DETERMINATION OF INTERFACIAL ENERGIES BETWEEN SOLID COPPER AND BINARY BISMUTH-THALLIUM LIQUID METAL COMPOSITIONS

by

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UNITED STATES ARMY FRANKFORD ARSENAL PHILADELPHIA, PA.

July 1965

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DETERMINATION OF INTERFACIAL ENERGIES BETWEEN SOLID COPPER AND BINARY BISMUTH-THALLIUM LIQUID METAL COMPOSITIONS

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July 1965
ABSTRACT

Interfacial energies were determined at 1250°F, 950°F, and 650°F between solid copper and binary bismuth-thallium liquid metal alloys. Interfacial energies were determined between the copper and the liquid metal environment as the relative proportions of bismuth and thallium in the liquid metal were varied.

Results showed that progressive additions of thallium to bismuth raises the interfacial energies between the resulting liquid metal environments and the solid copper. Interfacial energy values calculated for 1250°F ranged from 278 ergs/cm² for a liquid metal composition of 100 per cent bismuth to 360 ergs/cm² for a composition of 100 per cent thallium. Interfacial energies between solid copper and liquid bismuth-thallium environments increase as the temperature decreases in the range of 1250°F to 650°F. The effect of thallium on increasing the interfacial energy becomes more pronounced as the temperature decreases.
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INTRODUCTION

Certain gaseous and liquid environments have an embrittling effect on metals\(^1,2,3,4,5,6\). One such embrittling environment that is receiving increased attention is that of liquid metals. A review of work concerned with the embrittlement of metals by an environment of liquid metals has been presented by Rostoker, McCaughey, and Markus\(^7\). One factor that is related to embrittlement occurrence is the interfacial energy between the solid and the liquid metal\(^8,9\). However, much of the work on liquid metal embrittlement reported to date has not included quantitative determinations of interfacial energies because of the experimental difficulties involved. It has been shown by Morgan\(^8\) that the degree of embrittlement of copper in the presence of liquid bismuth-lead alloys increases as the interfacial energy decreases. In this system the interfacial energy decreases as the bismuth content of the liquid metal environment increases. Another system that embrittles copper is bismuth-thallium. However, no quantitative data on the interfacial energies of liquid bismuth-thallium alloys on solid copper are available. Therefore, the purpose of this investigation was to determine the interfacial energy for liquid bismuth-thallium alloys on copper. The interfacial energies were obtained by using the dihedral angle technique that has been explained by Smith\(^10\).

EXPERIMENTAL PROCEDURE

A. Material

Base metal

An annealed sheet of OFHC copper was used for the solid metal. Thickness of the sheet was 0.194 ± .001 in. The chemical analysis of the material is given in Table I.

### Table I

Chemical Analysis of Copper used in Interfacial Energy Determination Studies.

<table>
<thead>
<tr>
<th>Per Cent</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>99.97</td>
</tr>
<tr>
<td>Iron</td>
<td>Less than 0.005</td>
</tr>
<tr>
<td>Lead</td>
<td>Less than 0.01</td>
</tr>
<tr>
<td>Silver</td>
<td>Less than 0.01</td>
</tr>
<tr>
<td>Tin</td>
<td>Less than 0.005</td>
</tr>
<tr>
<td>Other elements</td>
<td>None detected</td>
</tr>
</tbody>
</table>
Liquid Metal Alloy Compositions

Eleven different alloy combinations were prepared from bismuth and thallium reagent chemicals. Prepared compositions ranged in 10 per cent weight increments between 100 per cent bismuth and 100 per cent thallium. Solid bismuth and thallium were mixed together in vycor test tubes and the atmosphere within the tubes was evacuated. The tubes were then sealed and heated in a furnace at 750 °F and were agitated after one hour at temperature to facilitate the formation of homogeneous liquid solutions. The samples were retained in the furnace at 750 °F for an additional hour and were then allowed to cool. The tubes were then broken and the cylindrical metal pieces removed. These homogenized alloy pieces weighed approximately 20 grams each.

B. Test Procedure

Preparation of Specimens

Circular disks, 1/2 in. in diameter, were punched from the copper sheet. The disks were annealed at 1300 °F for one hour to eliminate effects of possible cold work present in the copper as a result of the punching operation. After anneal the pieces were mounted in bakelite and polished metallographically to ensure that the flat circular faces were free of scratches or mirror defects. The disks were then broken out of the mounting medium, cleaned chemically, and placed flat on a stainless steel tray with the polished faces up. Using a jeweler's saw, approximately 0.2 g. of each prepared alloy combination of bismuth : thallium was cut from the homogenized samples. The alloy pieces were laid on the polished faces of the disks. The test was performed in quadruplicate for each composition of bismuth : thallium. The stainless steel tray was then placed into a vacuum furnace. Prior to heating, the furnace was evacuated and back filled with argon to a slight positive pressure. Three groups of specimens were prepared. The first group was held at 1250 °F, the second at 950 °F, and the third at 650 °F.

