was necessary to use the modified Brinell hardness tester used by Schaefer (34) and constructed in accordance with the specifications in the Metals Handbook (35). A lever system permitted the load (5.5 kilos) to be lowered slowly onto the specimen which was subjected to this load for 30 seconds. The indentor was a steel ball 2.35 mm in diameter which was held in place by a magnet set in the body of the load. Two measurements of the surface diameter were made at right angles to each other and the readings averaged. The diameters were read with a Zeiss ocular micrometer which took the place of the eyepiece of the microscope. The Brinell hardness numbers (Bhn) were calculated using the following formula:

$$\text{Bhn} = \frac{P}{\frac{D\pi}{2}\ D-\sqrt{D^2 - d^2}}$$

where P = test load in kilograms, D = diameter of the ball in mm and d = diameter of the impression in mm. The results, which agreed reasonably well, were averaged.

A Vickers-Armstrong tester with a 5 kilogram load was used to determine the hardness of the same specimens by the diamond pyramid method (DPH). This test employs a square based diamond pyramid indentor with an enclosed angle of 136° between opposite faces. The indentations were measured with a microscope fitted with an ocular micrometer which contains movable knife edges, the distance between the knife edges being registered on a calibrated counter. The impression was a square of which the lengths of the diagonals were measured, averaged, and used in the following formula:

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

where DPH = the diamond pyramid hardness number, L = load in kilograms, d = length of the diagonal of the impression in mm.

Two pieces of half inch brass strip six inches long soldered together in the form of a lap joint were used to determine the tensile strength of the alloys as solders. The area of the lap was one eighth of a square inch. Both pieces were 'tinned' with the solder under investigation then fused together. Any excess solder around the joint was removed with a file. A solution of zinc chloride was used for fluxing and the application of the solder as well as the fusing was done with a copper soldering iron. The strength of the joint was determined with an Olsen 10,000 lb. tester. This is a hand operated machine. One end of the specimen was attached to a scale capable of measuring loads to 10,000 lbs. and the load applied to the other end by means of a crank and screw. The load required to break the joint was recorded. Four tests were made with each solder and the results, which agreed reasonably well, were averaged.

## EXPERIMENTAL RESULTS

The experimental results will now be given in the order in which the investigation was carried out. Tables I and II show the composition of the homogeneous liquid in equilibrium with solid aluminum at 500°C and 600°C respectively, in the system Al-Pb-Sn. Table III represents the variation in the solubility of aluminum in tin with temperature at temperatures between 400 and 600°C. Top and bottom samples were withdrawn from each of the alloys represented in these tables. The resulting analyses, which agreed very well, were averaged. Finally, data concerning the ternary eutectic region are given in Tables IV and V. The former shows the temperature and composition of the binary Pb-Sn eutectic compared with the Al-Pb-Sn eutectic. The latter represents some of the mechanical properties of the pure metals and several alloys in the region of the ternary eutectic. The photomicrographs that follow the tables show the phases in equilibrium in the alloys which have the mechanical properties given in Table V.

## TABLE I

## Composition of the Liquidus in the 500°C Isotherm of the System Al-Pb-Sn

| Alloy No. | Composition by Weight Al | Pb | Sn |
|---|---|---|---|
| 2 | 3.5 | 27.5 | 69.1 |
| 3 | 4.0 | 16.1 | 80.0 |
| 4 | 4.9 | 6.2 | 88.8 |
| 5 | 5.7 | 0.0 | 93.9 |
| 5a | 5.5 | 0.0 | 94.4 |

Solid aluminum was present in all alloys.

## TABLE II

## Composition of the Liquidus in the 600°C Isotherm of the System Al-Pb-Sn

| Alloy No. | Composition by Weight Al | Pb | Sn |
|---|---|---|---|
| 6 | 5.0 | 43.0 | 52.5 |
| 7 | 6.6 | 18.3 | 75.2 |
| 8 | 8.4 | 26.5 | 65.2 |
| 9 | 9.1 | 30.4 | 60.5 |
| 10 | 10.3 | 26.2 | 63.5 |
| 11 | 0.45 | 85.0 | 15.1 |
| 12 | 29.2 | 0.0 | 68.8 |
| 12a | 30.3 | 0.0 | 68.9 |
| 13 | 2.7 | 61.3 | 36.5 |
| 14 | 5.5 | 40.2 | 54.5 |
| 15 | 9.4 | 27.7 | 63.1 |
| 16 | 15.9 | 12.2 | 70.5 |
| 17 | 23.8 | 5.2 | 71.4 |

Solid aluminum was present in all alloys.

## TABLE III

### Solubility of Aluminum in Tin Between 400 and 645°C

| Alloy No. | Temperature | Composition by Weight | |
|---|---|---|---|
| | °C | Al | Sn |
| 1 | 400 | 2.6 | 97.5 |
| 2 | 425 | 3.3 | 97.0 |
| 3 | 450 | 4.0 | 96.0 |
| 4 | 475 | 4.8 | 95.2 |
| 5 | 500 | 5.4 | 94.6 |
| 5a | 500 | 5.7 | 93.9 |
| 6 | 525 | 8.3 | 92.1 |
| 7 | 550 | 11.8 | 88.3 |
| 8 | 575 | 17.1 | 83.0 |
| 9 | 600 | 30.8 | 69.1 |
| 9a | 600 | 29.9 | 68.8 |
| 10 | 625 | 58.6 | 41.0 |
| 11 | 645 | 87.6 | 12.4 |

## TABLE IV

### Comparison of the Composition and Temperature in The Binary System Pb-Sn and the Ternary System Al-Pb-Sn

| Eutectic | Temperature | Composition of Liquid (wt. %) | | |
|---|---|---|---|---|
| | °C | Al | Pb | Sn |
| Pb-Sn | 183.3 | -- | 38.1 | 61.9 |
| Al-Pb-Sn | 183.0 | 0.08 | 38.1 | 61.7 |

