Silver Scavenging Inhibition of Some Silver Loaded Solders

The results of experiments show that silver dissolved in a solder alloy has an inhibiting effect on the scavenging of silver from a silver substrate.

BY R. A. BULWITH AND C. A. MACKAY

ABSTRACT. Comparisons of the rates of dissolution of silver in some binary tin/lead alloys and some silver-bearing alloys were reported. Activation energies for each alloy were calculated, and an alloy selection system was suggested together with a discussion on the dissolution inhibition mechanism.

Introduction

The use of silver loaded solders to prevent or reduce the rate of solution of silver from substrates during the soldering process has become widely accepted. However, development of alloys for this purpose have almost (Refs. 1,2) entirely been by analogy with the effect of copper on inhibition of copper solution by solders (Refs. 3-5). In fact, the analogy is an extremely good one; because in both cases — copper in tin/lead and silver in tin/lead — the systems are eutectic. Also, in both cases, the ternary eutectic being three phase involves tin-rich and lead-rich solid solutions and an intermetallic.

In copper containing alloys, the intermetallic was Cu₆Sn₅ while for silver-bearing alloys it was Ag₃Sn. The mechanism of solution inhibition would, therefore, presumably also be similar. Because silver-loaded alloys have been used for so long with apparent success, the analogy has not been challenged. However, the performance of different alloys, which have over the years been proposed and developed, have never been compared.

This paper reports the results of tests to measure the silver dissolution rates on sheet silver over a range of temperatures and for a range of alloys.

Materials

The materials used in this investigation were standard Alpha Metals production materials manufactured, where applicable, according to the ASTM standards. Where no standard existed, the alloys were made to the impurity levels as specified by ASTM (Ref. 6).

Table 1 lists the range of solders examined in this investigation together with their melting points. The silver strip used was 99.99% pure Ag.

Experimental

Silver strip of 0.05 in. (1.27 mm) thickness was cut into 0.20 X 1.0 in. (5 X 25.4 mm) coupons. A 0.20 X 0.40 in. (5 X 10 mm) area was then outlined by masking the remainder of the sample with a solder resistant compound (i.e., Alpha Solder Resist 2398).

Approximately constant volume samples of the solder alloys were melted into 10 ml pyrex glass beakers which fitted completely into a recess in a 5.25 X 1.5 in. steel guard ring heated on a Thermoline temperature controllable hot plate. The guard ring eliminated drafts from the sides of the beaker and, due to its large mass, served to stabilize and unify the alloy temperature. The silver strip samples were mounted in split

Table 1—Compositions (%) and Melting Points for Range of Solders Examined

<table>
<thead>
<tr>
<th>Sn</th>
<th>Pb</th>
<th>Ag</th>
<th>Sb</th>
<th>Cu</th>
<th>Bi</th>
<th>ASTM GRADE</th>
<th>Melting range</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0</td>
<td>40.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>60A</td>
<td>183-185 (361-365)</td>
</tr>
<tr>
<td>62.0</td>
<td>36.0</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>96.5TS</td>
<td>179-183 (354-361)</td>
</tr>
<tr>
<td>62.5</td>
<td>36.1</td>
<td>1.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>95A</td>
<td>179 (354)</td>
</tr>
<tr>
<td>96.5</td>
<td>3.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>221</td>
<td>227-280 (441-536)</td>
</tr>
<tr>
<td>98.5</td>
<td>-</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>232-240</td>
<td>232-240 (450-464)</td>
</tr>
<tr>
<td>95.0</td>
<td>-</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>268-302</td>
<td>268-302 (514-575)</td>
</tr>
<tr>
<td>10.0</td>
<td>88.0</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.5S</td>
<td>304 (580)</td>
</tr>
<tr>
<td>-</td>
<td>97.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>309</td>
<td>309 (588)</td>
</tr>
<tr>
<td>1.0</td>
<td>97.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.0</td>
<td>120-167 (248-333)</td>
</tr>
<tr>
<td>50.0</td>
<td>40.0</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.5S</td>
<td>179-210 (354-410)</td>
</tr>
<tr>
<td>49.0</td>
<td>50.0</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.5S</td>
<td></td>
</tr>
</tbody>
</table>

rubber holders and suspended in the molten alloys for times between 30 seconds (s) and 2 minutes (min).

