

Interfacial Compositions of Solders and Fluxes on Aluminum

Flux constituents have an important effect on the resulting solder-aluminum interface

BY A. E. SCHWANEKE, A. Y. LEE
AND W. L. FALKE

ABSTRACT. Metallography and x-ray microprobe scans have been used to show the interfacial compositions obtained with solders and fluxes on aluminum. A series of wetting tests on plates of aluminum was made using four commercial fluxes and four alloys specifically designed for aluminum soldering. Cross sections of the solder-aluminum interface show the location of the metals from the fluxes and solders, and their effects on the characteristics of the interfaces.

Introduction

In attempting to solder aluminum, the properties of the resulting interface between the solder and the aluminum substrate are of major importance. Penetration of the tenacious aluminum oxide to make contact with the aluminum metal, a primary difficulty in soldering aluminum, is usually accomplished by using highly reactive fluxes. Many proprietary fluxes and filler metals have been developed for soldering aluminum, but general use of these

by industry has been small. Most of the fluxes contain metallic ions that are very important to the formation of the interface. The claim has been made (Ref. 1) that the solder does not contact the aluminum directly, but instead wets and adheres to a plated layer formed on top of the aluminum by metals from the flux.

As part of the research on aluminum soldering, a series of wetting tests in which a measured quantity of solder is allowed to spread over an aluminum plate was made to investigate the properties of the resulting solder-aluminum interface. X-ray microprobe analyses and photomicrographs were made of the cross sections of the plates to show the alloying reaction products that occur at the interface.

Experimental Procedure

The experiments were performed using four different commercial fluxes and four soldering alloys specifically designed for aluminum soldering. The aluminum plates were 1-1/2 in. squares of commercial 1/16 in. thick rolled sheet, type 1100 aluminum. The fluxes were all low melting types with an organic vehicle or base, and are designated in this report by the letters "A" to "D". Chemical analyses for inorganic ions in the fluxes are given in Table 1. Compositions of the four solder alloys, identified by the numerals 1 through

4 in this report, are given in Table 2. In addition to the 4 × 4 matrix of solders and fluxes, two other alloys were spread on aluminum plates for reference purposes. One alloy was a 95Zn-5Al brazing filler metal which was applied for the wetting test with a dry mixed flux of 88% ZnCl₂-8% NH₄Cl-4% NaF by weight. The other alloy was regular 50-50 tin-lead solder; it was applied with flux A.

The wetting tests were performed by placing a sized pellet of solder and the necessary flux in the center of the 1 1/2 in. square plate. This combination was then placed on a temperature controlled hotplate, and 20 to 30 seconds after melting and spreading occurred, the aluminum test plate was carefully removed and placed on an asbestos board to cool. The temperature of the hotplate was generally between 500 and 600 F to give about a 140 F superheat over the melting point of the particular solder alloy for the test. The spread plates were eventually sectioned through the center of the spread area, mounted in plastic, polished, etched, and then subjected to optical metallography and x-ray microprobe analysis. Replicate spread tests were also subjected to corrosion and ductility tests, but are not reported here.

To further check the reactions of the fluxes used in the tests, a small amount of each flux, without any solder, was placed on aluminum substrates and heated to soldering tem-

The authors are associated with the Rolla Metallurgy Research Center, Bureau of Mines, U.S. Department of the Interior, Rolla, Missouri.

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Table 1 — Chemical Analyses of Fluxes

| Flux | Chemical elements — grams/liter | | | | | | | |
|------|---------------------------------|-----|------|------|------|-------|-----|------|
| | Al | B | Ca | Cd | Sn | Zn | F | Cl |
| A | .23 | .60 | <.01 | <.01 | 10.2 | 16.5 | 147 | 0.0 |
| B | .01 | .50 | <.01 | <.01 | <.01 | 94.8 | 34 | <.01 |
| C | .05 | .60 | <.01 | <.01 | 8.7 | 76.4 | 38 | <.01 |
| D | 1.7 | .50 | .54 | 36.8 | 30.0 | 220.0 | 157 | .81 |

Table 2 — Solder Compositions

| Solder | Elements — weight percent | | | | |
|--------|---------------------------|-----|-----|------|----|
| | Pb | Sn | Ag | Bi | Sb |
| 1 | 92.5 | 5 | 2.5 | — | — |
| 2 | 95 | 3.8 | 1.2 | — | — |
| 2 | 79.7 | .6 | 1.2 | 18.5 | — |
| 4 | 90 | — | — | 9 | 1 |

peratures. These plates were also sectioned and subjected to microprobe analysis.