## TABLE V

## Some Mechanical Properties of the Pure Metals and Certain Alloys of the System Al-Pb-Sn

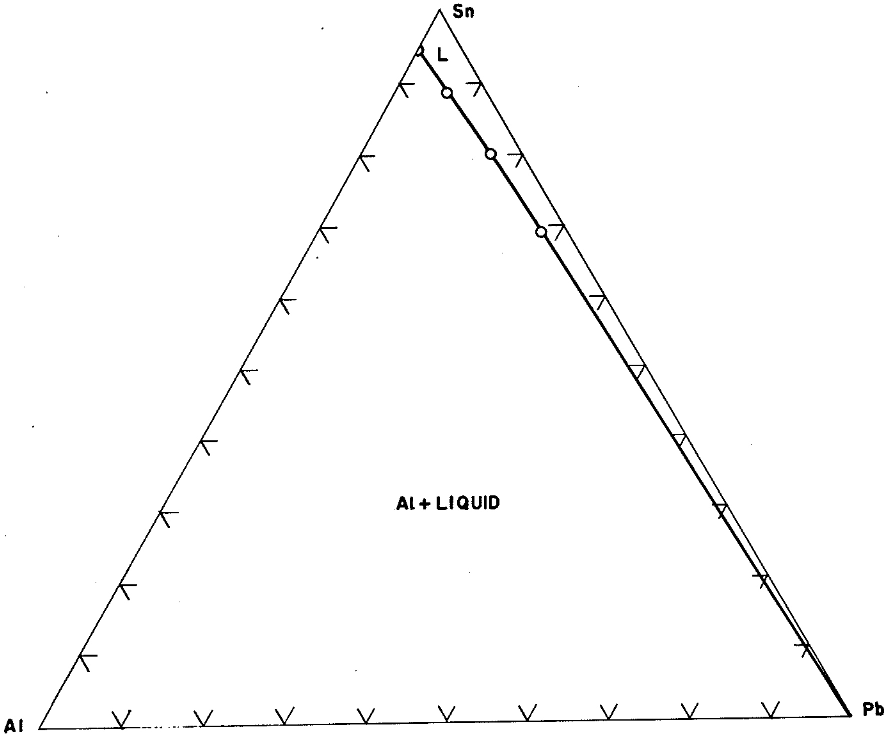
| Alloy | Hardness | | | | Tensile Strength |
|---|---|---|---|---|---|
| | Bhn | | | DPH | as a solder |
| | Dia. of ball | Load | Time of application | Load of 5.0 kilos. | Psi |
| | 2.5 mm | 5.5 kg. | 30 sec. | | |
| Al | | 14.9 | | 16.6 | ---- |
| Sn | | 5.0 | | 11.4 | ---- |
| Pb | | 3.4 | | 7.6 | ---- |
| Pb-Sn Eut. | | 14.2 | | 16.4 | 6200 |
| Al-Pb-Sn Eut. | | 18.2 | | 19.8 | 6450 |
| Pb-Sn Eut. + 1% Al | | 15.8 | | 18.4 | 5900 |
| Pb-Sn Eut. + 5% Al | | 14.2 | | 17.7 | ---- |

The shear strength of a soldered joint under prolonged load was determined also for the Pb-Sn eutectic. This solder supported 1360 psi. for 264 hours at room temperature.

The phase diagram shown in plate 7 is the result of plotting the data in table I. It shows the composition of the homogeneous liquid in equilibrium with solid aluminum, in the Al-Pb-Sn system at 500°C. Since there is only 3.5 per cent aluminum in the liquid when the tin content is 70 percent and since, according to Campbell and Ashley (13) the aluminum dissolved in lead at 500°C was 0.02 per cent there is little interest in the low tin region. Therefore no attempt was made to determine the exact nature of this portion of the curve. Top and bottom samples were withdrawn with alundum tubes and analysis showed the presence of a single homogeneous liquid in equilibrium with solid aluminum.

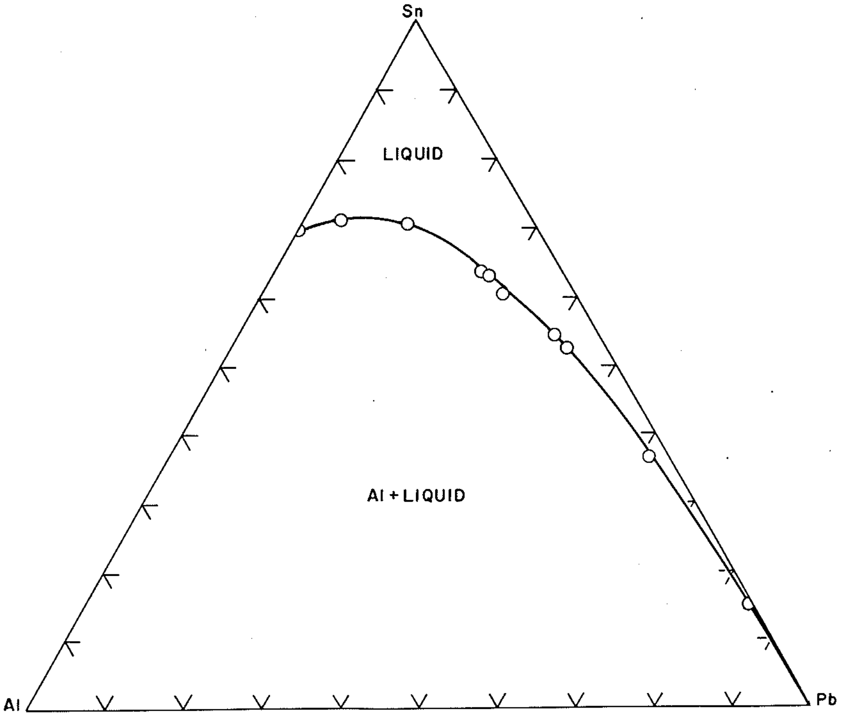
Plate 8 shows the phase diagram obtained when the data in table II were plotted. This continuous curve shows the composition of the homogeneous liquid in equilibrium with solid aluminum for the Al-Pb-Sn system at 600°C. All alloys in this table are represented on the diagram except numbers 7 and 8 which were unsaturated with respect to aluminum. These two alloys were prepared during the early stages of the investigation in an attempt to locate a region of partial miscibility which was thought to exist in this system at 600°C. There was solid phase present in all alloys plotted, and the sampling and analyzing was identical to that used for the 500°C isotherm. Analysis of alloy 11 gave 15 per cent tin, 0.45 per cent aluminum and 85.0 per cent lead. This was the alloy with the lowest tin content and since there was only 0.45 per cent aluminum present it indicated that the curve would intersect the binary at 0.02 per cent aluminum as determined by Campbell and Ashley (13).

