Lead Alloys for High Temperature Soldering of Magnet Wire

Low tin solders reduce the erosion of fine copper wire in coil soldering processes

BY W. G. BADER

ABSTRACT. Five lead-tin solders have been evaluated for potential use in soldering applications involving solderable polyurethane enamel coated magnet wire. The dissolution of copper by the five molten solders has been investigated in the temperature range from 600 F (316 C) to 900 F (482 C). The microstructures at the copper to solder interface are exhibited for selected samples.

Additional data show that copper additions to solders drastically reduce the dissolution of copper wire in molten solders at elevated temperatures. Lead solders with low tin contents and lead-tin solders containing copper are suitable for elevated temperature soldering of magnet wire terminations.

Introduction

Magnet assemblies for miniature relays employ coils wound with polyurethane enamel and polyurethanenylon insulated copper wire (Fig. 1). The polyurethane enamel coating provides electrical insulation and permits soldering of the wire without prior removal of the enamel coating. Soldering temperatures of 600 F (316 C) to 800 F (427 C) are required to remove the insulation depending on the composition and thickness of the polyurethane enamel coating. At these temperatures, the wire diam-

W. G. BADER is a member of the Technical Stall, Bell Telephone Laboratories, Murray Hill, New Jersey 07974.

Paper was presented at the 4th AWS International Soldering Conference held during the 56th AWS Annual Maeting, Cleveland, Ohio, April 21-25, 1975. eter is reduced as a result of erosion of copper by the molten tin-lead solders that are commonly used. The copper wire ranges in size from AWG 32 (0.0080 in. diam) to AWG 43 (0.0022 in. diam) depending on coil application. The soldering of the coil wires to terminals is usually performed by a wave soldering process (Refs. 1,2).

The time of exposure to molten solder in this process is short, 1 to 7 s, depending on conveyor speed, length of solder wave and depth of submer-



Fig. 1 - Magnet coil assembly X2, reduced 44%

Table 1 — Solder Alloys						
Solder no.	Composition	Solidus temp., F	Liquidus temp., F	Cost of ^(a) metal \$/Ib		
1	97.5 Pb-1 Sn-1.5 Ag	588 527	588 570	1.07		
3	80 Pb-20 Sn	361	531	0.93		
4	40 Pb-60 Sn	361	371	2.30		
6 7	94.75 Pb-3 Sn-2.25 Sb 80 Pb-14 Sn-6 Sb	460 455	575 514	0.39 0.83		
8 9	70 Pb-30 Sn+0.75 Cu 40 Pb-60 Sn+0.75 Cu					
10	40 Pb-60 Sn+2.3 Cu					

(a) Cost of metals on March 1, 1975

sion of the parts in the solder. However, even with the relatively short exposure time, breaks in the coil wire at the soldered termination have been encountered in service. Examination of these fractures has revealed severe erosion of the copper that reduced the strength and ductility of the soldered connection. In some cases the erosion of the wire was catastrophic. While control limits are imposed on solder temperature and immersion time in the manufacturing process, the extent of the copper erosion cannot be detected by visual inspection after soldering.

The dissolution of copper and other metals by molten lead-tin solders has been the subject of previous investigations (Refs. 3,4) which have shown the rate of dissolution of copper in solders to increase with increasing tin content. This study was undertaken to evaluate the suitability of various solders for high temperature soldering of fine gage magnet wire in terms of limiting the observed wire erosion.

Experimental Tests

Materials

The solders evaluated in this investigation are given in Table 1. The first seven solders are commercially available alloys that are commonly used in soldering applications. The last three solders are special alloys with additions of copper. A 3000 g bath of each alloy was prepared from metals with the following purity:

Lead	99.97 + %
Tin	99.97+%
Silver	99.9+%
Antimony	99.9+%
Copper OF	99.95+%
he colder bath was	thermostatic

The solder bath was thermostatically controlled to maintain the desired temperature to within ± 1.5 F.

Wetting Test and Solder Appearance

Copper OF sheet specimens, 0.008 in. \times 0.75 in. \times 1.5 in. were de-



Fig. 3 — Dissolution of copper wires in molten 97.5 Pb-1 Sn-1.5 Ag solder

greased with 1,1,1-Trichloroethane and scrubbed with grade 00 steel wool. They were immersed in a 90% ZnCl₂-10% NH₄Cl aqueous soldering flux and then immersed to a depth of 1 in. in the solder bath for 2 to 3 s. A temperature of 700 F (371 C) was used for alloys 1-7, 600 F (316 C) for Alloy 9 and 800 F (427 C) for alloys 8 and 10. Samples were allowed to cool and were rinsed thoroughly in water.