Results

Results of the experiments are presented as a series of photomicrographs accompanied by an equivalent series of scanning electron microprobe composites made from x-ray scans for each element of interest. The microprobe pictures were originally color composites with each element represented by a different color. However, for reproduction purposes, these color composites have been reduced to black and white photographs with varying shades of gray representing the location and distribution of the various elements in the interfacial phases. Although the black and white composites are not definitive in themselves, this format was chosen for publication as being more appropriate than single line scans or other methods that have been used to present x-ray microprobe data without color. By following the text closely, the information represented in the composites will become evident.

The photomicrographs were all made at 500X magnifications, while the microprobe composites used magnifications from 500X to 2,000X. Resolution of detail in the microprobe pictures is not as good as that in the photomicrographs for reasons associated with the generation of x-rays.

The first two photomicrographs, Fig. 1, show the contrast between the 95Zn-5Al brazing filler metal alloy and 50-50 tin-lead solder. A band of alloying occurred between the filler metal and the substrate for the zinc base alloy, while the tin-lead solder shows practically no interfacial diffusion. The interface between the tin-lead solder and the aluminum is very abrupt. The zinc base brazing alloy is used extensively to join aluminum and is very acceptable. The tin-lead solder forms a joint but is extremely susceptible to corrosion problems. The higher melting point for the zinc alloy (about 790 F) involved longer times for both heating and cooling, so, as is visible in the micrograph, some intergranular penetration of the substrate occurred — a problem that

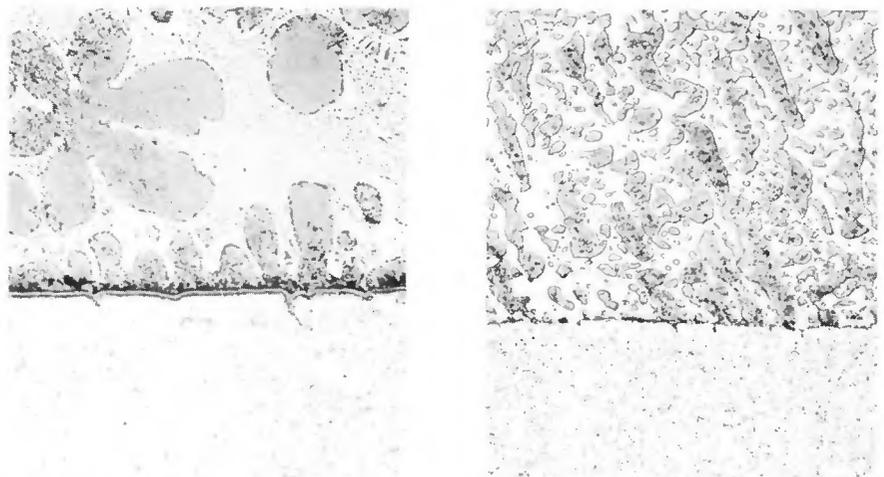


Fig. 1 — Brazing alloy and solder on aluminum substrates. (Left) 95Zn-5Al brazing alloy; (right) 50-50 Sn-Pb solder. (X500)