The results of the isothermal analysis of the Al-Sn system are given in table III. The phase equilibrium diagram represented in plate 9 was obtained from these results. It shows the variation in the solubility of aluminum in tin with temperature. Solid aluminum was present in all alloys and the



500°C ISOTHERM SYSTEM Al-Pb-Sn

Plate 7.



600°C ISOTHERM SYSTEM Al-Pb-Sn

Plate 8.

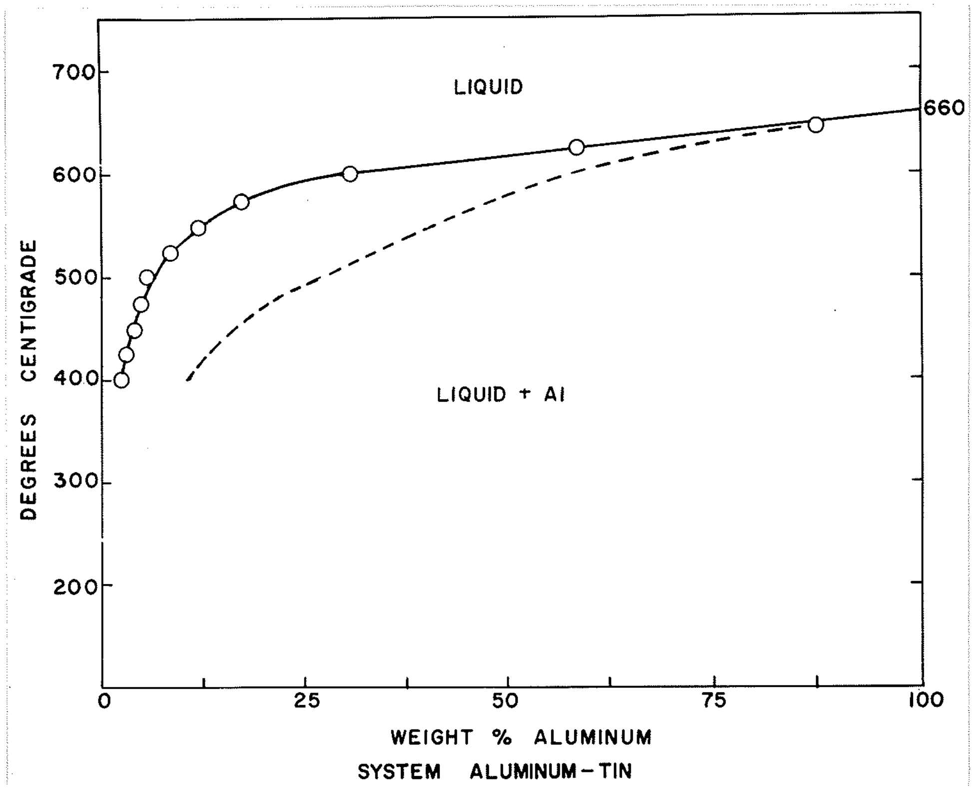


Plate 9.

method of sampling was the same as that used for the ternary system. No attempt was made to carry the investigation below 400°C.

The dotted curve shown in the Al-Sn diagram, plate 9 was calculated using the thermodynamic equations derived by Seltz (36). The difference between the ideal and experimental curves shows that the solubility of aluminum in tin deviates considerably from ideal behavior. According to the experimental curve aluminum is only slightly soluble in tin until the temperature approaches the melting point of aluminum, when the solubility increases rapidly for a small increase in temperature. It deviates from ideality to such an extent that a region of partial miscibility is approached as indicated by the flat portion of the curve.

Alloy 5a in Table I and alloy 12a in Table II were investigated at 500 and 600°C respectively during the investigation of the Al-Sn system. Similarly 5a and 9a in Table III correspond to determinations made during the isothermal investigation of the ternary system. Two months elapsed between the first determination and their repetition. This served as a check on the consistency of the method.

As shown in Table IV the Pb-Sn eutectic temperature was found to be 183.3°C which is in agreement with Stockdale's value (20). The composition data are due to Stockdale and were included for comparison with the ternary eutectic composition. The addition of aluminum to the Pb-Sn eutectic lowers the eutectic temperature to the extent of 0.3°C. The temperature of the ternary eutectic formed by the addition of aluminum to the Pb-Sn eutectic was determined to be 183.°C corresponding to 0.08% aluminum, 38.1% lead and 61.7% tin.

Plates 10 - 15 are photomicrographs (x 500) showing the various phases in equilibrium in the region of the ternary eutectic. Plates 10 and 13 show the lamellar structure of the Pb-Sn and Al-Pb-Sn eutectics respectively.

Plate 11 shows $\alpha$ lead imbedded in Pb-Sn eutectic matrix. The solubility of tin in lead at the eutectic temperature is 19.2% while at room temperature it is only 1.5%. The $\alpha$ phase