The dipped preweighed masked coupons were then stripped of the solder coating by immersion in an aqueous solution of 50 g/l NaOH with 35 g/l o-nitrophenol at 70°C (158°F). Weight loss was determined using a Sartorius 2462 precision balance capable of measuring to 0.1 mg.

In the first stage of the investigation, a single weight loss vs. time curve was established. Holding temperatures of liquidus + 50°C (90°F) for non-eutectics were used for this stage. Subsequently, the most common alloys used either in normal soldering or in microcircuitry were examined at three temperatures, melting point + 30°C, +50°C and +80°C (+54°F, +90°F, +144°F) from which Arrhenius plots were constructed.

**Results**

The effect of adding silver to a tin/lead alloy was demonstrated; the results, which are for both 60 Sn/40 Pb and 62Sn/36Pb/2Ag alloys, are shown in Fig. 1. Dissolution rates of various tin and tin/lead solders with tin/silver solder are compared in Fig. 2, which shows the weight losses in 95Sn/5Sb, 98.5Sn/1.5Cu, 60Sn/40Pb, 50Sn/40Pb/10Bi and 96.5Sn/3.5Ag.

The results for the higher tin content silver-containing alloys are shown in Fig. 3, while those for the high lead alloys are reported in Fig. 4. Those alloys showing the lowest dissolution rates were then further examined at superheats of +30°C and +80°C (+54°F and +144°F) so that Arrhenius plots could be obtained. These are shown in Fig. 5.

**Discussion**

Figure 1 shows the decrease in solubility of silver produced by saturation of the liquid alloy by silver at a melt superheat of 50°C (90°F). The rate of dissolution has been reduced from 0.20 mg/s to 0.07 mg/s, demonstrating the dissolution inhibition effect claimed.

Saturation of the tin constituent of solders — generally considered the active wetting component and also the reactive compound forming phase — with other elements such as copper or antimony does not appear to inhibit silver dissolution — Fig. 2. In addition, the rates of dissolution appear to increase as a function of the alloy melting point, thereby
When the results for silver-containing solders were examined, however, the same function of alloy melting point was not apparent in that some of the higher melting point solders had significantly lower dissolution rates. As an example, the 15Sn/97.5Pb/1.5Ag alloy shown in Fig. 3 with melting point 309°C (588°F), has a lower silver dissolution rate than does 96.5Sn/3.5Ag with a melting point of 221°C (430°F). Nor was there any obvious indication that a particular tin/silver or tin/lead or even lead/silver ratio was superior.

In absolute terms the lowest dissolution rate was exhibited by the 10Sn/88Pb/2Ag alloy both from the point of view of reaction rate (slope of curve) and weight loss measurements, by a considerable amount.

According to their measured reaction rates, both the 62.5Sn/36.1Pb/1.4Ag and 62Sn/36Pb/2Ag solders dissolve the silver at the same rates. However, owing to the nonlinear rate of dissolution at short times with the first of these solders, the weight loss curves were not identical. These differences are probably not significant, showing that eutectic and near eutectic alloys behave similarly. Both the lead rich alloys tested also fell in this region of reaction rate.

The same considerations that govern selection of a soldering alloy—in the case of say, PCB assembly and fabrication—come into play when selecting an alloy that will not dissolve away a silver coating or conductor track. When fabricating a hybrid component, for example, once the highest melting point alloy consistent with continued electronic performance of the device to be fixed and minimal dimensional distortion, has been used, subsequent assembly or fabrication stages must use lower melting point alloys to avoid destruction or disruption of the existing joints. Thus, although the 10Sn/88Pb/2Ag would appear to be the best alloy from a silver leaching standpoint, it could be necessary to use either 15Sn/97.5Pb/1.5Ag or 97.5Pb/2.5Ag on account of the melting points and so that 96.5Sn/3.5Ag alloy may be used at a later assembly stage.

