THE EFFECTS OF COMPOSITION ON THE DIHEDRAL ANGLES AND INTERFACE ENERGIES IN SOME TERNARY ALUMINUM ALLOYS

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SUMMARY

The purpose of the present investigation was to determine the changes in dihedral angle and interfacial energies with composition when small additions of copper, bismuth, cadmium and indium were made to an Al-Sn alloy containing nominally three percent tin. The work was a continuation of the work carried out by previous investigators, who studied the effects of small additions of a third element to an Al-Sn binary alloy.

To obtain the desired ternary alloys used in this work high purity (99.99+%) alloying elements were melted under carefully controlled conditions, cast into rods and machined into test specimens. The test specimens were cold worked and then annealed to change the as cast grain structure to one with uniform grain size and equilibriated grain boundaries. The specimens were then submitted for a spectrographic analysis. After analysis all specimens were reheated to the test temperature, held there for five hours, water quenched, polished and etched in preparation for microscopic examination of the shape of the liquid phase present at the test temperature.

The results obtained showed that the dihedral angles and interfacial energies exhibited by the Al-Sn binary alloy were increased appreciably by the addition of bismuth, cadmium, or indium in increasing quantities. This was attributed to the decreasing solubility of aluminum in the liquid phase caused by the addition of these elements (i.e. bismuth, cadmium, indium) which increased the amount of the liquid phase without increasing the amount of aluminum dissolved in it. The decrease in

solubility of aluminum in the liquid phase brought about an increase in composition difference between the solid and liquid phases which increased the solid-liquid interfacial energy and dihedral angle.

The addition of copper in increasing amounts to an Al-Sn alloy caused a slight but steady decrease in the relative interfacial energy. This was attributed to the decrease in compositional difference due to the solubility of copper in both solid and liquid phases. This decrease in compositional difference brought about a decrease in relative interfacial energy and dihedral angle. It is not possible to say precisely how this decrease in relative interfacial energy is brought about whether by a change in the grain boundary energy or by a change in the solid-liquid interfacial energy.

It was concluded that the relative composition of the two phases existing above the solidus is an important factor in determining the shape of intergranular liquid films at temperatures above the solidus. It was also noted that the solubility or percentage of the higher melting point constituent in the liquid phase and the interfacial energy between the solid and liquid phase appears to be related by the Gibbs adsorption equation.

CHAPTER I

INTRODUCTION

Definition of the Problem

The physical and mechanical properties of metals above the solidus have long been of interest to the foundry, welding and hot forming industries.

During the melting or solidification of an alloy a temperature range is usually found in which the presence of a liquid phase may be detected at the grain boundaries of a solid. It is generally believed that the presence of this liquid phase causes embrittlement of the alloy because a lack of sufficient cohesion exists between the solid grains. This embrittlement results in hot tearing in castings and welds and in hot shortness in the working of alloys at elevated temperatures. It has been found that relatively low mechanical and thermal stresses are sufficient to cause failure.

The degree of embrittlement and thereby the susceptibility of an alloy to hot shortness is believed to be determined by the shape of the intergranular liquid phase. Two factors which are known to control the shape of the intergranular liquid are the temperature and composition of the alloy.

In the present work the effects of changes in composition on the shape of the intergranular liquid is investigated. Additions of bismuth, cadmium, copper and indium are made to an aluminum alloy containing nominally three percent tin to determine the effects of variations in composition on the dihedral angle and relative interfacial energy at temperatures above the solidus.

Historical Background

A number of investigators have attempted to show the relationship between a liquid phase at the grain boundaries of an alloy and the hot shortness characteristics of that alloy. Pellini[1] conducted radiographic studies to show that the cracks associated with hot tearing occur at temperatures above the solidus. Singer and Cottrell[2] showed that the presence of a liquid phase has a marked effect on the super solidus strength and ductility. Rosenberg, Flemings and Taylor[3] in a study of the solidification of aluminum castings have indicated the importance of intergranular liquid films and shown that their shape and distribution at the end of solidification effect the hot tearing characteristics of the material. Rogerson and Borland[4] have also suggested that the shape of the intergranular liquid is an important factor in determining the susceptibility of a material to hot shortness. A convenient measure of the shape of the intergranular liquid is the dihedral angle. Rogerson and Borland[4] showed that on a comparative basis materials having the lowest dihedral angles at a given temperature gave the greatest severity of cracking. They stated that liquid in the form of globules should be less harmful than liquid in the form of extensive films, as more intergranular cohesion should be possible.

The shape of intergranular films are determined to a large extent by the ratio between the solid-liquid interfacial energy (γ_{LS}) and the grain boundary energy (γ_{SS}). This ratio, (γ_{LS}/γ_{SS}, relative interfacial energy) may be found from the following expression:

$$\gamma_{LS}/\gamma_{SS} = \frac{1}{2 \cos \frac{\theta}{2}}$$

where θ = dihedral angle

Ikeuye and Smith[5] investigated changes in the dihedral angle and relative interfacial energy with temperature for a number of ternary alloys formed when small additions of bismuth, cadmium, copper, lead and zinc were made to an aluminum-tin alloy. They found that in most instances changes in the dihedral angle were caused by compositional changes in the liquid phase; as the composition of the liquid approached that of the solid the dihedral angle decreased. They noted that the addition of a third element which was soluble in both the liquid and solid phases at a given temperature may decrease the dihedral angle (e.g. the addition of copper or zinc) but otherwise the ternary alloys formed exhibited dihedral angles between those of the aluminum-tin binary alloy and those of the binary alloy of aluminum with the added element.

Rogerson and Borland[4] showed that the susceptibility of an aluminum-tin alloy to hot cracking can be reduced by small additions of cadmium. It was found that the cadmium gave an increase in the dihedral angle at all temperatures above the solidus.

Dwarakadas and Krishnan[6] investigated the changes in dihedral angle and relative interfacial energy with temperature when small additions of magnesium, iron, silicon, maganese, sulphur, cobalt and silver were made to a copper alloy containing three percent bismuth. They found that in all cases the added elements gave an increase in the dihedral angle and relative interfacial energy when compared with the values obtained for the simple binary alloy at the same temperature.

Tundermann[7] investigated the changes in dihedral angle and relative interfacial energy with temperature when small additions of copper, silicon, antimony, indium, lithium and magnesium were made to an aluminum alloy containing nominally three percent tin. Tundermann[7] noted that: (1) When the added element was soluble in both the liquid and solid phases at a given temperature its addition decreased the dihedral angle (e.g. copper and silicon). (2) When the added element formed an intermetallic compound with the aluminum its addition had no effect on the dihedral angle (e.g. antimony). (3) When the added element was soluble in the tin only at a given temperature its addition caused a change in dihedral angle to a value which was between that of the aluminum tin binary alloy and that of the binary alloy of aluminum with the added element (e.g. indium). (4) When the added element formed an intermetallic compound with the tin its addition eliminated the effect of the tin and the resulting dihedral angle was approximately that of the binary alloy of aluminum with the added element (e.g. magnesium and lithium).

Taylor[8] has shown that it is possible to calculate the grain boundary energy (γ_{SS}) if it is assumed that: (1) The surface energy of a solid metal or alloy can be estimated from the value for the corresponding liquid phase by applying a correction for the increase of surface energy on freezing, amounting to one-third of the liquid value. (2) The grain boundary energy of a metal or alloy is taken as being one-third of the corresponding solid surface energy. From a knowledge of the grain boundary energy and relative interfacial energy $(\gamma_{LS}/\gamma_{SS})$ the solid-liquid interfacial energy (γ_{LS}) can be obtained. From an analysis of the data for the solid-liquid interfacial energies obtained for copper/lead plus bismuth systems and aluminum/tin plus lead, bismuth or cadmium systems Taylor[8] arrived at the following conclusions: (1) The magnitude of the solid-liquid interfacial energy appears to be closely related to the solubility of the solid phase in the liquid. (2) The solid-liquid interfacial energy apparently changes with solubility according to the Gibbs adsorption equation[9], which indicates that an incremental change in interfacial energy is proportional to a corresponding incremental change in the $\log_{10}$ of the solubility or concentration of the solid element in the liquid phase.

True Dihedral Angle, Measurement

Accurate measurement of the dihedral angles present in a specimen is difficult because the shape of the intergranular liquid region involves two planes in three dimensions and only a two dimensional section through the dihedral angle is possible. Provided that the two dimensional section is statistically random, then the true dihedral angle can be determined within set limits of accuracy.

Harker and Parker[10] showed that the mode of the frequency distribution of observed angles is within five degrees of the true angle if the true dihedral angle is 120 degrees. Smith[11] made calculations to show that the same generalization could apply to dihedral angles of 30, 60, 90 and 150 degrees. However, this procedure of the determination of the statistical mode is time consuming since experience has shown that more than 200 angle observations are necessary before the mode can be clearly indicated. Riegger and Van Vlack[12] found that the true dihedral angle could be determined just as accurately with a minimum of 25 observations if the median angle is used in place of the mode angle. They showed that the difference between the true dihedral angle and the median angle is never more than one degree.

The number of observations required to attain a desired accuracy using the Riegger and Van Vlack[12] technique varies with the true dihedral angle as shown in Figure 1. Riegger and Van Vlack[12] also stated that any attempt to determine the true dihedral angle with greater accuracy than that which is provided with 25 observations is seldom justified for two reasons: "(1) an individual's reproducibility in the reading of any one angle may vary from ±1 to ±5 degrees:" and "(2) dihedral angles of one type within a sample may have a variance." However, this variance can be readily detected by consideration of the cumulative distribution plot for the data obtained from any one specimen. Figure 2 shows how non-equilibrated specimens with a bimodal distribution can be detected by the deviation from the theoretical distribution of data.