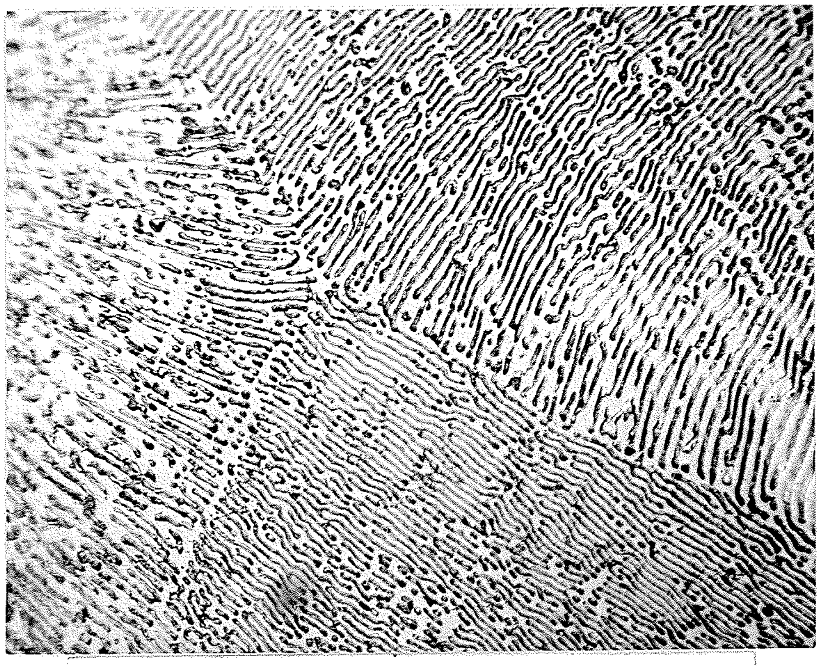


Plate 10. Pb-Sn Eutectic x 500

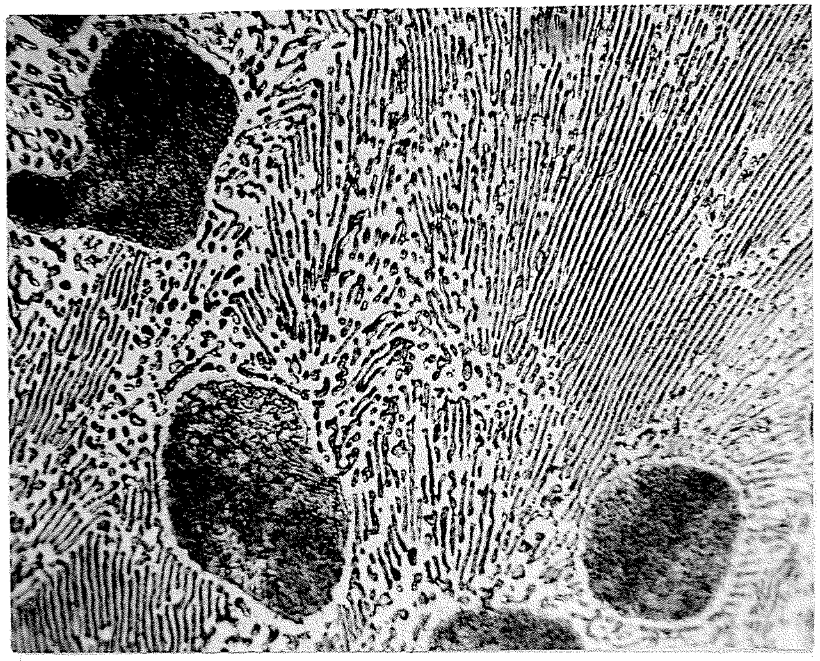


Plate 11. Alpha Lead Imbedded in Pb-Sn Eutectic Matrix. x 500.

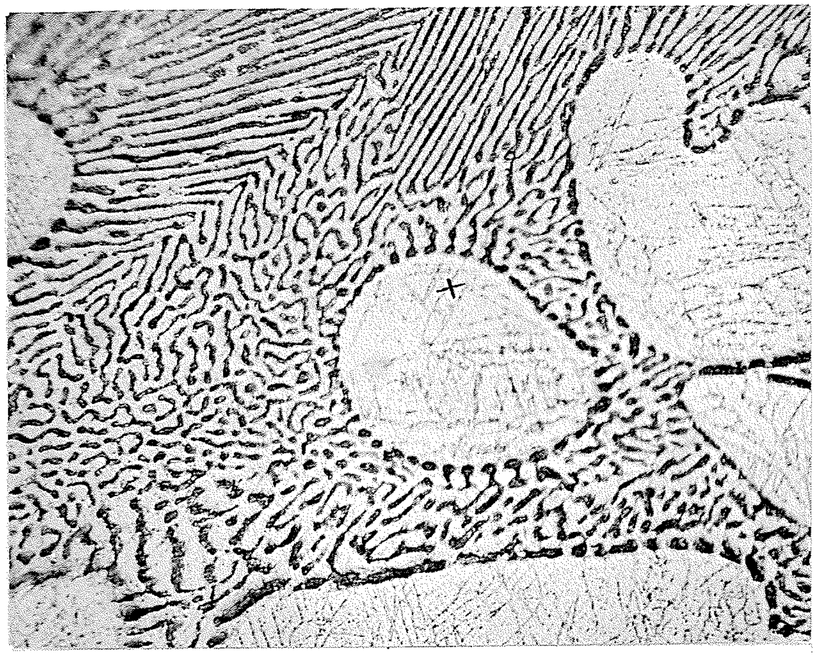


Plate 12. Beta Tin Imbedded in Al-Pb-Sn Eutectic Matrix. x 500.