The results of these tests are shown by Fig. 2 where the number designa-

tion identifies the alloy. All of the alloys except numbers 6 and 7 showed good wetting to the copper as evidenced by a continuous coating of solder. Dewetting of the copper, i.e., the withdrawal of molten solder from areas of the surface, was observed with the two alloys containing antimony. These results confirm those of other investigators (Refs. 5, 6).

The appearance of the alloy coatings was indicative of the melting



Fig. 2 — Wetting and appearance test specimens after immersion in solders from Table 1. X0.85, reduced 19%



Fig. 4 — Dissolution of copper wires in molten 90 Pb-10 Sn solder



Fig. 5 — Dissolution of copper wires in molten 80 Pb-20 Sn solder



Fig. 6 — Dissolution of copper wires in molten 70 Pb-30 Sn solder



Fig. 7 — Dissolution of copper wires in molten 40 Pb-60 Sn solder

range of the alloys, ie., the eutectic or near eutectic alloys were highly lustrous and glossy while those with wide melting ranges tended to be dull and frosty. For example, alloys 5 and 9 were highly lustrous, while alloys 8 and 4 were dull and slightly frosty. With the exception of alloys 6 and 7, all of the alloys produced coatings that would not cause difficulty during the inspection of soldered joints. Since alloys 6 and 7 exhibited poor wetting on copper, they were not included in subsequent evaluations.

Dissolution Tests on Copper Wire

The test procedures employed to determine the copper dissolution behavior were the same as those used in an earlier study (Ref. 4). Copper wire samples with a nominal diameter of 0.020 in. were degreased with 1,1,1-trichloroethane, dried and cleaned in

10% solution of HCl for 20 s. Each sample was fluxed with a 90% ZnCl2-10% NH₄Cl aqueous solution and immersed to a depth of 1 in. in the solder alloy bath being investigated. After the desired time interval the sample was removed and quenched in water. The tested samples were mounted. sectioned transverse to the wire axis, polished and etched to reveal the copper to solder boundary. The residual diameter was measured at three locations, 120 deg apart at a magnification of 100x using a filar eyepiece on a metallograph. Photomicrographs were taken to show the reaction products at the copper to solder interface.

Dissolution Tests Results

The residual diameter values were obtained from the average of three readings from each of two locations along the wire length. From these





data the decrease in radius was plotted as a function of immersion time for each temperature. These data are shown graphically in Fig. 3 through 7 for solder alloys 1 to 5. The data on alloy No. 5 were obtained in an earlier study (Ref. 4).

The dissolution rate lines were obtained from a least squares analysis of the test data except for the 97.5 Pb-1 Sn-1.5 Ag at 700 and 800 F. The dissolution rates of copper in the molten solders were obtained from the slopes of the linear plots and are given in Table 2. The temperature dependence of the dissolution rates for each solder are shown by the Arrhenius plot of Fig. 8. The reduced dissolution of copper by solder alloys containing copper is shown by Fig. 9.

Discussion of Results

All of the solder alloys that were investigated showed compound formation at the copper-to-solder interface. The compound layer was extremely thin with Alloy 1. Evidently the low tin content and the presence of silver retard the formation of the compound layer. With the lead-tin alloys, Nos. 2-5, the intermetallic compound Cu₆Sn₅ layer was observed on samples tested at temperatures below 779 F (415 C). For temperatures greater than 779 F the compound Cu_sSn₅ decomposes and the compound Cu₃Sn is formed. This compound does not appear to form an adherent layer as shown by Fig. 10, where Cu₃Sn particles are only seen within the solder layer. The Cu₆Sn₅ compound layer commonly encountered with tin-lead solders at lower temperatures is shown by Fig. 11.

The increased thickness of the Cu_6Sn_5 compound layer encountered with Alloy 9, 40 Pb-60 Sn + 0.75 Cu is shown by Fig. 12. The Cu_6Sn_5 particles formed from the copper addition are readily seen within the solder coating.

The addition of copper to solder alloys as a means of reducing subsequent copper dissolution is based on work conducted on copper buildup in solder pots (Ref. 7). The quantity of copper necessary for this purpose was estimated from the analysis of those solder baths that were contaminated over a range of temperatures. For the solder baths in this study, the dissolution of copper wires was reduced to a negligible amount as shown in Fig. 9 even though it is likely that the copper additions were not large enough to saturate the solder at the test temperature. For a copper-saturated bath the dissolution of the copper wires should be reduced to essentially zero. Copper additions to solders have also been employed to reduce the erosion of copper soldering bits (Ref. 8).