Stickels and Hucke[13] have criticized the work of Riegger and Van Vlack[12] from the standpoint that a 25 angle sample of any one specimen can not satisfactorily determine the true median angle, since this sample almost certainly does not describe a normal distribution with the same mean and standard deviation. However, Stickels and Hucke[13] never obtained more than one degree higher than and never lower than the same median angle as found by the Riegger and Van Vlack[12] method when using samples of 100 angle observations or more.

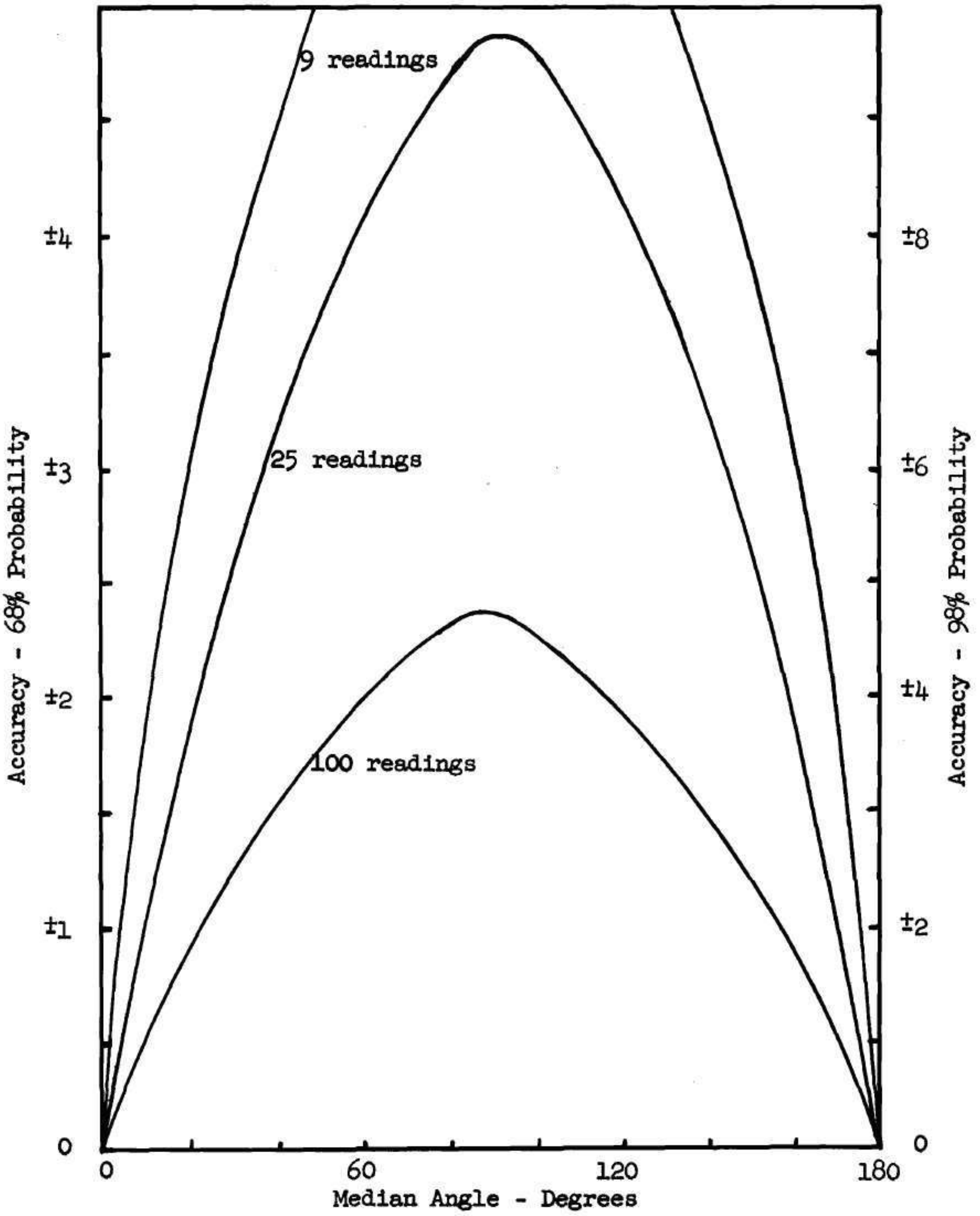

Figure 1. Statistical Accuracy of Random Angle Measurements.[12]

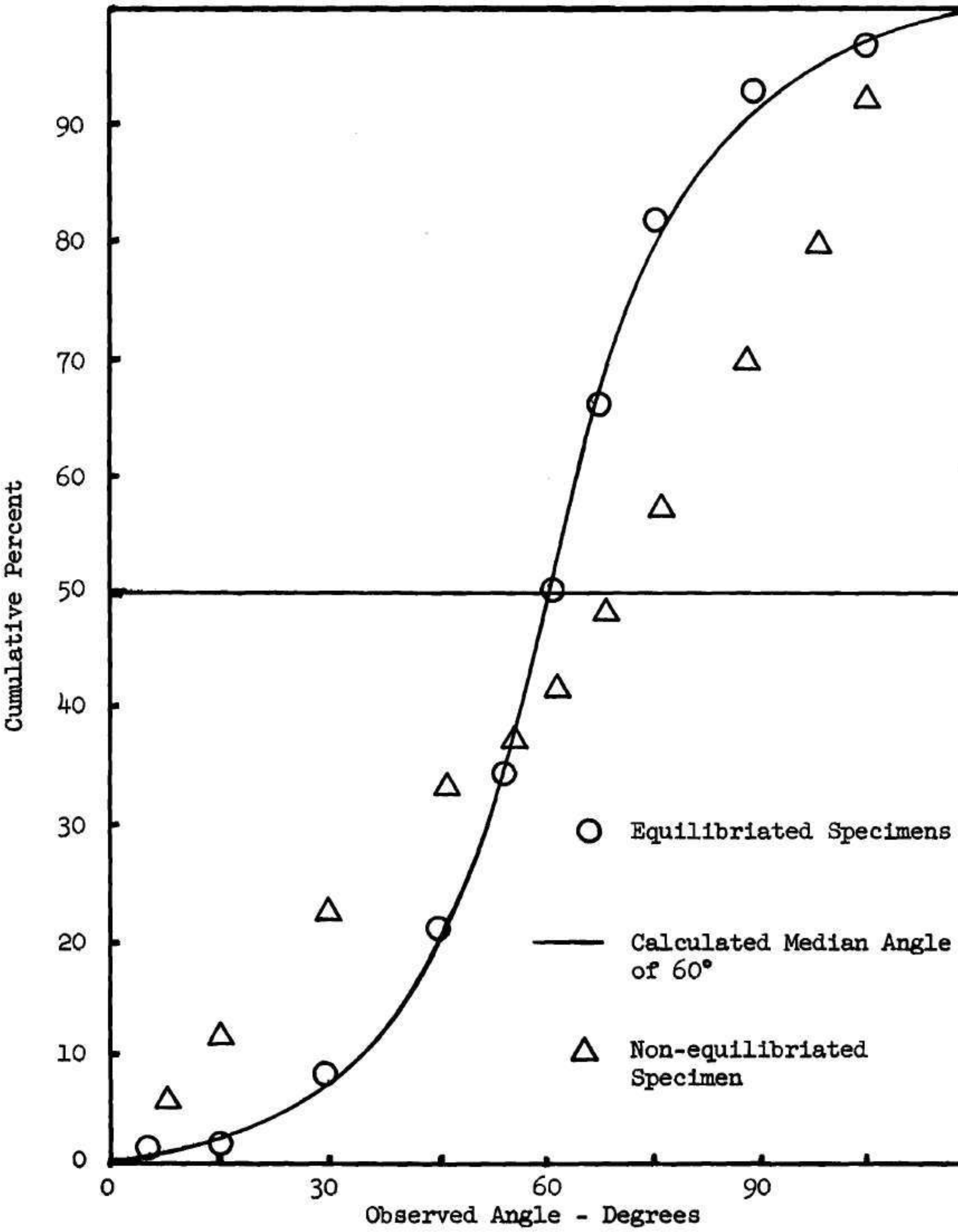

Figure 2. Statistical Distribution of Observed Angles.[12]

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

General

The equipment used to perform the work reported in this thesis can be separated into four sections. These are (1) casting, (2) heat treating, (3) polishing and (4) micro-examination. The second and third sections are described in Appendices A and B respectively. The remaining two sections are described below.

Casting Equipment

A natural gas fired pot furnace and a high purity graphite crucible were used to cast all of the specimens for this work. The graphite crucible was machined from available bar stock and had approximate dimensions of five inches outside diameter, three inches inside diameter and six inches height initially. It was found that the gas flame of the pot furnace burned away the crucible to such an extent that it became necessary to enclose the crucible in a stainless steel cage so that it might be gripped securely for pouring the molten alloy.

The temperature of the melt was measured by means of a thermoelectric pyrometer. A stainless steel skimmer was used in fluxing and skimming slag from the melt. The metal was cast into a split cast iron mold containing three five inch by one-half inch diameter casting holes and one five inch by three-fourths inch diameter sprue which were connected at the bottom by a gate.