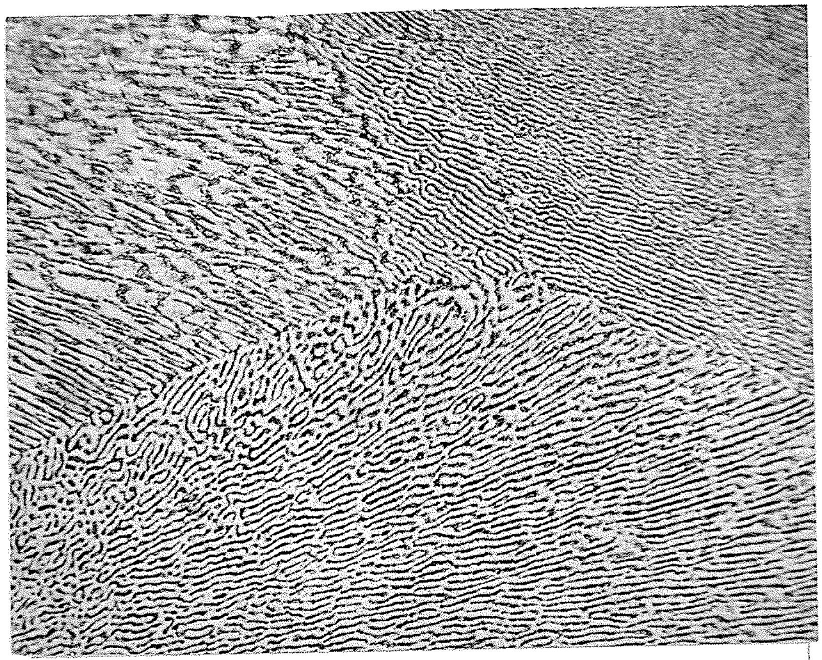


Plate 13. Al-Pb-Sn Eutectic x 500

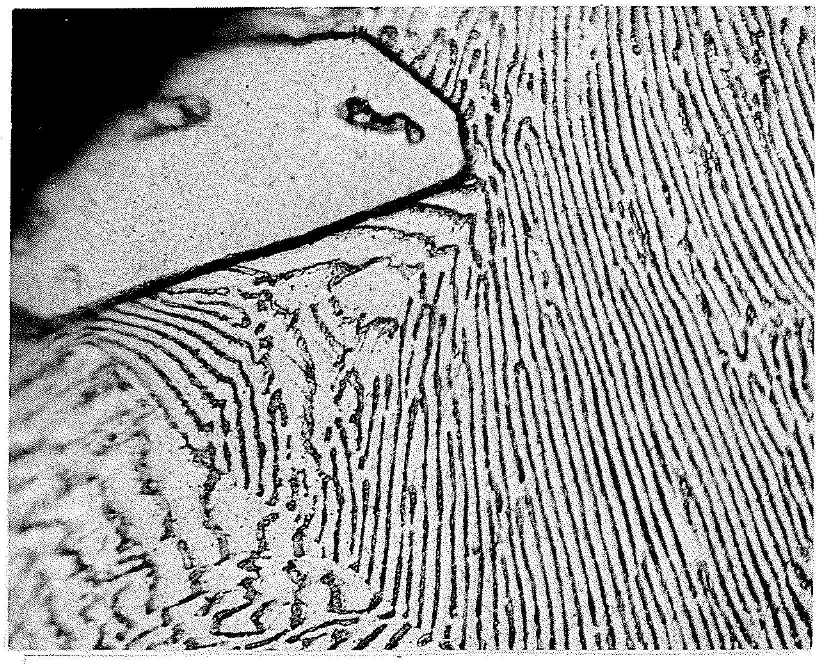


Plate 14. Primary Aluminum in Al-Pb-Sn Eutectic Matrix. x 500.

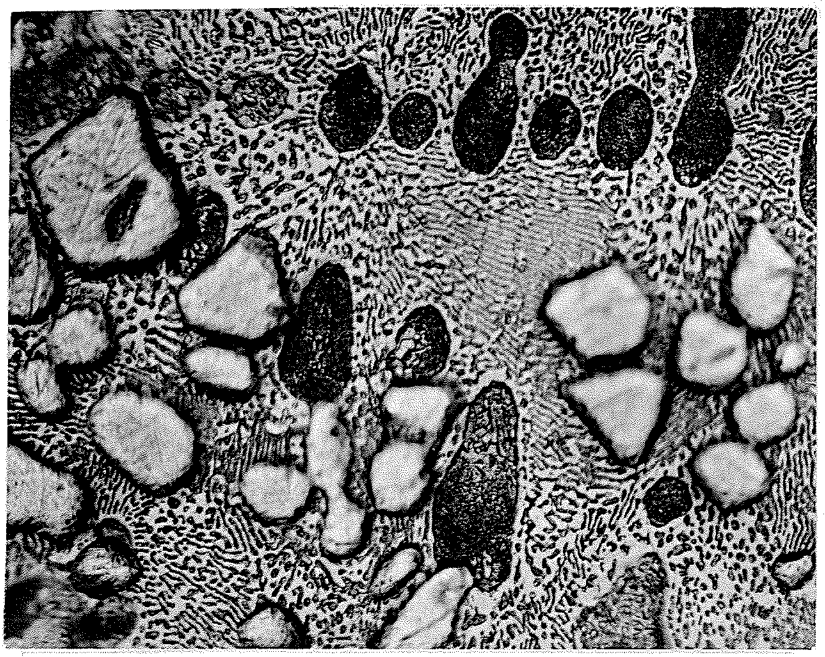


Plate 15. Alpha Lead (dark), Primary Aluminum (light) in Al-Pb-Sn Eutectic Matrix. x 500.

exhibits a white outline and light spots due to the precipitation of tin in the solid phase as the temperature is lowered.

Plate 12 is a photomicrograph of a ternary alloy that had been allowed to solidify in the furnace then thrust into powdered dry ice for quenching. It shows β tin imbedded in eutectic matrix. Tin contains 2.5 per cent lead in solid solution at the eutectic temperature but a negligible amount at room temperature. The β phase here shows lead precipitated at the grain boundaries and in the crystallographic planes. This structure is called Widmannstatten. The portion marked with an 'x' is an example of twinning through cold working. Tin forms mechanical twins when it is cold worked and the creaking sound called the 'cry' of tin when it is bent is due to this twinning process.

Primary separation of aluminum imbedded in an Al-Pb-Sn matrix is shown in plate 14. The sample was selected so that the outside edge of the ingot formed one side of the specimen, then one of the sides perpendicular to this edge was polished and etched. This alloy contained 1 per cent aluminum in the Pb-Sn eutectic composition and shows a primary aluminum crystal formed at the outer edge of the ingot.

The phases present in an alloy containing 5 per cent aluminum in the Pb-Sn eutectic are shown in plate 15. α lead is the dark phase with some tin precipitated. The light polygonal shaped crystallites are primary aluminum. Because aluminum is more resistant to the polishing abrasive these crystallites are not in the same plane as the α lead and eutectic matrix, hence are slightly out of focus.

Table V shows the relationship between the hardness of the pure metals, the Pb-Sn eutectic and two alloys having primary separated aluminum. Brinell Ball and Vickers Diamond Pyramid hardness numbers are given. The trend in the hardness is the same on both scales. The binary eutectic alloy was found to have a greater hardness than lead or tin, the two pure components. Likewise the ternary eutectic alloy had a greater hardness than both the binary Pb-Sn eutectic and aluminum, the third alloying component. The alloy made by adding 1 per cent aluminum to the Pb-Sn eutectic, thus forming an alloy that was mainly ternary eutectic surrounding primary separated aluminum, had a hardness less than the eutectic and approached that of pure aluminum. Aluminum occupies about 20 per cent of the volume in the alloy containing 5 weight per cent aluminum plus the Pb-Sn eutectic composition. Consequently the hardness of this alloy was almost equal to that of pure aluminum.

The effect of aluminum on the shear strength of the Pb-Sn eutectic solder was determined. As shown in Table V the shear strength and the hardness, were greater for the ternary eutectic than for the binary. The alloy containing 1 per cent aluminum showed a marked decrease in shear strength due to the appearance of primary aluminum. The 5 per cent aluminum alloy could not be used as a solder due to the large volume of aluminum present. Aluminum does not fuse at soldering temperatures.