After 24 hours equilibration at temperature, the pieces were allowed to cool in the argon atmosphere until the liquid metal solidified. The pieces were then quenched in water. Using a jeweler's saw the disks were cut in half along a diameter so that the copper-metal interface could be examined on the cross section. The pieces were then mounted in bakelite and the sectioned faces were polished metallographically and then etched with potassium dichromate solution. Microscopic examination was made of the copper-alloy interfaces using a magnification of 1000X.
**Dihedral Angle Measurements**

Grain boundary dihedral angles were measured on external angles formed where the copper grain boundaries came to the surface at the copper-alloy interface. Typical dihedral angles are shown in Figure 1. Measurements were made by rotating the calibrated stage of a Bausch and Lomb metallograph to align the grain boundaries with a cross hair located within the eyepiece. Measurements were made of all clearly delineated angles along the copper-alloy interface for each disk section and were recorded to ±0.5°. Preliminary measurements were made of representative angles in order to check the reproducibility of the measuring process. Three typical angles were selected and each was measured 10 separate times. The reproducibility was such that the measured values for an individual angle were within ±1.5° of the mean of the 10 measurements recorded for that angle.

A minimum of 60 angles were read for each condition of composition at the two higher temperatures. For the specimens equilibrated at 650°F, a fewer number of measurements could be recorded since many angles were poorly formed.

**RESULTS**

The equilibrium grain boundary dihedral angle for an individual condition of temperature and composition was taken to be the median of the angles measured for that condition. These angles are given in Table II. The table also shows the number of angles measured as well as the minimum and maximum angle values recorded for each condition. Interfacial energies were calculated by using the expression of equilibrium as presented by Smith(O). The expression is of the form:

\[
\gamma_B = 2\gamma_{SL}\cos\frac{\theta}{2}
\]

where \(\gamma_B\) = grain boundary energy of copper (ergs/cm²)

\(\gamma_{SL}\) = interfacial energy between solid copper and the liquid metal (ergs/cm²)

\(\theta\) = dihedral angle at equilibrium (degrees)

A constant value of 350 ergs/cm² was used for \(\gamma_B\). This value is the mean value calculated by Fisher and Binn(11) from interface angle ratios experimentally developed by Smith(10), Van Vlack(12), Bailey and Watkins(13), and Fullman(14).
Figure 1. Diagram and photomicrographs showing method of measuring dihedral angles


**TABLE II**

Dihedral Angles after Heating Copper Specimens in the Presence of Liquid Bi-Tl Compositions for 24 hours at the Temperature Indicated.

<table>
<thead>
<tr>
<th>Composition (by weight)</th>
<th>1250 F</th>
<th>950 F</th>
<th>650 F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of Angles</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>100 Bi 0 Tl</td>
<td>60</td>
<td>12°</td>
<td>49°</td>
</tr>
<tr>
<td>90 Bi 10 Tl</td>
<td>60</td>
<td>13°</td>
<td>36°</td>
</tr>
<tr>
<td>80 Bi 20 Tl</td>
<td>60</td>
<td>20°</td>
<td>50°</td>
</tr>
<tr>
<td>70 Bi 30 Tl</td>
<td>60</td>
<td>9°</td>
<td>53°</td>
</tr>
<tr>
<td>60 Bi 40 Tl</td>
<td>60</td>
<td>25°</td>
<td>57°</td>
</tr>
<tr>
<td>50 Bi 50 Tl</td>
<td>60</td>
<td>28°</td>
<td>75°</td>
</tr>
<tr>
<td>40 Bi 60 Tl</td>
<td>60</td>
<td>22°</td>
<td>77°</td>
</tr>
<tr>
<td>30 Bi 70 Tl</td>
<td>60</td>
<td>32°</td>
<td>82°</td>
</tr>
<tr>
<td>20 Bi 80 Tl</td>
<td>60</td>
<td>42°</td>
<td>90°</td>
</tr>
<tr>
<td>10 Bi 90 Tl</td>
<td>60</td>
<td>49°</td>
<td>89°</td>
</tr>
<tr>
<td>0 Bi 100 Tl</td>
<td>60</td>
<td>30°</td>
<td>117°</td>
</tr>
</tbody>
</table>

5
An accurate evaluation of dihedral angles requires that the surface of the specimen, the plane of the microsection, and the plane of the grain boundary be mutually perpendicular. It should be noted that compliance with the condition that the plane of the grain boundary must be perpendicular to the microsection is clearly impractical when polycrystalline specimens are used. Non-perpendicularity between the plane of the grain boundary and that of the microsection causes the measured angle to be either larger or smaller than the true dihedral angle.