Micro-Examination Instruments

Micro-examination of each of the specimens was accomplished using a Unitron Metallograph and Universal Camera Microscope equipped with a Xenon-Tungsten illuminator. This instrument has a revolving objective and photo-eyepiece turret which permits magnifications of 50X, 75X, 100X, 150X, 200X, 300X, 400X, 600X and 800X. The magnified images were cast on a 3-1/4" x 4-1/4" ground glass screen. The specimens were placed on an inverted stage which could be moved in any direction in the plane of the stage by two mechanical adjusting screws. All photomicrographs in this thesis were made using a Unitron Inverted Metallurgical Microscope, Series MEC, equipped with a high intensity Koehler illuminator and a Polaroid Land Camera attachment, type PRM.

CHAPTER III

PROCEDURE

In preparation for melting the materials, each constituent was weighed out on a set of chain-O-matic balance scales according to the percentage desired in the final alloy of 200 grams total weight. Initially only the high purity aluminum was placed in the crucible and melted. After the aluminum was melted, the other constituents of the desired alloy were added and pushed below the surface of the melt with the skimmer. This minimized any possible oxidation of the added elements.

At a melt temperature of approximately 1400°F. the furnace was turned off and the melt fluxed using a chlorine base flux, Foseco degaser No. 450. The flux was held below the melt surface with the skimmer and the chlorine gas allowed to bubble through the melt. Casting was begun at a melt temperature of 1350°F. The mold was preheated to approximately 600°F. before pouring by placing it on top of the furnace while the material was being melted.

To prepare the test specimens, each of the five inch by one-half inch castings was broken off and machined to seven-sixteenths inch diameter, cut into one inch lengths and compressed to approximately one-half inch lengths. This cold working was necessary to produce grain refinement during the subsequent heating and annealing operations. All specimens were heated to a temperature of 1000°F. for a period of three hours and then allowed to cool over night in the closed furnace. This process gave an evenly distributed grain structure of sufficient size to be viewed and inspected by microscopic examination.

Once the desired grain structure had been obtained the specimens were placed in a steel wire basket and put back into the furnace. All of the specimens were heated to the test temperature of 1023°F. at the same time for five hours to insure that the same temperature equilibrium was reached throughout each specimen. The basket containing the specimens was then taken from the furnace and quickly immersed in water. The time taken to transfer the specimens from the furnace to the water quench was approximately one second. This process of quenching all specimens at the same time should preserve that structure present in each specimen at the test temperature. Test temperatures should not vary between specimens. The specimens were now ready for spectrographic analysis and mounting as described in Appendices D and B respectively.

CHAPTER IV

DISCUSSION OF RESULTS

Introduction

The addition of a third element to a binary alloy may result in a change in the type and number of phases present at any particular temperature. At temperatures above the solidus the added element may:

1. Enter into solution in either the liquid or solid phases or possibly both.

2. Be insoluble in either liquid or solid phases.

3. Form intermetallic compounds with either metal from the binary alloy.

Without a complete knowledge of the ternary equilibrium diagram it is difficult to determine the nature of the phases present at a given temperature and composition. Therefore, any discussion must be limited to those phases inferred from the binary equilibrium diagrams[14] of the elements involved.

The Al-Sn equilibrium diagram[14] indicates that at the test temperature of 1023°F. an alloy containing nominally three percent tin would consist of solid grains of pure aluminum with a homogeneous liquid phase of aluminum and tin probably situated at the grain boundaries. Any addition of bismuth, cadmium or indium to the Al-Sn alloy can only add to the liquid phase present since the binary diagrams[14] show them to be soluble in the liquid tin and insoluble in solid aluminum. The test temperature is well above the liquidus lines on any of the binary equilibrium diagrams of tin with the added element. The copper, however, is known to be soluble in both aluminum and tin. Therefore, a certain percentage of the copper will be contained in the solid grains of aluminum and a percentage miscible in the liquid tin and aluminum. It is not possible to say precisely how much copper is contained in either the liquid or solid phases at the test temperature. The distribution and shape of the intergranular liquid films phases present at the test temperature should be retained upon quenching, with the possible exception of any precipitation of intermetallic compounds upon aging.

Calculation of Energies

The relative interfacial energy $(\gamma_{LS}/\gamma_{SS})$ of any specimen for which the median dihedral angle is known may be found by use of the following expression:

$$\gamma_{LS}/\gamma_{SS} = \frac{1}{2 \text{ Cos } \frac{\theta}{2}}$$

where θ = dihedral angle

However, in this work the solid-liquid interfacial energy (γ_{LS}) is of most interest. The relative interfacial energy can be used to calculate the solid-liquid interfacial energy if a good estimate of the grain boundary energy (γ_{SS}) can be obtained. A method of estimating grain boundary energy suggested by Taylor[8] is used in this work. Taylor[8] found from previous experimental work that the surface energy of aluminum at the melting point was 915 ergs/cm^2. By assuming that upon freezing the surface energy would be increased by one-third of the value in the liquid state a value of (915 + 305) = 1220 ergs/cm^2 was estimated for the solid surface energy. He further assumed that the grain boundary energy (γ_{SS}) was one-third of the solid surface energy (1220 ergs/cm^2) and estimated a value of (1220/3) = 405 ergs/cm^2 for the grain boundary energy (γ_{SS}). The value of the solid-liquid interfacial energy (γ_{LS}) may now be obtained from the product of the relative interfacial energy (γ_{LS}/γ_{SS}) calculated from the median dihedral angle, and the grain boundary energy (γ_{SS}). In the above calculations the grain boundary energy (γ_{SS}) is assumed to be independent of temperature.

Values of the median dihedral angle (θ), relative interfacial energy (γ_{LS}/γ_{SS}) and solid-liquid interfacial energy (γ_{LS}) for each alloy in this work are listed in Tables 1 through 4.

It is realized that the grain boundary energy (γ_{SS}) may not be independent of temperature, but its variation, if any, should be small. Rogerson and Borland[4] have estimated the temperature coefficient of grain boundary energy to be about 0.5 ergs $\cdot$ cm^{-2} $\cdot$ deg^{-1} C. Since this work was all conducted at the same temperature, even if the estimated value of grain boundary energy (γ_{SS}) is not exact, the derived solid-liquid interfacial energies will vary from the true values by some constant factor and all trends indicated will remain the same.

Bismuth, Cadmium and Indium Alloys

Since the effects of bismuth, cadmium and indium additions on the Al-Sn binary system seem to be almost identical they will be discussed simultaneously. An explanation of these effects can be found from the pertinent binary equilibrium diagrams (i.e. Al-Sn, Al-Bi, Bi-Sn for bismuth alloys).[14] Bismuth, cadmium and indium are relatively insoluble in aluminum in the solid state, and immiscible with aluminum in the liquid state. However, bismuth, cadmium and indium are miscible with tin in the liquid state. As previously mentioned, at the test temperature any addition of bismuth, cadmium or indium to the Al-Sn alloy can only add to the liquid phase present. This would effectively reduce the concentration of aluminum in the liquid phase. According to Taylor[8] this reduction in concentration of aluminum in the liquid phase should result in an increase in the solid-liquid interfacial energy (γ_{LS}). This increase in solid-liquid interfacial energy would be readily observed as an increase in dihedral angle. The present work agrees with Taylor's[8] generalization in that the dihedral angle and interfacial energy were found to increase with an increase in the amount of bismuth, cadmium or indium present in the alloy (tin content relatively constant) as shown in Figures 3 through 5. Photomicrographs of representative angles of bismuth, cadnium and indium alloys are found in Figures 8 through 13 respectively. Note that there are apparently no intermetallic compounds present in the alloys.

Other investigators[4,5] have shown that as the bismuth, cadmium or indium content in the ternary alloy with aluminum and tin increased at any temperature above the solidus the relative liquid interfacial energy increased. They stated that the values found for any one of the ternary systems would be somewhere between those values found for the Al-Sn binary alloy and the binary alloy of the added element with aluminum. This is true in the present case.

Tables 1 through 3 show the solubility of aluminum in the liquid phase, the median dihedral angle (θ), the relative interfacial energy $(\gamma_{LS}/\gamma_{SS})$ and the solid-liquid interfacial energy (γ_{LS}) of the alloys

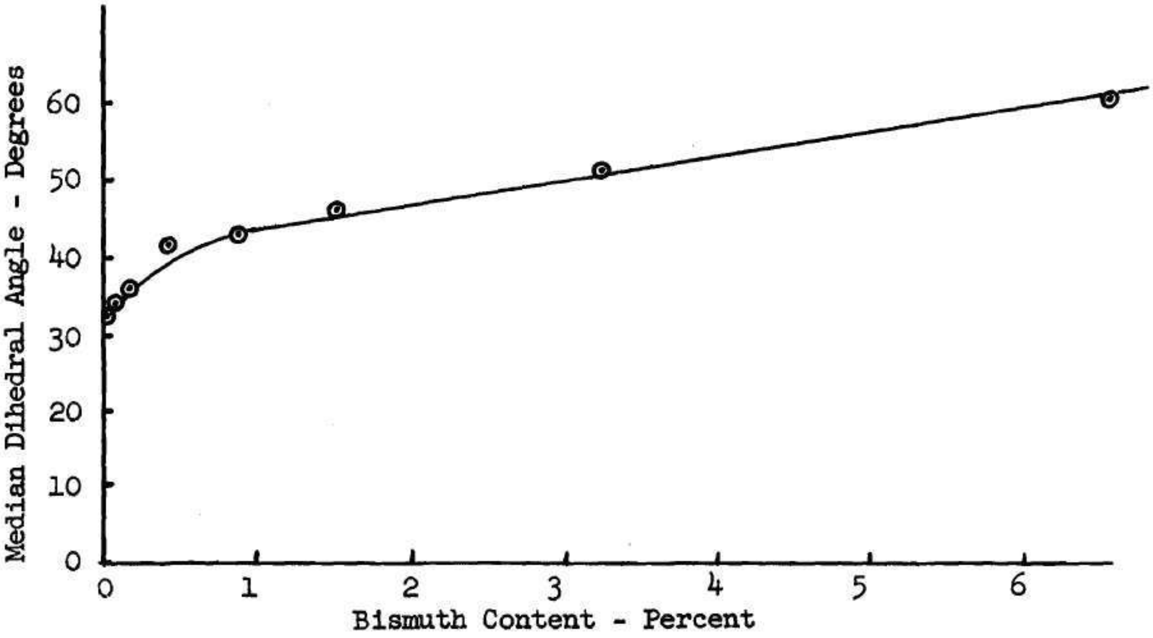

Figure 3. Effect of Bismuth Content on Dihedral Angle.