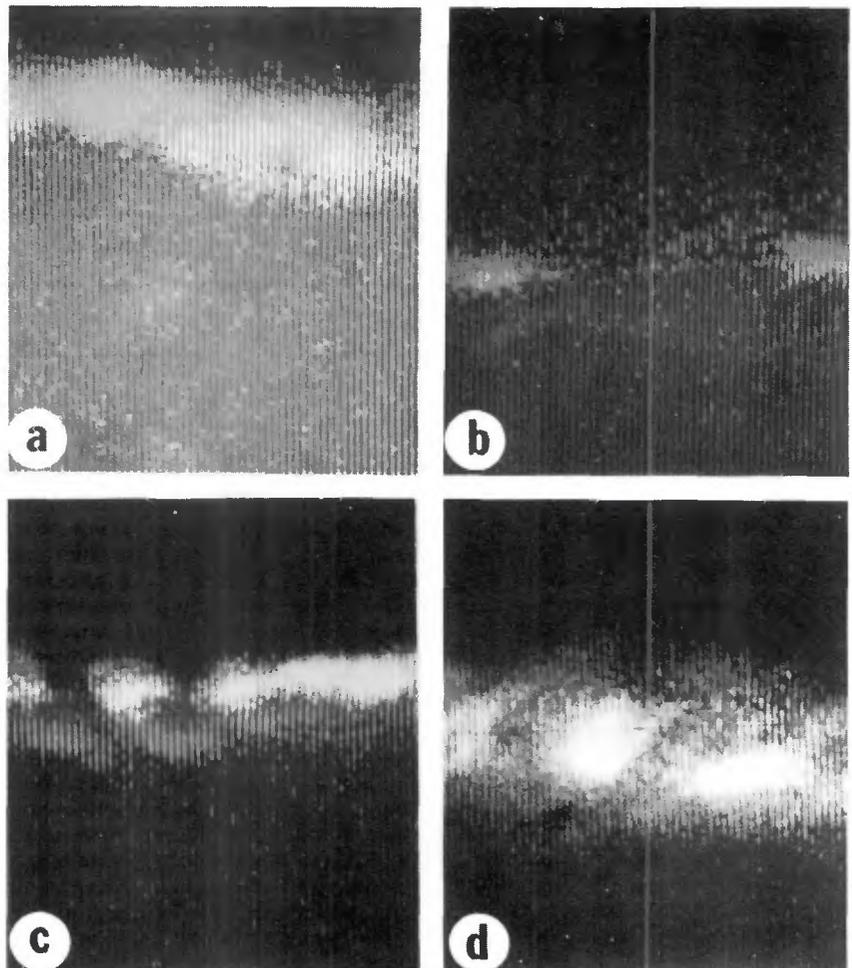


Fig. 2 — Fluxes on aluminum substrates (X1,600). Letter designations match the identification of fluxes in Table 1

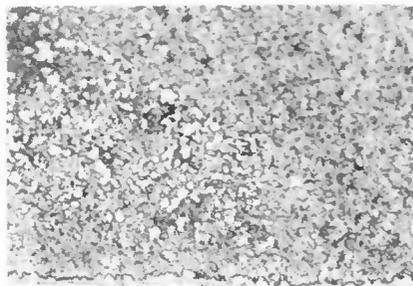


Fig. 3 — Solder 1 (92.5Pb-5Sn-2.5Ag) with flux A. (Left) photomicrograph (X500), right x-ray microprobe composite (X2,000)

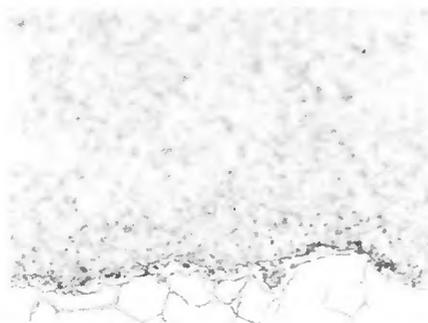


Fig. 4 — Solder 1 (92.5Pb-5Sn-2.5Ag) with flux B. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X500)



Fig. 5 — Solder 1 (92.5Pb-5Sn-2.5Ag) with flux C. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

further complicates aluminum soldering or brazing.

The first four microprobe composites, Fig. 2, are of the fluxes alone on the aluminum substrate (without solder). Magnification is 1,600X, and the aluminum substrate is at the bottom. The letter designation for each picture matches the identification of the fluxes listed in Table 1. In Fig. 2a (flux A) the medium gray strip is mainly zinc, while the two smaller light areas represent the location of tin. In this case, most of the zinc rests on the aluminum surface, but the tin penetrated into the aluminum a short distance. In Fig. 2b (flux B) the two light-gray spots show zinc on the surface with a slight penetration into the aluminum below. In Fig. 2c (flux C) the lower strip represents zinc penetrating into the aluminum substrate; the light spots are tin. Figure 2d for flux D shows about the same effect as Fig. 2c except that a weak cadmium signal detected was associated with the lightest spots. Without a covering layer of solder, most of the cadmium probably evaporated during heating. Although each flux contained boron, scans for this element are not included because the amount present was below the detection capabilities of the microprobe.

A consistent format is used for presenting the balance of the visual data representing the 4×4 matrix of solders and fluxes. In each case the photomicrograph on the left was made metallographically at 500X magnification. On the right is the black and white composite of x-ray microprobe scans. In every picture the aluminum substrate is at the bottom.