Rieggers and Van Vlack(15) made statistical analysis studies of the relationship between observed angles and true dihedral angles. They proposed a method by which the median of the measured angles could be used as the true dihedral angle for an individual condition of composition and temperature. Their computations showed that the probable error between the obtained median angle and the true dihedral angle became greater as the dihedral angles increased toward 90°. Moreover, the confidence level which could be attributed to selected limits of probable error was shown to increase as a greater number of angles was measured to determine the median. For example, Rieggers and Van Vlack showed that the measurement of 25 angles assured an accuracy of ± 5° in 96 per cent of the cases if the true dihedral angle is 30° or less, and ± 5° in 68 per cent of the cases for angles close to 90°. In order to increase the confidence level to 96 per cent for angles close to 90° would require the measurement of approximately 90 angles.

Interfacial energies were calculated for each composition of bismuth : thallium for each of the three equilibrium temperatures investigated. Calculations were made using the median dihedral angles recorded in Table II and the value of 550 ergs/cm² for Υ₂. Interfacial energy values for the 1250 °F equilibrium temperature are plotted in Figure 2. Values for the 950 °F condition are plotted in Figure 3 and the values for 650 °F are plotted in Figure 4. The ranges of values shown in these plots were obtained by considering the probable limits of error of the median angle in the manner described by Rieggers and Van Vlack. For the two higher temperatures, the 96 per cent confidence level for the probable limits of error was based on the measurement of 60 angles. For the 650 °F condition the same limits of error were maintained but the confidence level was thereby reduced to 68 per cent since the number of angles measured was less. The interfacial energy curves obtained for the three individual test temperatures are shown together in Figure 5.

For each of the three temperatures investigated the interfacial energies, Υ_sl, between the solid copper and the liquid bismuth-thallium alloy compositions increased as the thallium content increased. Interfacial energies calculated for the 1250 °F temperature ranged from 273 ergs/cm² for 100 per cent bismuth to 360 ergs/cm² for 100 per cent thallium. It can be seen from Figure 5 that the interfacial energies increased gradually as the equilibrium temperature decreased in the range of 1250 °F to 650 °F. As can be seen from Table II the spread of measured dihedral angles for an individual liquid metal composition was smallest for the 1250 °F temperature condition. As the temperature decreased, the spread of measured dihedral angles increased.
Figure 2. Interfacial Energies between Copper and Liquid Metal Alloys of Bismuth-Thallium. Specimens Equilibrated 24 Hours at 1250F. (Confidence Level of 96 percent.)
Figure 3. Interfacial Energies between Copper and Liquid Metal Alloys of Bismuth-Thallium. Specimens Equilibrated 24 Hours at 950°F. (Confidence Level of 96 percent.)
Figure 4. Interfacial Energies between Copper and Liquid Metal Alloys of Bismuth-Thallium. Specimens Equilibrated 24 Hours at 650°F. (Confidence Level of 68 percent.)
Figure 5. Interfacial Energies between Copper and Liquid Metal Alloys of Bismuth-Thallium. Specimens Equilibrated 24 Hours at Temperatures Indicated.
DISCUSSION

The interfacial energy value of 282 ergs/cm$^2$ calculated for a liquid metal composition of 100 per cent bismuth at 650°F agrees fairly well with the value of 280.5 ergs/cm$^2$ reported by Morgan (8) on copper-bismuth. Morgan, however, heated his specimens for 10 hours at 662°F and used the most frequently observed dihedral angle as the equilibrium grain boundary angle. In the present study the specimens were heated for 24 hours at 650°F and the median of the measured angles was used as the equilibrium angle.

The addition of lead to bismuth increases the interfacial energy between the liquid bismuth-lead alloy and the copper (8). This study has shown that the addition of thallium to bismuth also increases the interfacial energy between copper and the liquid metal environment. Morgan's work showed a value of 390.5 ergs/cm$^2$ for a liquid metal composition of 100 per cent lead. In our experiments a value of 402 ergs/cm$^2$ was obtained for a liquid metal composition of 100 per cent thallium at 650°F.

The values reported by Morgan for the copper-bismuth-lead system were for one temperature condition. With regard to the present study, examination of Figure 5 showed that the interfacial energies increase gradually as the equilibration temperature decreases. Moreover, the addition of thallium was seen to have a greater effect in increasing the interfacial energy as the temperature decreases.