Figure 6 shows a selection diagram indicating the melting points of the various alloys, their suggested usable temperature ranges, and their observed silver dissolution rates. The best solder choice would be that showing the lowest solution rates which lie in the temperature block corresponding to the use, i.e., those in the cross-hatched region. Judging from this chart, the preferred solders for the whole range of possible applications are 62Sn/36Pb/2Ag, 10Sn/88Pb/2Ag and 15Sn/97.5Pb/1.5Ag.
Figure 5 shows the Arrhenius plots for these soldering. From this, the dissolution rate for each alloy for any temperature can be found and the weight loss curve reconstructed. From each line, the activation energy for solution of silver from a solid surface into the melt can be calculated, and these are listed in Table 2.

As mentioned previously, the results for non-silver containing solders appear to increase as a function of temperature. If the natural log of the dissolution rates for these solders was plotted against the inverse of the melting points in K, then a near straightline plot is obtained. In fact, Fig. 7 shows such a plot, although it is for the melting point + 50°C (90°F) temperature (the actual experimental temperature).

The implication of such a curve is that the activation energies of dissolution of silver into each molten alloy were identical. In other words, neither antimony, copper, lead nor lead + bismuth has any effect on the energy barrier which the silver atom must surmount in order to dissolve into the melt. From the slope of this line and the Arrhenius equation given as:

\[ \text{Ln (rate)} = \frac{E}{RT} + A \]  

an activation energy value of 17.6 (Kcal units) was obtained. When the corresponding value for 96.5Sn/3.5Ag alloy was plotted, was this below the line shown.

Our assumption is that alloying with antimony, copper or bismuth did not affect the silver dissolution rate. If this is correct, then both the activation energy value for the binary tin-lead solder in Fig. 5 and the value for the range of non-silver bearing solders in Fig. 7 should be similar. In fact, the agreement between the two is quite good.

Plotting the results for the silver-containing alloys in Fig. 7 showed that all fall below the line to differing extents. If we can assume that all alloys tested will make the same intercept with the y (ln (rate)) axis (i.e., that they have the same frequency factor), then the straightline through the point for each silver bearing alloy would have a steeper slope, thus, indicating an increased activation energy. From Fig. 3 the intercepts for each alloy except 10Sn/88Pb/2Ag lay in the range (-13 to -24) cm\(^{-s}\)\(^{-1}\), and from Fig. 7 it was -16 cm\(^{-s}\)\(^{-1}\). Considering the closeness of the temperature range from which they were determined, this was probably an acceptable agreement.

From equation (1) it was clear that:

\[ T (\text{Ln (rate)} - A) = \text{constant}. \]

For the point on the straight line relationship in Fig. 7 this was sensibly the same and equal to the slope of the line. For the silver-containing alloys it was reduced by an amount indicative of the distance of the point for that alloy from the straightline. The ratio of any two constants, therefore, indicates the relative order of merit for silver dissolution inhibition for that alloy.

Using this hypothesis, the differences between the constant for points off the line with those defining the line represent some measure of the effectiveness of that alloy inhibiting silver dissolution. Table 3 indicates the relative order of

<table>
<thead>
<tr>
<th>Table 2—Activation Energies for Five Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
</tr>
<tr>
<td>60/40</td>
</tr>
<tr>
<td>62/36/2</td>
</tr>
<tr>
<td>1/97.5/1.5</td>
</tr>
<tr>
<td>−/97.5/2.5</td>
</tr>
<tr>
<td>10/88/2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3—A Relative Order of Merit for Eleven Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
</tr>
<tr>
<td>60/40</td>
</tr>
<tr>
<td>98.5/1.5Cu</td>
</tr>
<tr>
<td>95/5Sb</td>
</tr>
<tr>
<td>50/40/1.1Ag</td>
</tr>
<tr>
<td>49/50/1.1Ag</td>
</tr>
<tr>
<td>52/30/1.4Ag</td>
</tr>
<tr>
<td>62/36/2Ag</td>
</tr>
<tr>
<td>7/97.5/2.5Ag</td>
</tr>
<tr>
<td>1/97.5/1.5Ag</td>
</tr>
<tr>
<td>10/88/2</td>
</tr>
</tbody>
</table>

WELDING RESEARCH SUPPLEMENT | 89-s
merit for the alloys tested, the % inhibition figures being the difference of these same ratios expressed as a percentage (constant determined from Fig. 7 = -8873).