Figures 3 through 6 show solder 1 (92.5Pb-5Sn-2.5Ag) with the four different fluxes. In Fig. 3 (flux A) the photomicrograph shows a band at the interface with some intergranular penetration. Also, a scattered second phase appears spread through the solder bulk. In the microprobe composite the interfacial band shows primarily silver which, at the edge next to the aluminum, contains zinc, tin, and some dissolved aluminum. The upper part of the band (layer), a slightly darker gray, is silver alloyed with lead and some separate particles of silver. The dark area above the band is lead with scattered particles of tin and silver. These particles, the tin-silver phase, are visible in the micrograph.

The photomicrograph in Fig. 4 (flux B) shows substantial intergranular penetration, and the usual band along the interface. The microprobe revealed that the interface band is zinc and silver with some dissolved aluminum. The high zinc content of

flux B accounts for the high intergranular penetration. The smaller scattered particles in the lead solder which do not show in the photomicrograph are tin-silver alloy. The tin is associated with the silver except at the interfacial band.

The photomicrograph in Fig. 5 (flux C) shows a very narrow band at the interface and a second band some distance from the substrate. The intergranular penetration is less than for flux B although C contains proportionately more zinc. The microprobe composite showed that the interfacial band is zinc and silver. The lower darker gray edge of this band shows dissolved aluminum with the silver and zinc. The tin is distributed above and in the solder and does not appear at the interface. The second band up in the solder is primarily tin with some small particles of silver. Incidentally, the large hole at the left edge of the photomicrograph is the result of a gas bubble probably developed from the flux vehicle. Such bubbles are not unusual.

Most of the features in Fig. 6 (flux D) are the same as those in Fig. 5 except that the cadmium from the flux appears in the band along with the zinc, silver, and dissolved aluminum. The interfacial band, or layer, also detaches or splits away from the surface where the aluminum has been penetrated by the zinc. This, as will be seen in subsequent pictures, is a characteristic of cadmium in the flux. The portion of the specimen shown in the microprobe composite did not exhibit the splitting.

Figures 7 to 10 show solder 2 (95Pb-3.8Sn-1.2Ag) used with the four fluxes. Because this solder is similar to 1, except for slightly less tin and silver, the results were anticipated to be somewhat similar. In Fig. 7 (flux A) the silver from the solder and the zinc from the flux are located in the interfacial layer. Very little intergranular penetration was found in this specimen, but experience has shown that both the quantity of zinc available in the system and the amount of time the solder is molten have a decided influence on the amount of penetration. In this case the silver is concentrated at the lower edge of the interfacial layer and probably had some effect on the penetration. Most of the tin is located in the bulk solder with the lead, and very little is located at the interface. Some attack of the aluminum is evident also.

Figure 8 (flux B) shows the effect of additional zinc in the flux. The photomicrograph shows the intergranular penetration by the zinc. The interfacial layer again contains silver and zinc, with the silver located mainly at the lower edge of the layer. That is, the silver has greater affinity for the

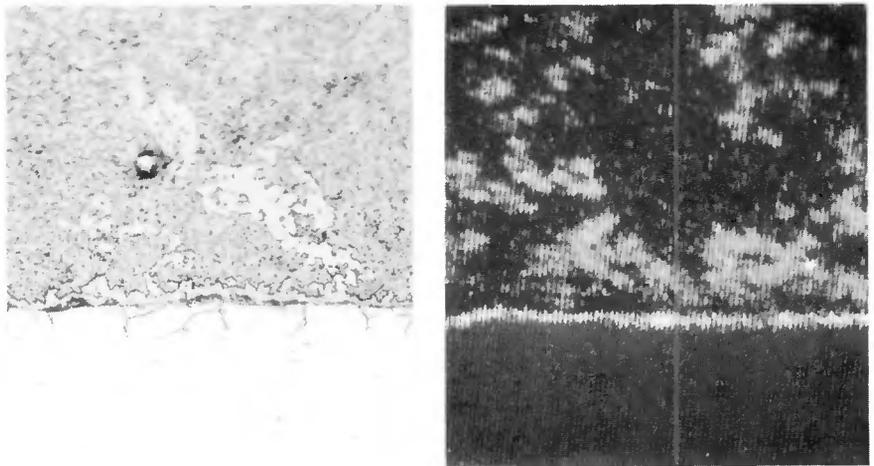


Fig. 6 — Solder 1 (92.5Pb-5Sn-2.5Ag) with flux D. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X500)