# GENERAL DISCUSSION

Since an investigation of the Al-Sn system had not been anticipated when the original work was planned it will now be shown why it was included in the present study. The latter part of this section will deal with the Al-Pb-Sn system in terms of the solid model.

A study of the three binaries, Al-Sn, Pb-Sn, and Al-Pb and the previous work on the Al-Pb-Sn ternary were used to determine the temperature at which the present investigation was to be carried out. It was found that Pb-Sn and Al-Sn were miscible in all proportions in the liquid state but Al-Pb possessed a miscibility gap above 658°C. All the previous work on the ternary system (30) was above 650°C and showed the effect produced when tin was added to the Al-Pb system. These results are shown in the diagram plate 4. This diagram shows that the partially miscible region moved towards the tin end of the diagram as the temperature was lowered. At 650°C this region extends beyond 55 per cent tin and it seemed reasonable to assume that it would move even closer to the tin end with decreasing temperature. At the same time solid aluminum would intrude into the partially miscible region since the temperature would be lower than the melting point of aluminum. According to the published work on the Al-Sn system, the liquid in equilibrium with solid aluminum contained 50 per cent aluminum at 600°C. The solubility of aluminum in lead at the same temperature was 0.02 per cent. A curve joining these two points would cut the partially miscibility region. It was therefore decided to investigate the 600°C isotherm of the Al-Pb-Sn system and outline the partially miscible region. If a region of partial immiscibility did exist then an invariant triangle would occur. The base of the triangle would form the base of the partially miscible region. Any alloy whose composition was represented by a point in this triangle would separate into solid aluminum and two congruent liquid layers. The tie-line joining the two points which represented the compositions of the two liquid layers would lie on the base of the invariant triangle. By the same argument it was decided that the gap would be non-existent at 500°C and this temperature was chosen to determine the nature of the curve below the region of partial miscibility. This line of reasoning indicated that the partial miscibility dome outlined in plate 18 would be intruded along the base by solid aluminum below 658°C, the amount of intrusion varying with temperature until the partially miscible region was completely obliterated.

A smooth curve very similar to the one postulated was obtained at 500°C. The region of partial miscibility was completely intruded by solid aluminum at 500°C. The subsequent investigation of the 600°C isotherm also showed the partially miscible region to be non-existent. But the solubility of aluminum in tin at this temperature was found to be only 30 per cent instead of 50 per cent which is the published value. This showed that there was a large error in the published data on the Al-Sn system. Therefore the solubility of aluminum in tin, as a function of temperature was determined. The results plotted along with those of Sully, Hardy and Heal (27) are shown in plate 16. The dotted line represents the results of the latter group. It can be seen that the curves coincide between 400 and 450°C, and between 450 and 550°C the deviation in percentage composition was small, being less than 2 per cent. Above 550°C the curve starts to flatten out and although the difference in temperature between the two curves was only about 10°C, in this region, the difference in composition was as great as 20 per cent. The curve due to Sully, Hardy and Heal (27) was determined by the method of thermal analysis. This method does not usually yield accurate results when there is a large change in composition for a small variation in temperature. Therefore the large difference between the results obtained isothermally by the present author and the published results is explained.

With the aid of these new data on the solubility of aluminum in tin it can be readily seen that a region of partial miscibility is not to be expected in the Al-Pb-Sn system at 600°C and this was found to be the case. Thus the miscibility gap that was present at 650°C was completely intruded by solid aluminum at 600°C. Plate 17 shows the 650°C isotherm superimposed on the 600°C isotherm. From this diagram it can be seen to what extent the solid aluminum had moved across the liquid region of the diagram when the tempera-

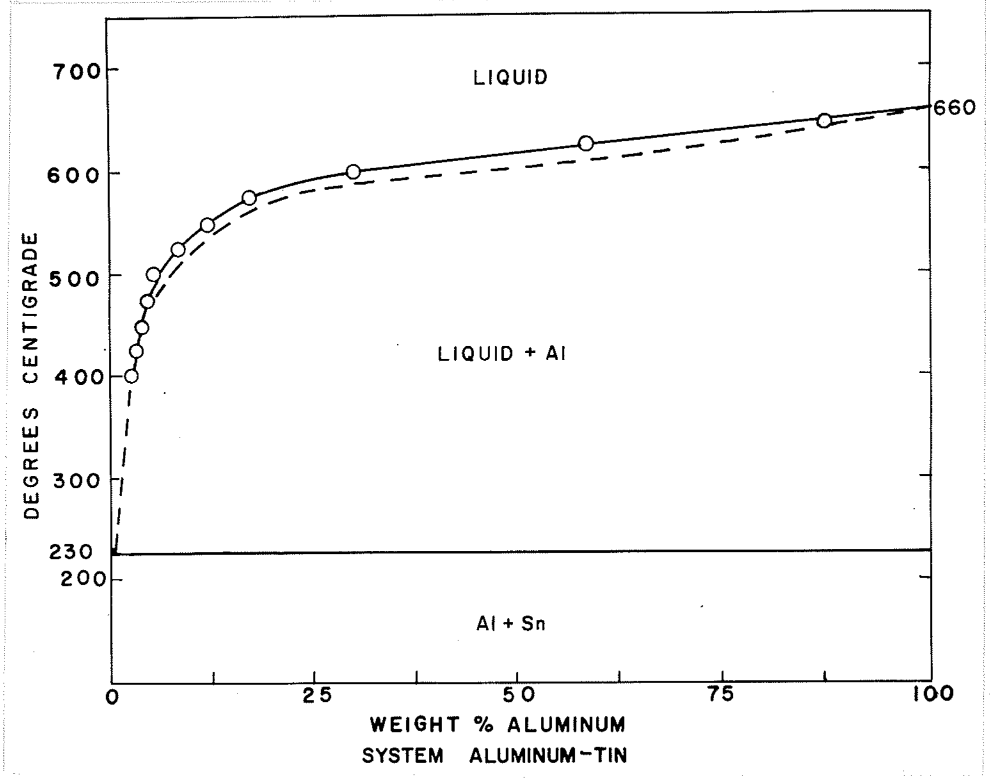


Plate 16.