On the basis of these results some comments may be made about the mechanism of silver dissolution inhibition. Using a different dissolution measuring technique, both Bader (Ref. 3) and Berg and Hall (Ref. 2) showed a similar near linear relationship between the quantity of dissolved metal and immersion to those reported in Figs. 1–4. On the basis of the work of Lommel and Chalmers (Ref. 7), they showed that the dissolution mechanism must be either governed by a surface reaction or limited by extreme thermal agitation or stirring producing continuous limitation of the interface boundary layer.

In support of this theory, Berg and Hall recalculated Bader’s results and obtained an activation energy for silver dissolving into 60Sn/40Pb alloy of 11.5 kcal, which agrees with the results presented here. This model, however, does not explain the marked increase in activation energy for silver dissolving inhibiting alloy found by Berg and Hall or as reported in this research.

It has been well documented that the rate of transfer of atoms for a high concentration region was dependent upon the concentration gradient because of the concentration dependence of the diffusion constant. Thus, for example, annealing times for low levels of alloying addition in the iron/tin system were longer than for higher levels (Refs. 8,9). It could be argued, therefore, that the reduction in concentration gradient brought about by small alloying additions to the molten alloy could modify the dissolution rates. However, this does not appear to be the case, since results reported here do not indicate a monotonic decrease in dissolution rate with increasing level of tin addition.

Another explanation could be that the rate limiting function was the formation of intermetallic compound from saturated solid solution so that dissolution material was always attempting to supersaturate the molten alloy. In such an instance, it might be expected either that the more silver saturated alloys would show greater inhibition. This, however, was not the case. Compare, for example, 62Sn/36Pb/2Ag with 62.5Sn/36.1Pb/1.4Ag and 15Sn/97.5Pb/1.5Ag or consider that since all alloys tested were at or exceeded their eutectic silver content then all would behave equally, which again was not the case.

The effect appears to be due to a change in the activation energy of dissolution so that an atom of silver in the solid had to be excited to a higher energy level to dissolve into a molten silver bearing solder than for molten silver free alloys.

Conclusion

These experiments have shown that silver dissolved in a solder does have an inhibiting effect on the scavenging of silver from a silver substrate. The effectiveness of the various alloys commonly used for this purpose does not appear to be readily predictable.

Recommendations of most suitable alloys for particular temperature intervals should be based on experimental results. Such recommendations have been offered in this paper.

The effect of dissolved silver in the molten alloy appears to be to increase the activation energy for dissolution; consequently, a silver atom in the solid must be raised to a higher energy level in order to dissolve into a silver containing solder than was necessary with silver free alloys. Accordingly, for a given temperature, correspondingly fewer atoms pass into solution in a fixed time interval, and a silver substrate does not dissolve away.

Acknowledgments

The authors thank the management of Alpha Metals for permission to publish this paper and Paul Lotosky for his help with the experimental work.

References

6. ASTM B-32.
AN INVITATION TO AUTHORS

to present Brazing Papers at the
17th AWS International Brazing and Soldering Conference

Atlanta, Georgia, April 15-17, 1986

The American Welding Society's C3 Committee on Brazing and Soldering invites you to present your outstanding and unpublished work in the field of brazing development, research or application at the 17th International AWS Brazing and Soldering Conference. This event will be held in conjunction with the Society's 67th Annual Convention at the Georgia World Congress Center, Atlanta, Georgia.