The decrease in dissolution rate of copper in molten solders with de-



Fig. 9 — Dissolution of copper wires in molten solders containing copper



Fig. 10 — Copper-to-solder (80 Pb-20 Sn) interface after 3 min at 900 F showing Cu_3Sn compound particles in solder. X800, reduced 19%

Fig. 11 — Copper-to-solder (70 Pb-30 Sn) interface after 2 min at 600 F showing $Cu_{e}Sn_{5}$ layer. X800, reduced 19%

creasing tin content observed in earlier studies was confirmed in this work. The lowest dissolution rates were exhibited by the solder alloy containing 1 percent tin, while the highest rates were encountered with the 40 Pb-60 Sn bath. In this investigation, the dissolution rates of copper in solders were determined in a static bath.

However, in production soldering operations employing wave ma-

chines, the dissolution of copper will occur under dynamic conditions. It has been shown by Howes and Saperstein (Ref. 3) that even mild agitation can increase the dissolution rate by a factor of 3 to 4 and Ward and Taylor (Ref. 9) have shown that a relative velocity of 0.052 ft/s increases the static rate of solution of copper in liquid lead and liquid bismuth by a factor of 2 to 3. Since the velocity of solder in wave machines varies between 0.5 ft per s and 1.5 ft per s (Ref. 10), the dynamic dissolution rates of copper in solder in production wave soldering can be expected to be greater than the static rates of this study by a factor of at least 4.

A comparison was made of the dissolution of fine copper wire in a production wave soldering operation



Fig. 12 — Copper-to-solder (40 Pb-60 Sn $^+$ 0.75 Cu) interface after 3 min at 600 F showing Cu_{6}Sn_{5} compound layer. X800, reduced 19%

with the dissolution predicted from the rate values obtained in this study. Magnet assemblies employing AWG 40 coil wire with a nominal diameter of 0.0031 in. were measured after wave soldering with a 40 Pb-60 Sn solder at \sim 700 F for 2 s. The residual diameters were 0.002 in. or a reduction of 0.0011 in. From Table 2, the radial dissolu-

Table	2		Rac	lial	Disa	olution	Rates	of
Coppe	r	Wire	In	Var	ious	Solder	Alloys	

		Dissolu-
Solder alloy	Temper- ature, F	tion rate 10 ⁻⁶ in./s
97.5 Pb-1 Sn -1.5 Ag	700 800 900	0.56 2.8 6.4
90 Pb-10 Sn	700 800 900	1.8 4.3 8.7
80 Pb-20 Sn	700 800 900	3.8 9.4 22.7
70 Pb-30 Sn	600 700 800	2.3 8.8 27.5
40 Pb-60 Sn	450 600 700 800 900	4.1 21.2 61.5 143. 248.

tion rate of copper in 40 Pb-60 Sn solder at 700 F is 61.5×10-6 in. per s. Using a dynamic rate factor of 4, a time of 2 s, and multiplying by 2 to convert to diameter, the predicted dissolution is 0.00098 in. The agreement between the predicted and the measured values Is quite good and indicates that for those tests a value of 4 for the dynamic rate factor is reasonable. For these same conditions, the reduction in diameter would be expected to be 0.000009 in. with the 97.5 Pb-1 Sn-1.5 Ag solder and 0.000028 in. with the 90 Pb-10 Sn solder.

Solder Test on Magnet Wire TermInations

Samples of magnet wire terminations were soldered in static baths of solder alloy Nos, 1, 2, 4, 5, 8 and 10. These tests were performed with a 25% rosin-alcohol flux and solder bath temperatures of 700 F. All of the soldered joints revealed evidence of good wetting to the wire and the terminal. Very little difference in the appearance of the soldered joints was observed with the rapid solidification of the small amount of solder contained at the joint. The results of these tests are shown in Fig. 13.

Conclusions

The dissolution rates of copper in five lead-tin solders have been determined and given in graphical form.



Fig. 13 - Coil wire-terminal soldered joints with solders from Table 1. X6, reduced 23%

374-s | OCTOBER 1975

These results indicate that the lowest tin content solders will produce the least erosion of fine gage copper wire at elevated temperatures. Of the solders studied, the 97.5 Pb-1 Sn-1.5 Ag produced the least erosion of copper.

The addition of copper to lead-tin solders provides an alternate method of reducing the rapid dissolution of copper wires in molten solder. In wave soldering operations, saturation of the soldering bath should be possible in short times by immersing copper rods in the flowing solders.

The appearance of high lead solders or solders with wide melting ranges should not present difficulty in the inspection of soldered joints.

Acknowledgments

The author wishes to express his appreciation to M. E. Davis who prepared the metallographic sections, photomicrographs and measured the wire samples and to thank P. L. Key, T. D. Schlabach and P. R. White for helpful comments on the manuscript.