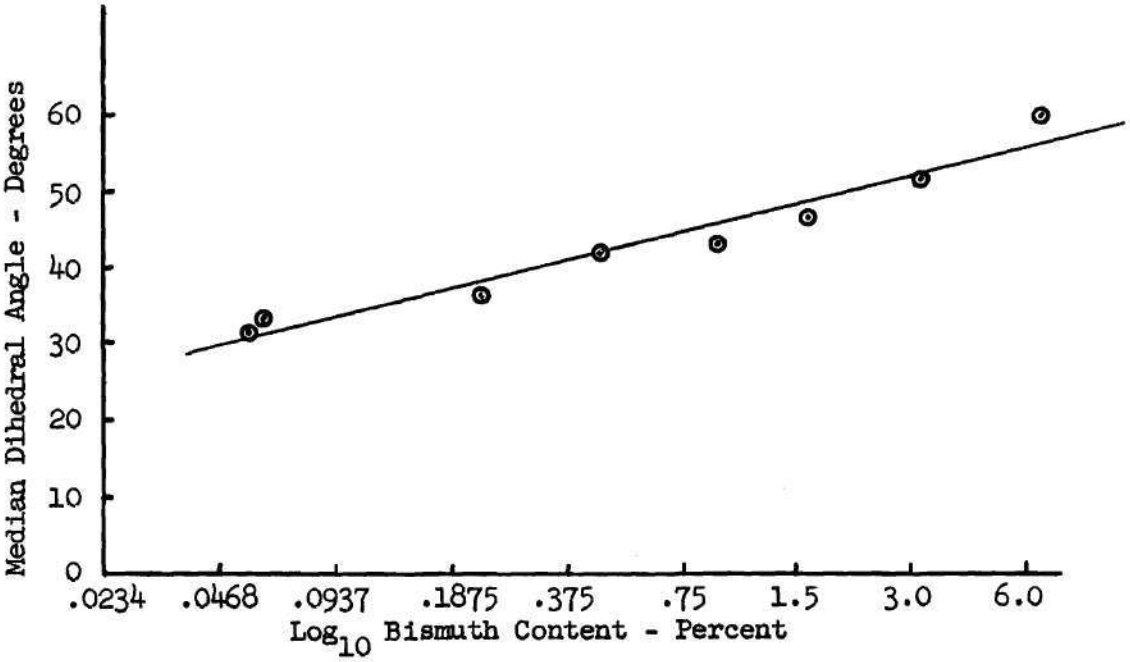

Figure 3A. Effect of Log_{10} Bismuth Content on Dihedral Angle.

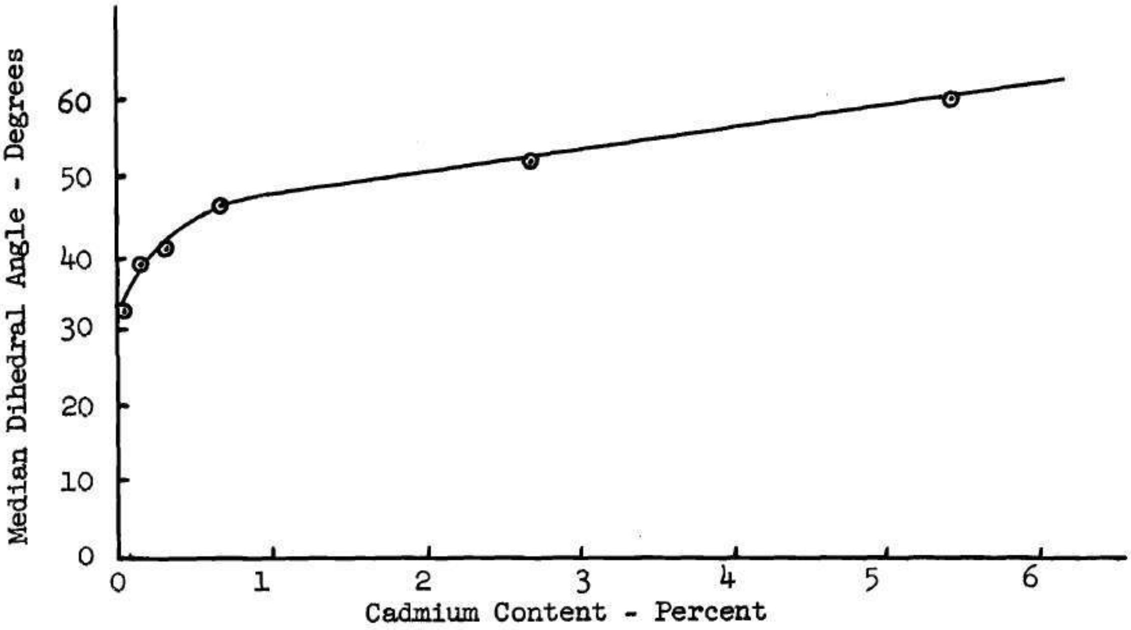

Figure 4. Effect of Cadmium Content on Dihedral Angle.

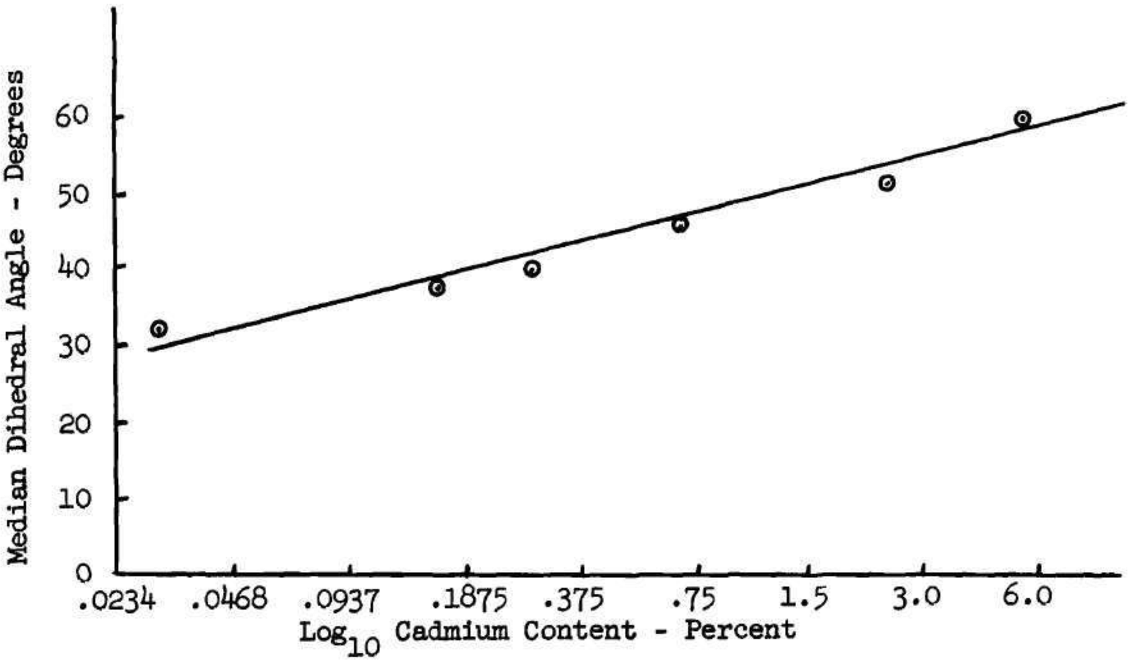

Figure 4A. Effect of Log_{10} Cadmium Content on Dihedral Angle.