Please submit your abstract(s) by August 15, 1985, to be screened by the C3 Papers Selection Committee for the 1986 conference. Authors will be notified sometime in November, 1985, regarding acceptance of their papers.

Each abstract should be sufficiently descriptive to give a clear idea of the content of the proposed paper. In any case, it must contain not less than 500—but preferably not more than 1000—words. Manuscripts of approximately 5,000 words must be submitted before final approval is given. Repeated references to a company and/or the use of advertisement, trade names, trade marks (or expressions considered as such by the industry) are not permitted. Suitable generic terms must be used, in accordance with those standardized by the American Welding Society, where applicable.

Papers may be considered for publication in the Welding Journal regardless of acceptance for presentation at the conference. Topics of particular interest in brazing are:

Applied technologies of (1) aerospace structures, (2) machine tools, (3) nuclear assemblies, (4) automotive assemblies, (5) electronic equipment, (6) food processing equipment and (7) pressure vessels. Of special interest is the application of brazing to titanium, aluminum and other base metals including brazement strength data.

New research and development on (1) brazing filler metals, (2) brazing filler metal/base metal interaction, (3) nuclear properties of brazements, (4) electronic properties of brazements, (5) corrosion of brazements and (6) strength of brazed joints.

In addition, papers dealing with educational and informative aspects of brazing production, engineering, research and metallurgy are welcomed if the subject falls within the scope of the session.

Please fill out the Author's Application Form (reverse side), attach abstract thereto and return to AWS. To assure your paper's consideration for the 1986 conference, your abstract must be postmarked no later than August 15, 1985.

Paul W. Ramsey
Executive Director

IMPORTANT: ABSTRACTS MUST BE AT LEAST 500 WORDS AND BE POSTMARKED NO LATER THAN AUGUST 15, 1985, TO ASSURE CONSIDERATION.
AUTHOR APPLICATION FORM
FOR
BRAZING PAPERS

Complete in Full and Return to American Welding Society, Inc., 550 N.W. LeJeune Rd., P. O. Box 351040, Miami, Florida 33135

Date Mailed .................................................................

Author's Name ...........................................................

Check how addressed: Mr. □ Ms. □ Dr. □ Other □

Title or Position ...........................................................

Company or Operation ..................................................

Mailing Address ..........................................................

City ................................................................. State ................................................................. Zip

Telephone (including Area Code) ........................................

If there are to be joint Authorships, give name(s)
of other author(s)

Name ................................................................. Address ..........................................................

Name ................................................................. Address ..........................................................

Proposed title (10 words or less):

ABSTRACT:

• Type, double spaced, an abstract of not less than 500—but preferably not more than 1000—words on separate sheets and attach to this form.
• Be sure to give sufficient information to enable the Papers Selection Committee to obtain a clear idea of content of the proposed paper; confine background to about 100 words. Also be sure to emphasize Results and Conclusions since this material, together with information on what is NEW, will have a very important bearing on the final decision of the AWS C3 Papers Selection Committee.
• If complete manuscript is available, in addition to abstract, please attach two copies to this form.
• Application Form and Abstract must be postmarked not later than August 15, 1985, to assure consideration.

MANUSCRIPT DEADLINES:

• All manuscripts must be in the hands of the Papers Selection Committee no later than March 15, 1986. If received by that date, every effort will be made to publish them in a special Brazing and Soldering issue.
• It is expected that the Committee's selections will be announced sometime in November, 1985.
• If your paper is made a part of the program, which of the following manuscript deadlines will you be able to meet?

PRESENTATION AND PUBLICATION OF PAPERS:

• Has material in this paper been previously presented in a meeting or published?
  Yes □ No □ When? ________ Where? ________
• Following presentation at the Conference, would you accept invitations to present this paper before AWS Sections? Yes □ No □
• Papers accepted for presentation become the property of the Society with original publication rights assigned to the Welding Journal.

RETURN TO AWS HEADQUARTERS. MUST BE POSTMARKED NOT LATER THAN AUGUST 15, 1985, TO ENSURE CONSIDERATION.

Author’s Signature