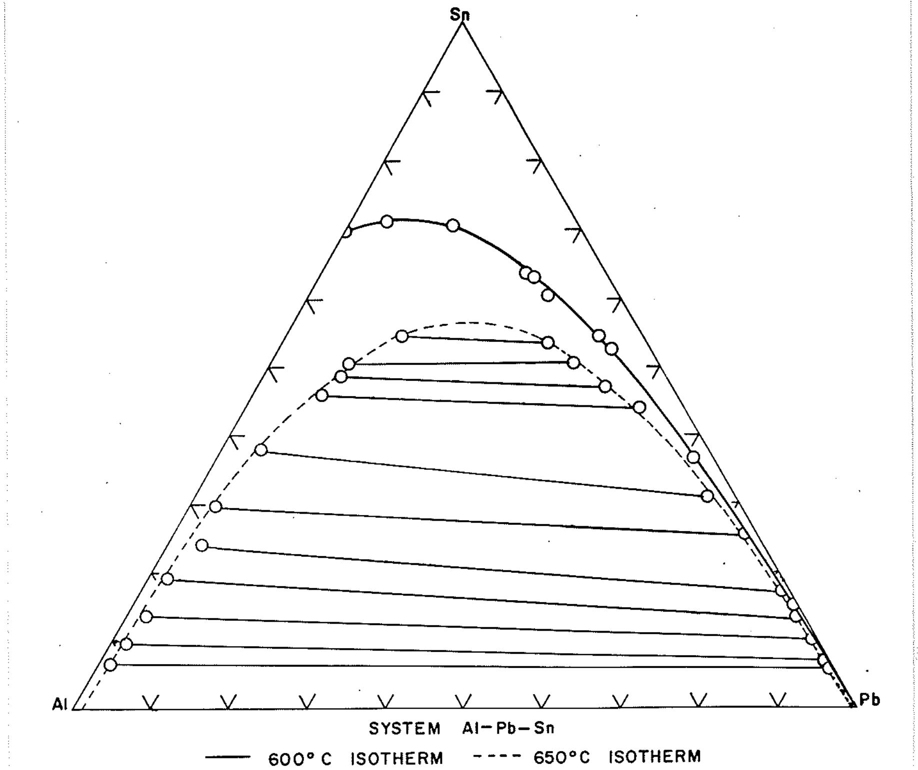


Plate 17

ture was decreased by 50°C. In terms of plate 18 this means that a large "plateau" of aluminum which makes its appearance at 658°C (even though it was undetected by Davies at 650°C) has moved into the solid figure from the Al-Pb side and has covered three quarters of the cross sectional area by the time the temperature has dropped to 600°C. This rapid intrusion made this ternary investigation rather uninteresting from the point of view of a phase study.

It was found that the ternary eutectic temperature was only 0.3°C below the Pb-Sn eutectic temperature and contained not more than 0.08% aluminum. This was to be expected since the Al-Sn eutectic contains 0.5% aluminum and the Al-Pb eutectic 0.02% aluminum and a line joining these two binary eutectics almost always includes the ternary eutectic composition. This meant the aluminum content of the ternary eutectic was less than 0.5 per cent and more than 0.02 per cent. The ternary eutectic was very near the Pb-Sn eutectic since this was the binary with the lowest temperature. In plate 18 it was found impossible to indicate the eutectic troughs leading from each binary eutectic to the ternary eutectic because they are so close to the Pb-Sn side of the diagram. The solid phases present in this system are primary aluminum, $\alpha$ lead and $\beta$ tin.

The upper critical solution temperature and composition have not yet been determined for the partially miscible region in the Al-Pb-Sn system. The other region of interest is the solid phase of Pb-Sn at approximately 150°C. Almost everyone who has studied the Pb-Sn system has reported an evolution of heat upon cooling alloys of certain compositions. The number of theories presented to explain this heat effect is almost equal to the number of investigators but no real evidence has been given to support any of the theories.