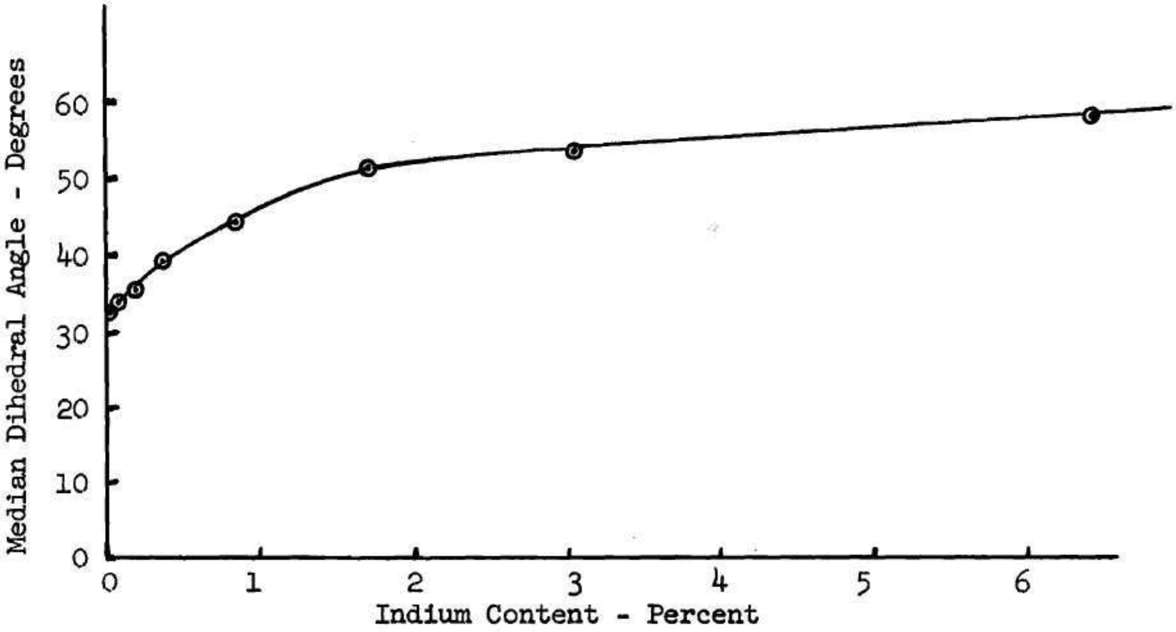

Figure 5. Effect of Indium Content on Dihedral Angle.

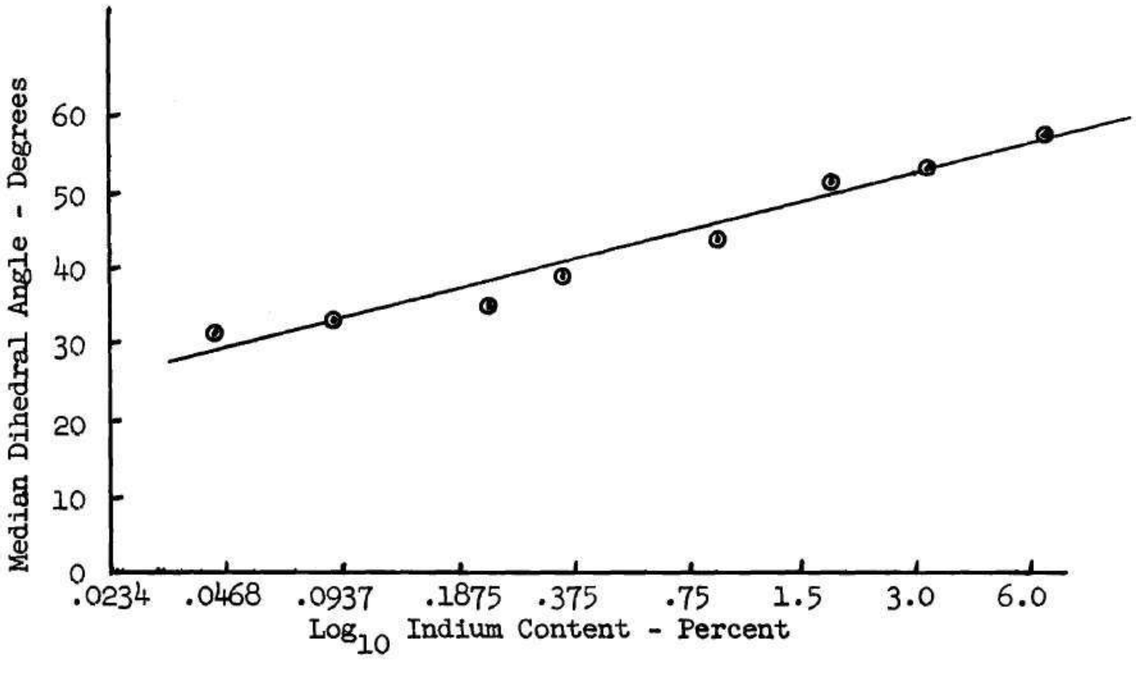

Figure 5A. Effect of Log$_{10}$ Indium Content on Dihedral Angle.

investigated.

Gibbs[9] has proposed that in multiphase systems such as those discussed a surface phase would exist at the solid-liquid interface would contain the same components as the solid and liquid phases but in different proportions. Gibbs[9] stated that the composition of the surface phase would largely control the solid-liquid interfacial energy (γ_{LS}). In the present case it is believed that the aluminum content of the surface phase would control the solid-liquid interfacial energy. As the aluminum content of the liquid increases the aluminum content of the surface phase would also increase. The decrease in the composition difference between the liquid and solid phases would then bring about a decrease in interfacial energy. If the system involved was the binary of bismuth, cadmium or indium with aluminum at temperature in the melting range there would be very little or no aluminum in the liquid phase (therefore no surface phase would exist) since aluminum is insoluble in these metals in this temperature range. If there is tin present in the alloy then the surface phase will contain some tin in which some aluminum will be soluble. When tin is added to these binary systems (Al-Bi, Cd or In) the solid-liquid interfacial energy (γ_{LS}) drops very rapidly initially, then as more tin is added the decrease is much less marked. Taylor[8] has explained this initial rapid drop as occurring while the so-called monolayer is first forming. Once the monolayer has formed the surface adsorption and corresponding reduction in solid-liquid interface energy (γ_{LS}) becomes less marked and finally becomes proportional to the log of the change in concentration of aluminum in the liquid.

The work in this thesis was in the region of composition after the monolayer had formed because of the comparatively large tin content. Indications are that there is no marked initial change in interfacial energy as the initial amount of the added element is made to the Al-Sn system and the solid-liquid interfacial energy (γ_{LS}) changes proportional to the log change in solubility of aluminum in the liquid phase. Figure 6 shows a plot of Log solubility of aluminum in the liquid phase vs solid-liquid interfacial energy (γ_{LS}).

Copper Alloys

An explanation of the effects of copper additions to the Al-Sn system can be found by reference to the Al-Cu, Al-Sn and Cu-Sn binary diagrams[14]. These diagrams indicate that at the test temperature the copper is soluble in both aluminum and tin, which as previously mentioned means that a percentage of the added copper is contained in the solid aluminum grains and in the liquid mixture of aluminum and tin. Tundermann[7] stated that copper has a greater solubility in aluminum than in tin and suggested that at a temperature a few degrees above the solidus the ternary alloy of Al-Sn-Cu would consist of a liquid phase of tin and a solid solution of copper in aluminum. As the temperature increased toward the liquidus the solubility of copper in tin would increase until the copper was more evenly proportioned between the aluminum and tin. At the test temperature of 1023°F. it is not possible to say precisely how much copper is contained in either the liquid or solid phase. However it is probably reasonable to assume that the compositional difference between the solid and liquid phases is lower at test temperature than at a temperature a few degrees about the solidus. As greater quantities of copper are added to the Al-Sn

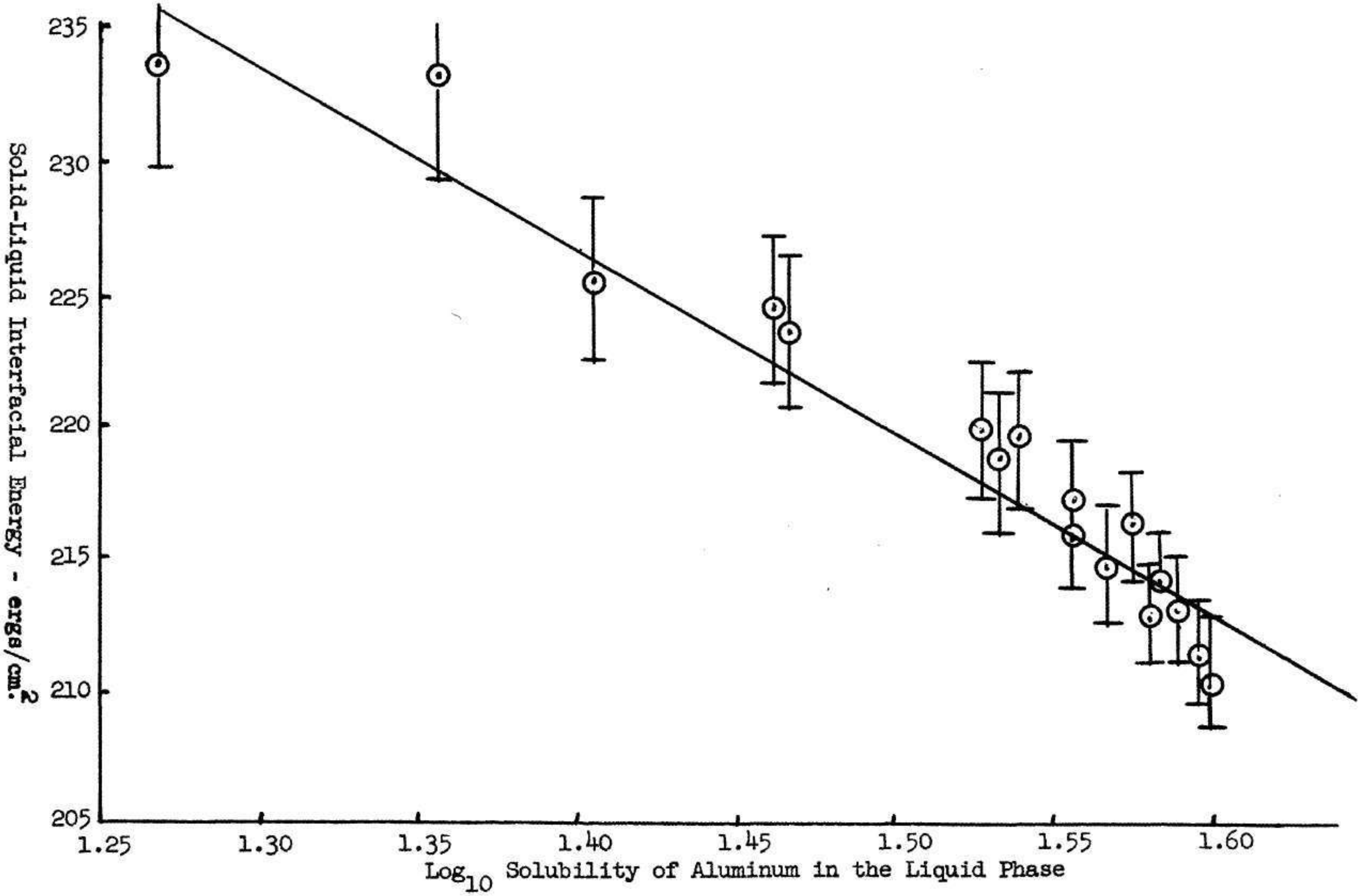

Figure 6. Effect of Log$_{10}$ Solubility of Aluminum in the Liquid Phase on Solid-Liquid Interfacial Energy.