Interfacial energy values determined from the measurement of dihedral angles may be influenced by factors such as the time and temperature of specimen equilibration as well as by possible effects on the grain boundary energy of copper of temperature and relative grain orientation. Some mention should be made of the possible effects of these factors.

In the current study, the holding of specimens for 24 hours at temperature was considered adequate to ensure equilibrium of angles at grain boundary intersections. Smith (10), for his measurements of dihedral angles of the copper-lead system, found 16 hours at 1382°F to be sufficient for equilibrium purposes. Sears (16), for similar studies of lead drops on copper, heated his specimens for 8 hours at 1472°F. Bailey and Watkins (13) measured groove angles at the intersection of grain boundaries and a free copper surface which were thermally etched in a lead atmosphere and reported identical results for specimens held 2 hours at 1652°F and those held 8 hours at 1472°F.
The equilibrium adjustment of interfaces probably is the result of diffusion\(^{12}\). Therefore, comparisons of the effect of different holding times to achieve equilibrium on the depth of penetration of the liquid metal can be made in terms of reaction-rate principles. Application of the Arrhenius reaction rate equation would tend to indicate that comparable results would be expected between the work of the other investigators\(^{10,13,16}\) and that of the present study for the 1250 °F equilibrium temperature. To achieve comparable depths of penetration for the 950 °F and 650 °F temperature conditions would have required much longer holding times.

In the opinion of Bailey and Watkins\(^ {13}\), it is reasonable to suppose that the equilibrium dihedral angle is established as soon as thermal etching begins, and that, as etching proceeds, the grooves merely become deeper, while maintaining the same dihedral angle. With respect to the present study, no noticeable differences in dihedral angle were observed between holding times of 20 and 24 hours at 1250 °F. It was noticeable, however, that the depth of penetration of the liquid metal into the grain boundary intersections was less at 20 hours than at 24 hours.

Under certain conditions the depth of penetration tends to influence the measurement of dihedral angles. As the depth of penetration decreases it tends to become more difficult to judge the exact limits of the dihedral angles. This factor was believed responsible for the observation that as the equilibrium temperature was decreased the spread of the measured dihedral angles increased. However, even though the angles for the 650 °F condition were more difficult to measure, the obtained interfacial energy values appeared similar in nature with those for the higher temperatures. Values for all three temperatures are considered representative of equilibrium conditions for those temperatures.

The grain boundary energy of copper, \(\gamma_B\), probably varies somewhat with temperature. The interfacial energies calculated in this study were obtained using a grain boundary energy value of 550 ergs/cm\(^2\). Ikeuye and Smith\(^ {17}\), from studies of the ratio of the solid-liquid interface energy to that of the grain boundary, for the copper-lead system, reported that the major change in the ratio with temperature was due to a change in the liquid-solid interface energy. This change was chiefly the result of the change in composition of the liquid and did not become pronounced until the monotectic temperature was nearly reached, at which point the copper content of the liquid discontinuously increased. Below a temperature of 1470 °F the ratio of the interface energies for the copper-lead system was seen to be constant. Therefore, interfacial energy calculations made in this study based on \(\gamma_B\) being considered constant over a temperature range of 1250 °F to 650 °F were believed to be meaningful.
The grain boundary energy, $\gamma_B$, of copper polycrystals also depends on the orientation of the boundary with respect to the crystal axis of the adjoining grains. However, as noted by Cottrell(18), this dependence of the boundary energy on relative grain orientation is pronounced only for small-angle boundaries. It is a fair approximation to regard the energies of large-angle boundaries as being independent of orientation. The value of 550 ergs/cm$^2$ for the grain boundary energy of copper was adopted by Fisher and Dunn(11) based on large-angle boundaries. With respect to our experiments, microscopic examination of the copper sheet material showed no pronounced indications of the presence of textures. Moreover, after the preliminary anneal of 1300 $^\circ$F for one hour the grains were essentially equiaxed with large-angle grain boundaries. If a different value were used for $\gamma_B$, the calculated values of $\gamma_{SL}$ would change but the relative shape of the $\gamma_{SL}$ vs. composition curves would remain the same.

CONCLUSIONS

1. At temperatures of 1250 $^\circ$F, 950 $^\circ$F, and 650 $^\circ$F, progressive additions of thallium to bismuth increases the interfacial energy between solid copper and the resulting bismuth-thallium alloys in the liquid state.

2. Interfacial energy values between solid copper and liquid bismuth-thallium compositions increase slightly as the temperature decreases from 1250 $^\circ$F to 650 $^\circ$F.

3. The effect of thallium on increasing the interfacial energy between solid copper and liquid bismuth-thallium compositions becomes more pronounced as the temperature decreases.
REFERENCES


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