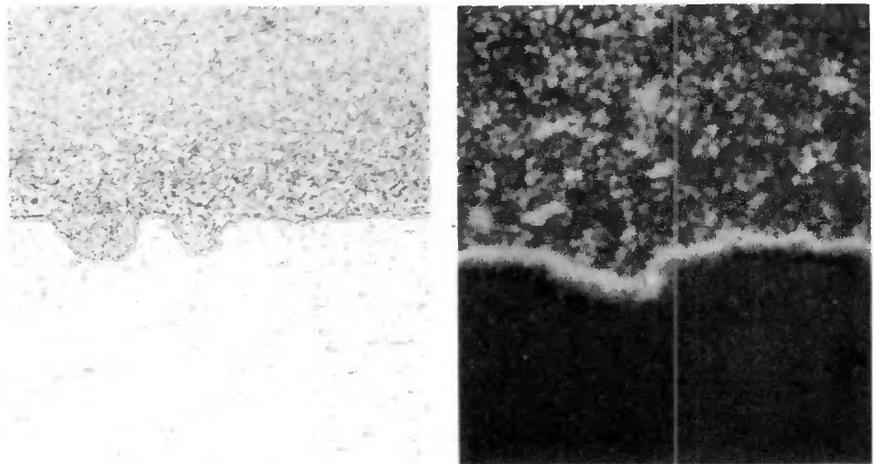


Fig. 7 — Solder 2 (95Pb-3.8Sn-1.2Ag) with flux A. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

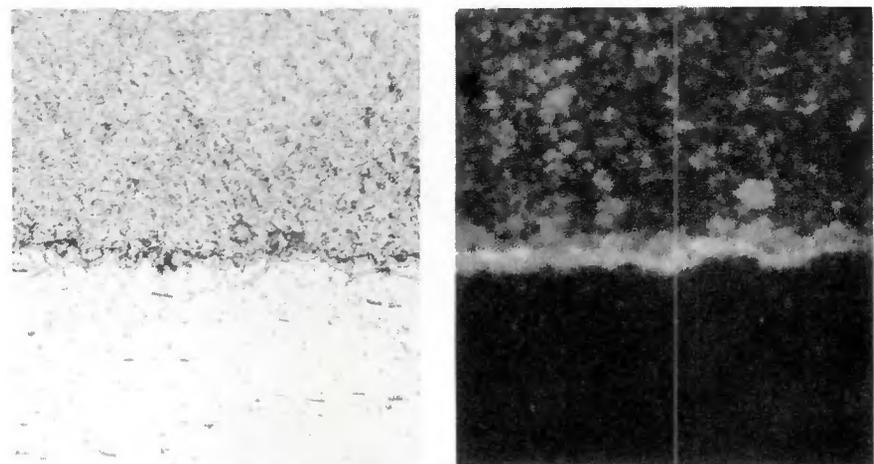


Fig. 8 — Solder 2 (95Pb-3.8Sn-1.2Ag) with flux B. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

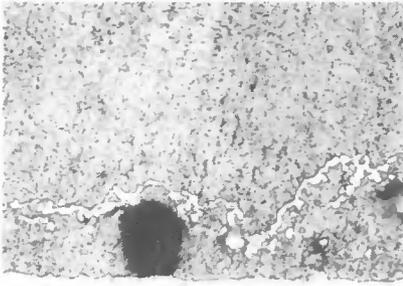


Fig. 9 — Solder 2 (95Pb-3.8Sn-1.2Ag) with flux C. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

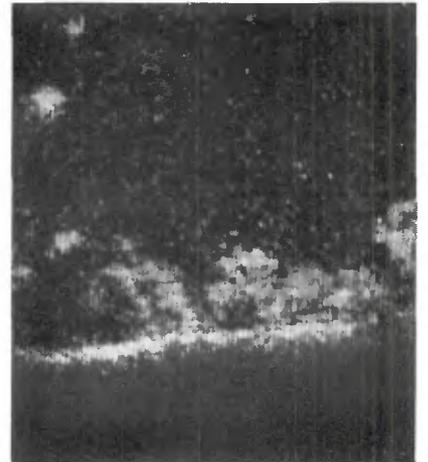
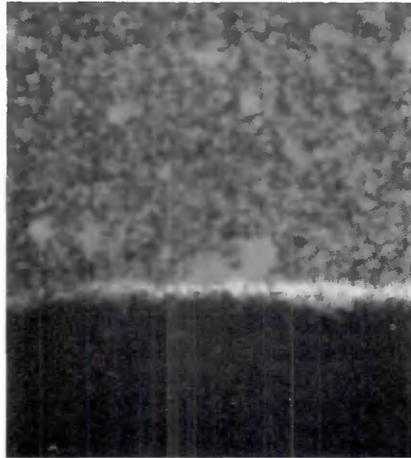