alloy at the test temperature we might also expect a decrease in the compositional difference between the liquid and solid phases. This decrease in compositional difference would result in a decrease in the solid-liquid interfacial energy which would be observed as a decrease in dihedral angle. The results of this work support this line of thought in that the median dihedral angle (θ) and relative interfacial energy $(\gamma_{LS}/\gamma_{SS})$ were found to decrease with an increase in the amount of copper present in the alloy as shown in Figure 7. It should be noted that the grain boundary energy (γ_{SS}) would be different in this case where the solid grains are something other than pure aluminum than in the case of the bismuth, cadmium or indium alloys where the solid grains were almost pure aluminum. The grain boundary energy (γ_{SS}) cannot be computed here since the exact composition of the solid grains is unknown. It is also not known whether the grain boundary energy remains constant or changes with an increase in copper content. Ikeuye and Smith[5] obtained similar experimental results with three Al-Sn-Cu alloys. They stated that; "Copper is soluble in both the solid and liquid phases in Al-Sn alloys and acts slightly in the direction of decreasing the value of relative interfacial energy -- whether by modification of the grain boundary energy (γ_{SS}) or of the solid-liquid interface cannot be said."

Photomicrographs of representative specimens for the copper alloys are found in Figures 14 and 15. Note the presence of intermetallic compounds $(CuAl_2)$ within the grains and at the grain boundaries. These compounds are believed to have been precipitated during an aging process occurring sometime after quenching. They did not exist as compounds at test temperature since the aluminum is capable of holding up to six percent

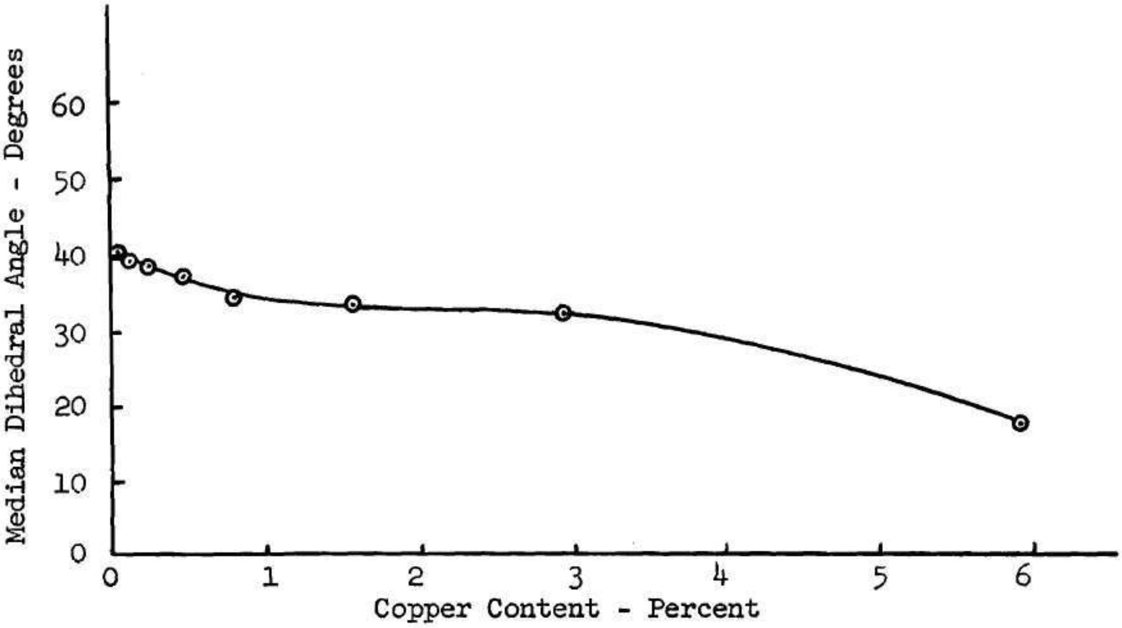

Figure 7. Effect of Copper Content on Dihedral Angle.

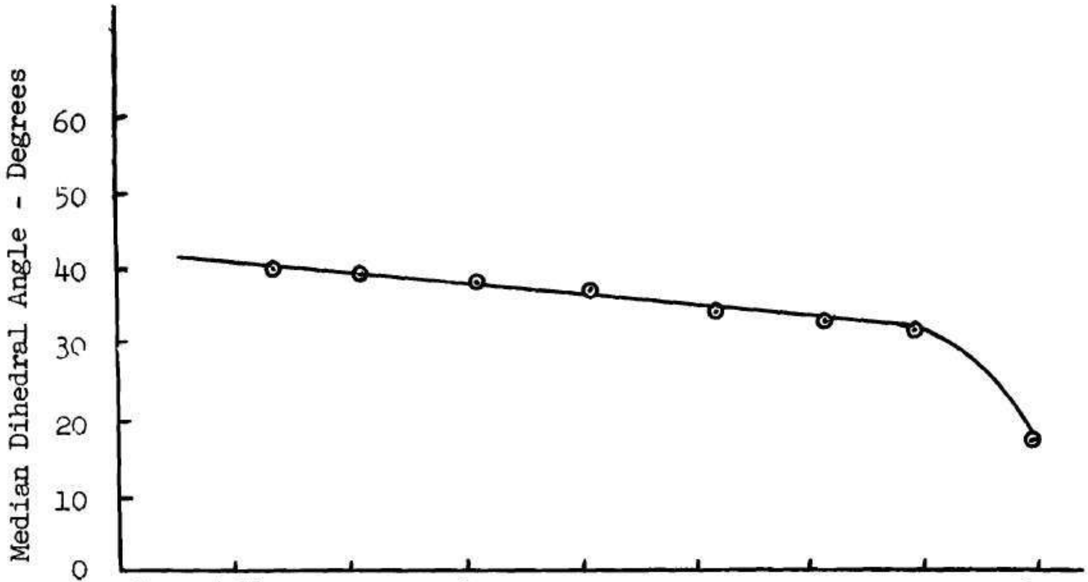

Figure 7A. Effect of Log$_{10}$ Copper Content on Dihedral Angle.

copper in the alpha (α) solution at this temperature. No attempt was made to fit the results for the copper alloys to the Gibbs equation[9] since the solubility of the solid phase elements in the liquid phase was unknown.

The results obtained by Tundermann[7] (see Figure 6) for the addition of lithium and magnesium to the Al-Sn alloy seem to fit the Gibbs equation very well. This would seem to indicate that the effects of temperature and composition on the relative interfacial energies in metallic systems can be satisfactorily interpreted by means of the Gibbs adsorption equation providing the solubility of the high melting point constituent in the liquid phase can be determined.

Reliability of Obtained Data

Reliability of Technique and Results

The study of the alloys in this work was conducted not only to compare data obtained with some previous work, but to check the techniques used in analyzing the data. The results obtained are consistent with the works of Taylor (bismuth and cadmium alloys)[8], Rogerson and Borland (cadmium and indium alloys)[4], Ikeuye and Smith (copper, cadmium and bismuth alloys)[5], and Tundermann (copper and indium alloys)[7] which were conducted on a more limited range of composition. The present work is a more detailed investigation of the effects of composition than others previously undertaken.

The technique of obtaining median dihedral angle by graphically plotting cumulative percent versus observed angle as suggested by Riegger and Van Vlack[12] proved as accurate as other techniques if 100 observations were recorded rather than the 25 observations previously suggested. For a sample of 100 observations and a confidence limit of 98 percent the maximum deviation of median dihedral angle is ±4 degrees. But for a sample of only 25 observations the maximum deviation is ±8 degrees.

To check the calculated statistical deviation of median dihedral angle samples of 25 and 100 angle observations from the entire population were recorded for each of a number of specimens. The median dihedral angle indicated by the sample of 25 observations was for some specimens as much as six degrees below that median dihedral angle indicated by the sample of 100 observations on the same specimen. In many cases the data for samples of only 25 observations did not coincide with the theoretical frequency distributions as indicated by Riegger and Van Vlack[12]. This would indicate that Stickels and Hucke[13] were correct when they stated that a sample of only 25 observations did not accurately describe the entire population since it would not give a normal distribution with the same mean and standard deviation. However, samples of 100 observations did fit the theoretical frequency distribution very closely, which would indicate that this larger sample did represent the entire population in that it was a normal distribution with the same mean and standard deviation as the population.