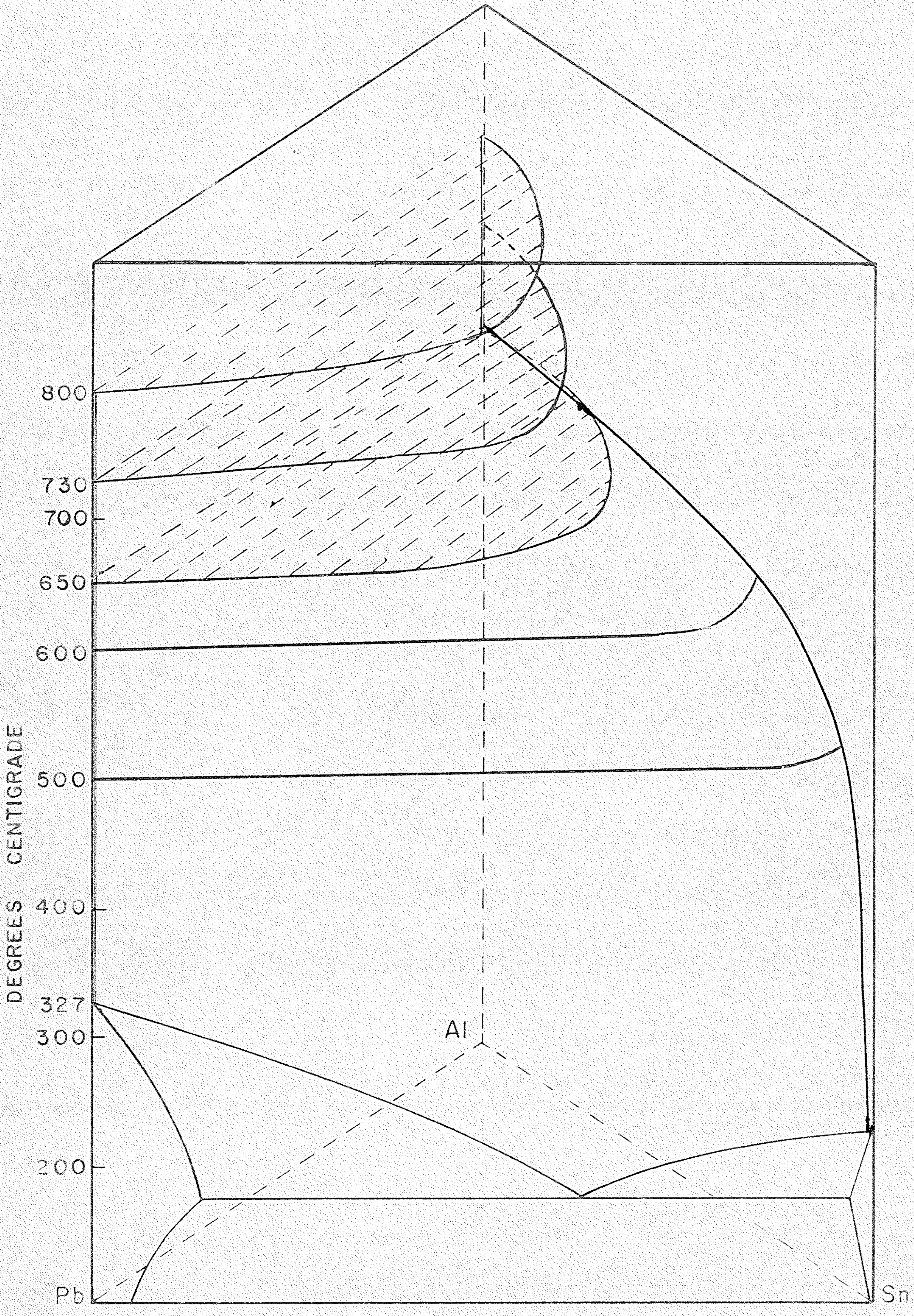

800
730
700
650
600
500
400
327
300
200
DEGREES CENTIGRADE
Al
Pb
Sn

PLATE 18.

## SUMMARY

1. The equilibrium diagram of the system Al-Pb-Sn has been investigated between 660°C. and room temperature.

2. The 500 and 600°C. isotherms are continuous curves, extending from the Al-Pb binary system to the Al-Sn binary system. The phases present are solid aluminum and homogeneous liquid.

3. The solubility of aluminum in tin, between 400 and 645°C, as determined by the isothermal method, was found to be less than previously reported.

4. The ternary eutectic temperature of the Al-Pb-Sn system was found to be 183.0°C with an eutectic composition of 0.08 weight per cent aluminum, 38.1 weight per cent lead, 61.7 weight per cent tin.

5. The solid phases present in this system at room temperature are primary aluminum, $\alpha$ lead and $\beta$ tin.

6. Hardness tests (Brinell Ball and Diamond Pyramid) show that the ternary eutectic alloy is the hardest of this system.

7. When the alloys are used as solder the joint made using Al-Pb-Sn eutectic composition has the greatest shear strength.

## BIBLIOGRAPHY

1. Alexjeff; Bull. Soc. Chem., 38, 145 (1882).
2. Plato, W.; Z. Physikal Chem., 55, 721 (1906).
3. Roberts-Austen, W.C.; "Fifth Report, Alloys Research Committee", Proc. Inst. Mech. Eng., 35, (1899).
4. Beilby, G.T.; Proc. Roy. Soc. 72, 227 (1903).
5. Mantell, C.L.; "Tin", Second Edition, Reinhold Publishing Corp.
6. Mayuyama, Y.; Science Repts. Tohoku Imp. Univ., First Ser., 20, 649 (1931).
7. Wright, C.R.A.; J. Soc. Chem. Ind., 9, 944 (1890). 11, 492 (1892
8. Pecheux. H.; Compt. Rend. 138, 1042 (1904).
9. Gwyer, A.G.C.; Z. Anorg. Allegem. Chem., 57, 113 (1908).
10. Hansen, M. and Blumenthal, B.; Metalwirtschaft 10 925 (1931).
11. Claus, W.; Aluminium, 18, 544 (1936).
12. Kempf, L.W. and Van Horn, K.R., Amer. Inst. Mining Met. Engrs. Inst. Metals Division, Tech. Publ. No. 990, 12 (1938).
13. Campbell, A.N. and Ashley, R.W.; Can. Jour. Res. B, 18, 281 (1940).
14. Roberts-Austen, W.C.; Fourth Report to Alloys Research Committee Inst. Mech. Engrs., (1897).
15. Rosenhain, W. and Tucker, P.A.; Phil. Trans. Roy. Soc. (London). A209, 89 (1908).
16. Degens, P.N.; Z. Anorg. Chem. 63, 207 (1909).
17. Parravano, N. and Scortecci, A; Gazz. Chem. ital. 50, 83 (1920).
18. Feffery, F.H.; Trans. Faraday Society, 24, 209 (1928).
19. Honda, K. and Abe, W.; Sci. Rep. Tohoskei Imp. Univ. 19, (1), 315 (1938).
20. Stockdale, D.; J. Inst. Metals, 49, 267 (1932).
21. Heycock, C.T. and Neville, F.H.; J. Chem. Soc., 57, 376 (1890).

22. Gautier, H.; Bull. Soc. Encour. Ind. Nat., 1, 1293 (1896).

23. Gwyer, A.G.C.; Z. Anorg. Chem., 49, 311 (1900).

24. Campbell, W. and Matthews, J.A.; J. Amer. Chem. Soc., 24, 253 (1902).

25. Lorenz, R. and Plumbridge, D.; J. Anorg. Allgem. Chem., 83, 243 (1913).

26. Losana, L. and Carozzi, E.; Gazz. Chim. ital., 53, 546 (1923).

27. Sully, A.H., Hardy, H.K. and Heal, T.J.; J. Inst. Metals, 76, 269 (1949).

28. Wright, C.R.A.; Proc. Roy. Soc. 52, 14 (1892).

29. Lorenz, R. and Erbe, F.; Z. Anorg. Chem. 183, 328 (1929).

30. Davies, M.H.; J. Inst. Metals, 81, 415 (1953).

31. Lutz, B.C. and Wood, J.H.; Can. Jour. Res. A., 26, 145 (1948).

32. Symposium, "Temperature-Its measurement and Control in Science Industry, Am. Inst. Phys. (Rheinhold Publishing Company pp. 1294-95 (1941).

33. Villela and Beregekoff; Ind. Eng. Chem., 19, 1049 (1927).

34. Schaefer, T.P.; M.Sc. Thesis, University of Manitoba, (1955).

35. "Metals Handbook", The American Society for Metals, pp. 93-94.

36. Seltz, H.; J. Amer. Chem. Soc., 56, 307 (1934).