References

 Bud, P. J., "Wave Soldering at Elevated Temperatures," *Welding Journal*, Vol. 53 (2), 1974, pp 79 to 87.
Bud, P. J., "Wave-soldering Tech-

2. Bud, P. J., "Wave-soldering Techniques For the Soldering and Tinning of Coils, Windings, and Wire," *Insulation/Circuits*, Vol. 20 (5), 1974, pp 65 to 67.

3. Howes, M. A. R., and Saperstein, Z. P., "The Reaction of Lead-Tin Solders

with Copper Alloys," *Welding Journal,* Vol. 48 (2), 1969, Research Suppl., pp 80-s to 85-s.

4. Bader, W. G., "Dissolution of Au, Ag, Pd, Pt, Cu and Ni in a Molten Tin-Lead Solder," *Welding Journal*, Vol. 48, (12), 1969, Research Suppl., pp 551-s to 557-s. 5. Lewis, W. R., "Notes on Soldering,"

5. Lewis, W. R., "Notes on Soldering," Tin Research Institute, October 1959, pp 87 to 88.

6. Manko, H. H., Solders and Soldering, McGraw-Hill, New York, 1964, pp 91-92.

7. F. G. Foster unpublished research.

8. U.S. Patent 2,671,844.

9. Ward, A. G., and Taylor, J. W. "Dynamic Solution — Rate Studies of Solid Metals in Liquid Metals," *Journal of Institute of Metals*, Vol. 86, 1957-58, pp 36 to 42.

10. P. J. Bud, private communication.

WRC Bulletin

No. 187

Sept. 1973

"High-Temperature Brazing"

by H. E. Pattee

This paper, prepared for the Interpretive Reports Committee of the Welding Research Council, is a comprehensive state-of-the-art review. Details are presented on protective atmospheres, heating methods and equipment, and brazing procedures and filler metals for the high-temperature brazing of stainless steels, nickel base alloys, superalloys, and reactive and refractory metals. Also included are an extensive list of references and a bibliography.

The price of WRC Bulletin 187 is \$5.00 per copy. Orders should be sent to the Welding Research Council, 345 East 47th Street, New York, N.Y. 10017.

WRC Bulletin

No. 197

August 1974

"A Review of Underclad Cracking in Pressure-Vessel Components"

by A. G. Vinckier and A. W. Pense

This report is a summary of data obtained by the PVRC Task Group on Underclad Cracking from the open technical literature and privately sponsored research programs on the topic of underclad cracking, that is, cracking underneath weld cladding in pressure-vessel components. The purpose of the review was to determine what factors contribute to this condition, and to outline means by which it could be either alleviated or eliminated. In the course of the review, a substantial data bank was created on the manufacture, heat treatment, and cladding of heavy-section pressure-vessel steels for nuclear service.

Publication of this report was sponsored by the Pressure-Vessel Research Committee of the Welding Research Council. The price of WRC Bulletin 197 is \$5.50. Orders should be sent to the Welding Research Council, 345 E: 47th St., New York, N.Y. 10017.

WRC Bulletin No. 184

"Submerged Arc Weld Hardness and Cracking in Wet Sulfide Service"

by D. J. Kotecki and D. G. Howden

This study was undertaken to determine:

(1) The causes of higher-than-normal hardness in submerged-arc welds in plaincarbon steels

(2) The levels of strength or hardness which will not be susceptible to sulfidecorrosion cracking

(3) Welding procedures which will assure that nonsusceptible welds will be produced.

Concentration is primarily on weld metal, though some consideration to the weld heat-affected zone is given. The study covered a two-year period. The first year was concerned with a macroscopic view of the weldments. In that first-year study, some inhomogeneities were observed in weldments which are not obvious in a macroscopic view of the weldment. It appeared likely that these inhomogeneities could affect the behavior of the weldment in aqueous hydrogensulfide service. Accordingly, their presence and effects were investigated during the second year. The price of WRC Bulletin 184 is \$3.50 per copy. Orders should be sent to the

The price of WRC Bulletin 184 is \$3.50 per copy. Orders should be sent to the Welding Research Council, 345 East 47th Street, New York, N.Y. 10017.

WRC Bulletin

No. 185

July 1973

"Improved Discontinuity Detection Using Computer-Aided Ultrasonic Pulse-Echo Techniques"

by J. R. Frederick and J. A. Seydel

The purpose of this project, sponsored by the Pressure Vessel Research Committee of the Welding Research Council, was to investigate means for obtaining improved characterization of the size, shape and location of subsurface discontinuities in metals. This objective was met by applying computerized dataprocessing techniques to the signal obtained in conventional ultrasonic pulseecho systems. The principal benefits were improved signal-to-noise ratio and resolution.

The price of WRC Bulletin 185 is \$3.50 per copy. Orders should be sent to the Welding Research Council, 345 East 47th Street, New York, N.Y. 10017.