Reproducibility

The reproducibility of the tests was checked while studying the Al-Sn-Cd and Al-Sn-In alloys. Two of the cadmium alloys cast had only a very small percentage difference in cadmium content. The two alloys were analyzed independently, not knowing the composition of either.

The indicated median dihedral angles were identical for the two alloys. A similar check was made on the indium alloys in that two samples of 100 observations of the same alloy were independently recorded and analyzed. The deviation between the median dihedral angles indicated was only one degree.

CHAPTER V

CONCLUSIONS

The effects of increasing additions of bismuth, cadmium, indium and copper on the dihedral angles and relative interfacial energies of the Al-Sn binary system have been studied. As a result of this work, the following conclusions can be drawn:

1. The dihedral angle and relative interfacial energy of the Al-Sn alloy is increased at any particular temperature by increasing additions of bismuth, cadmium or indium.

2. The addition of bismuth, cadmium or indium to the Al-Sn alloy apparently does not change the grain boundary energy by any significant amount, but does increase the solid-liquid interfacial energy by decreasing the solubility of aluminum in the liquid phase.

3. The change in solid-liquid interfacial energy appears to be related to the change in solubility of aluminum in the liquid phase by the Gibbs adsorption equation.

4. The effects of temperature and composition on the relative interfacial energies in any metallic system apparently can be satisfactorily interpreted by means of the Gibbs adsorption equation providing the solubility of the higher melting point constituent in the liquid phase can be determined.

5. The dihedral angle and relative interfacial energy of the Al-Sn alloy are decreased at any particular temperature by increasing

additions of copper.

6. This decrease in dihedral angle and relative interfacial energy brought about by an increase in the copper content of the alloy is caused by a decrease in composition difference between the solid and liquid phases.

CHAPTER VI

RECOMMENDATIONS

In the course of this work several interesting points arose which were beyond the scope of the work as originally visualized. Investigation of these points would be an important and logical extension of the work as completed to date in the study of material properties above the solidus temperature. These points are as follows:

1. With the aid of a micro-probe analyser, identify the constituents present in both phases of the Al-Sn-Cu alloys considered in this investigation and determine the relative composition of each so that the location of added amounts of copper at the test temperature might be known.

2. With a knowledge of the percent of copper in each phase at the test temperature determine the grain boundary energy (γ_{SS}) of the alloy and see if it varies appreciably with composition.

3. With some knowledge of grain boundary energy (γ_{SS}) and relative interfacial energy $(\gamma_{LS}/\gamma_{SS})$ compute the solid-liquid interfacial energy (γ_{LS}) of the Al-Sn-Cu alloys to see if compositional effects can also be described by the Gibbs adsorption equation.

APPENDIX

APPENDIX A

HEAT TREATING

An electrical multiple unit furnace with a Honeywell Electronik 15 temperature controller and recorder was used for heating all specimens. The furnace was also spot checked during heating and soaking by the use of chromel-alumel thermocouples and a Leeds and Northrup millivolt potentiometer. An ice bath cold junction was used as a reference for determining temperature. The thermocouples were guaranteed to have an accuracy within ±7°F. at the temperature used in this work. The thermocouple-potentiometer check on the furnace showed that the specimens had only a ±2°F. variation during the on-off cycling of the furnace temperature control.

All quenching was done in water.

APPENDIX B

POLISHING AND ETCHING PROCEDURES

The specimens containing cadmium, copper and bismuth were mounted in bakelite, in preparation for polishing. The specimens containing indium were mounted in a cold curing plastic since the setting or hardening temperature of bakelite is above the melting temperature of pure indium and it was feared that some indium on the surface of the specimens might be lost. After all specimens had been mounted in plastic blocks the blocks were placed in a lathe and the face containing one surface of the specimen was machined off to a depth of about three-sixteenths inch. This insured that the surface to be inspected would be that of the interior of the specimen.

Each specimen was then ground on grades 180, 240, 320, 400 and 600 silicon carbide paper using a rotating wheel and continuously running water. With each paper care was taken to be sure that all scratches obtained through using the previous grade paper had been removed.

Initially polishing was attempted using 14, 9 and 3 micron diamond abrasives respectively. This gave a usable surface finish but proved to be a slow operation. In order to obtain a better surface more quickly two grades of aluminum oxide abrasive were readily available and proved to give an acceptable surface finish very quickly. After grinding the specimens on the 600 grade paper, the more coarse of the aluminum oxides (a grade M309W polishing compound produced by American

Optical Company) was mixed with water on a rotating polishing wheel covered with an A. Buehler Microcloth and used to remove all of the scratches left by the 600 grade paper. In order to improve the surface finish still more another A. Buehler Microcloth was mounted on a stationary, flat glass plate and covered with a thick paste of 0.3 Micron Linde Metallographic Polishing Compound. This stationary plate was used to remove most of the minute scratches left by the previous abrasive.

With a satisfactory polish obtained all specimens were initially etched by swabbing with a cotton swab saturated in 0.5 percent hydrofluoric acid in water for 15 seconds and rinsing in running water. This process removed all of the plastically flowed surface distorted during polishing. This also gave the dihedral angles of the indium and copper alloys a distinguishable outline. However, the cadmium and bismuth alloys required further etching to outline their dihedral angles. A 2.0 percent nitric acid in ethanol solution was used to outline the cadmium alloys and a 1.0 percent hydrochloric acid in water solution used on the bismuth alloys. These etchants were applied by swabbing as with the initial etch for varying lengths of time (5 to 15 sec.). It was found that the etching times were dependent largely on the alloy composition. The alloys with the highest percentages of cadmium and bismuth etched more quickly than those of lower content.

APPENDIX C

ANGLE MEASUREMENT

To measure the dihedral angles in each alloy, the Unitron Metallograph and Universal Camera Microscope, previously described was used with the Xenon illuminator. The images of the grain structure and dihedral angles cast on the 3-1/4" x 4-1/4" ground glass screen at 600X and 800X were of sufficient size to be accurately measured. A clear plastic template containing a series of angles at 5° intervals from 5° to 60° was used to measure the dihedral angle as cast on the screen. It was found that any two readings taken on the same angle varied by no more than two degrees. Also by representing the data on cumulative percentage basis at 5° intervals the 5° interval on the template was sufficient to give very accurate and repeatible results.

In order to obtain a random selection of angles the specimen was placed in position on the inverted stage and brought into focus at the power required to accurately measure the existing angles. The stage was then randomly positioned in relation to the objective and all angles appearing on the screen measured and recorded. This operation was repeated until about 100 observations had been made and recorded.

Cumulative percent versus observed angle graphs were constructed for each specimen using the data as collected. The median dihedral angle, that is the angle at which the curve fitting the data crosses the 50 percent cumulative percent line was found. The angles shown in the results are median angles and have not been corrected to true dihedral angles.

Table 1. Dihedral Angles and Solid-Liquid Interfacial Energies for the Bismuth Alloys

Percent Bismuth	Solubility of Aluminum in Liquid Phase At. Percent	Median Dihedral Angle Deg.	Relative Interfacial Energy	Solid-Liquid Interfacial Energy $ergs/cm^2$
0	40.0	31°	0.51858	210.00
0.052	39.5	32°	0.52015	210.66
0.060	39.4	34°	0.52285	211.75
0.22	38.8	36°	0.52576	212.93
0.47	37.75	42°	0.53556	216.90
0.91	36.1	43°	0.53740	217.65
1.58	33.7	46°	0.54318	219.99
3.26	29.0	51°	0.55396	224.35
6.61	22.7	60°	0.57737	233.83

Table 2. Dihedral Angles and Solid-Liquid Interfacial Energies for the Cadmium Alloys

Percent Cadmium	Solubility of Aluminum in Liquid Phase At. Percent	Median Dihedral Angle Deg.	Relative Interfacial Energy	Solid-Liquid Interfacial Energy $ergs/cm^2$
0	40.0	31°	0.51858	210.0
0.019	39.60	32°	0.52015	210.66
0.032	39.50	33°	0.52149	211.20
0.152	38.55	38°	0.52882	214.17
0.296	37.40	40°	0.53208	215.49
0.680	34.75	46°	0.54318	219.99
0.672	34.80	46°	0.54318	219.99
2.66	25.40	52°	0.55630	225.30
5.40	18.55	60°	0.57737	233.83

Table 3. Dihedral Angle and Solid-Liquid Interfacial Energies for the Indium Alloys

Percent Indium	Solubility of Aluminum in Liquid Phase At. Percent	Median Dihedral Angle Deg.	Relative Interfacial Energy	Solid-Liquid Interfacial Energy ergs/cm^2
0	40.0	31°	0.51858	210.00
0.042	39.5	32°	0.52015	210.66
0.091	39.0	33°	0.52149	211.20
0.21	38.1	35°	0.52427	212.33
0.35	37.0	39°	0.53042	214.82
0.80	34.1	44°	0.53928	218.41
1.71	29.4	51°	0.55396	224.35
6.40	17.1	57°	0.56896	230.43

Table 4. Dihedral Angle and Relative Interfacial Energies for the Copper Alloys

Percent Copper	Median Dihedral Angle Deg.	Relative Interfacial Energy
0	31°	0.51858
0.052	40°	0.53208
0.106	39°	0.53042
0.202	38°	0.52882
0.406	37°	0.52724
0.777	34°	0.52285
1.516	33°	0.52149
2.89	32°	0.52015
5.88	17°	0.50556

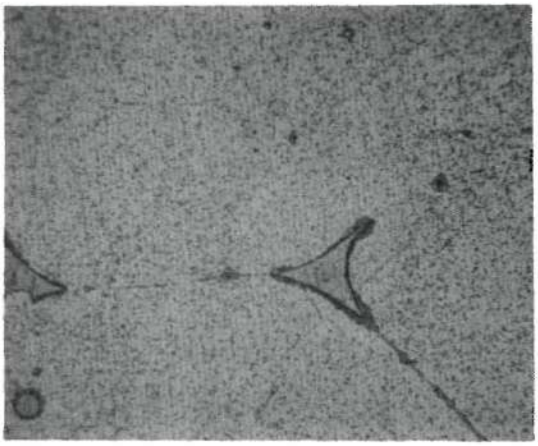

Figure 8. Microstructure of Al-2.75% Sn-0.052% Bi. 400X.

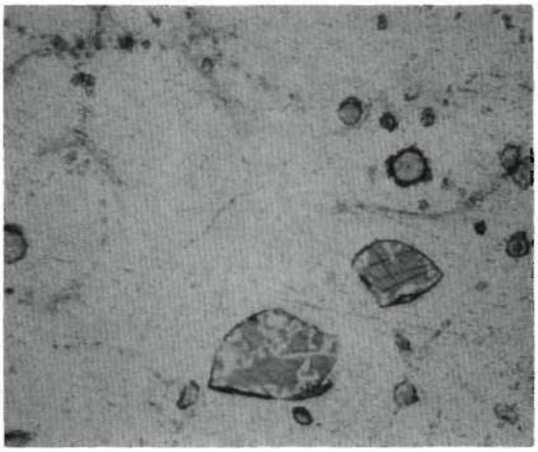

Figure 9. Microstructure of Al-2.95% Sn-6.61% Bi. 400X.

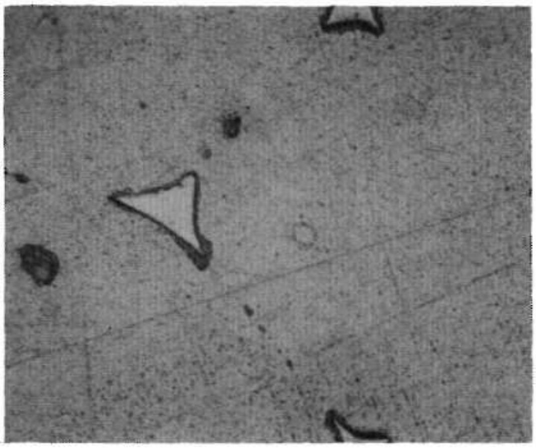

Figure 10. Microstructure of Al-3.16% Sn-0.032% Cd. 400X.

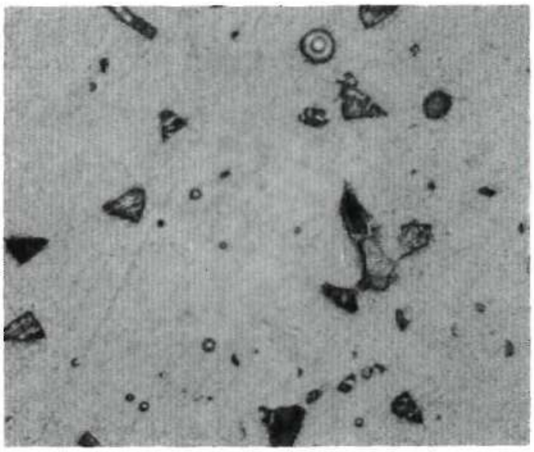

Figure 11. Microstructure of Al-3.10% Sn-5.40% Cd. 400X.

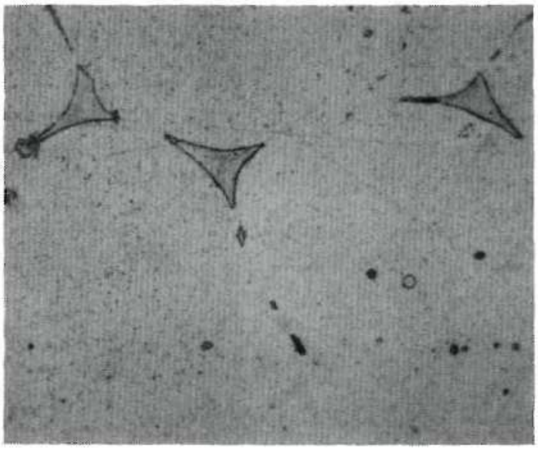

Figure 12. Microstructure of Al-3.06% Sn-0.042% In. 400X.

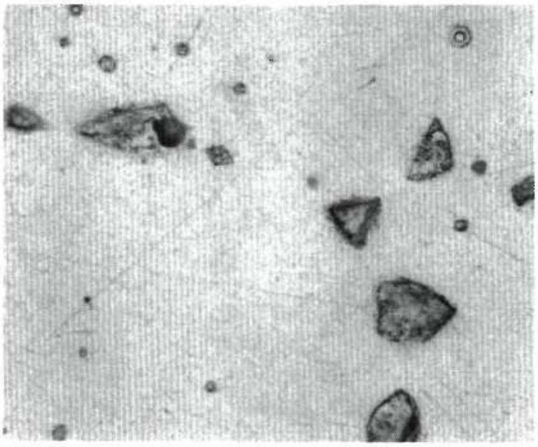

Figure 13. Microstructure of Al-3.39% Sn-6.40% In. 400X.

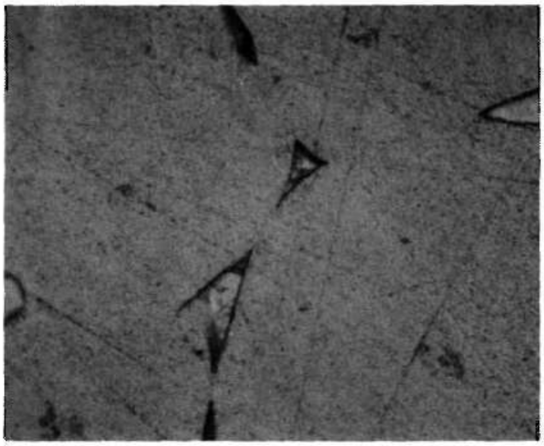

Figure 14. Microstructure of Al-2.80% Sn-0.106% Cu. 400X.

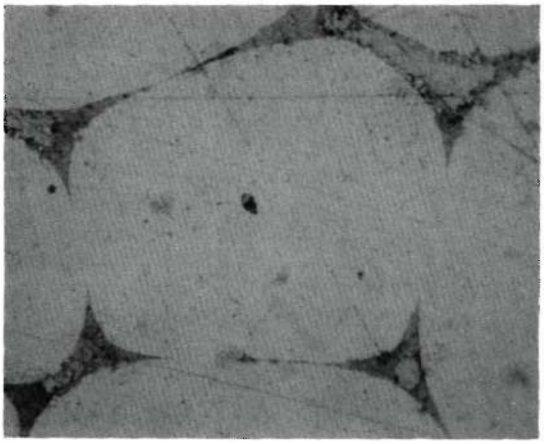

Figure 15. Microstructure of Al-2.72% Sn-5.88% Cu. 400X.

APPENDIX D

ALLOY ANALYSIS

After all specimens were heat treated they were submitted to MacMillan Laboratories of Atlanta, Georgia for a spectrographic analysis.

The elements and amounts of each indicated by the analysis are tabulated below. Each specimen contained traces of elements in the amounts as given in Table 5 and the amounts of tin and copper, cadmium, bismuth or indium as given in Tables 6 to 9.

Table 5. Spectrographic Analysis of Trace Elements Appearing in All Alloys

Element	Percentage	Element	Percentage
Mg.	0.05	Cr.	L.T. 0.01
Cu.	0.06	Ti.	L.T. 0.01
Ni.	0.01	Pb.	0.002
Mn.	0.01	Fe.	0.24
Zn.	0.09	Si.	0.06

Table 6. Spectrographic Analysis of Al-Sn-Bi Alloys

Specimen	Tin Percentage	Bismuth Percentage
B-1	2.75	0.052
B-2	2.80	0.060
B-3	2.84	0.22
B-4	2.91	0.47
B-5	2.77	0.91
B-6	2.92	1.58
B-7	2.91	3.26
B-8	2.95	6.61

Table 7. Spectrographic Analysis of Al-Sn-Cd Alloys

Specimen	Tin Percentage	Cadmium Percentage
C-1	3.20	0.019
C-2	3.16	0.032
C-3	3.04	0.152
C-4	3.12	0.296
C-5	3.22	0.680
C-6	3.07	0.672
C-7	3.38	2.66
C-8	3.10	5.40

Table 8. Spectrographic Analysis of Al-Sn-In Alloys

Specimen	Tin Percentage	Indium Percentage
D-1	3.06	0.042
D-2	3.10	0.091
D-3	3.20	0.21
D-4	2.99	0.35
D-5	3.00	0.80
D-6	3.12	1.71
D-7	3.39	6.40

Table 9. Spectrographic Analysis of Al-Sn-Cu Alloys

Specimen	Tin Percentage	Copper Percentage
A-1	2.76	0.052
A-2	2.80	0.106
A-3	2.81	0.202
A-4	2.98	0.406
A-5	3.06	0.777
A-6	2.40	1.615
A-7	2.72	5.88

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