Fig. 12 — Solder 3 (79.7Pb-0.6Sn-18.5Bi-1.2Ag) with flux B. (Top) photomicrograph (X500); (bottom) x-ray microprobe composite (X1,000)

Fig. 10 — Solder 2 (95Pb-3.8Sn-1.2Ag) with flux D. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

shows in the microprobe composite. This strip is mainly tin in association with a small amount of zinc. This reduces the zinc in the interfacial band and thus the width of the band (thickness of the interfacial layer).

Figure 10 (flux D) also shows intergranular penetration resulting from the increased zinc in the flux. Zinc is the most prominent feature at the interface, and silver and cadmium concentrations are very low. The tin appears mainly scattered through the bulk of the solder.

Figures 11 to 14 are for solder 3 (79.7Pb-0.6Sn-18.5Bi-1.2Ag). All four photomicrographs and accompanying microprobe composites have similar features. These are (a) a very thin interfacial band or layer, (b) a general etching of the aluminum surface, and (c) a prominent broken and scattered phase directly above the interfacial band, or in some places lightly attached to the band. In general, no intergranular penetration is evident. The interfacial layer consists of dissolved aluminum, zinc, and silver. The bismuth in the solder is associated with the lead. Tin is found associated with the silver in the inter-

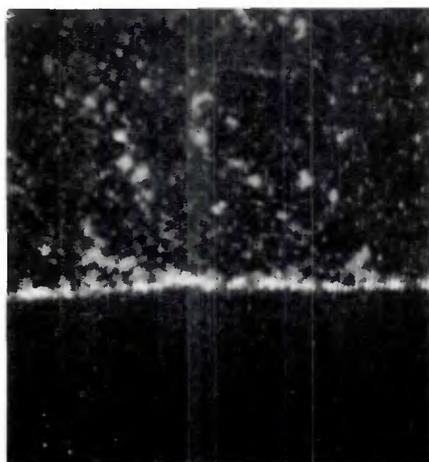


Fig. 11 — Solder 3 (79.7Pb-0.6Sn-18.5Bi-1.2Ag) with flux A. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X500)

aluminum than for the lead in the solder.

Additional tin in the system as characterized by Fig. 9 (flux C) has lit-

tle effect on the interfacial band, but gives rise to larger tin particles in the solder. The strip across above the interface in the photomicrograph also

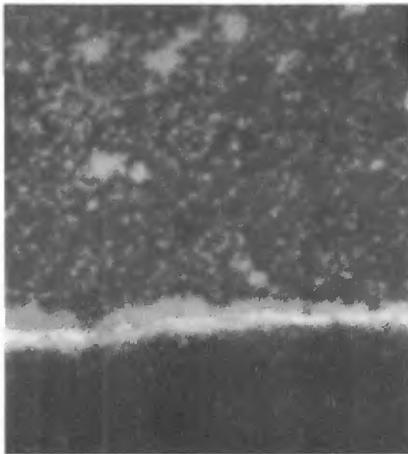


Fig. 13 — Solder 3(79.7Pb-0.6Sn-18.5Bi-1.2Ag) with flux C. (Top) photomicrograph (x500); (bottom) x-ray microprobe composite (x900)

face, and also as isolated particles through the bulk of the solder. The particles just above the interface are silver and zinc. The sizes of these particles are somewhat proportional to the amount of zinc in the flux. The cadmium from flux D, Fig. 14, is also found in the broken particles just above the interface.

The last four Figures (15 to 18) are for solder 4 (90Pb-9Bi-1Sb). Before pointing out the features shown in the micrographs it should be noted that this solder, without silver or tin, spreads very slowly. It requires an extra 30 to 50 F superheat before it begins spreading, and the spreading is relatively sluggish, although complete. This will explain the excessive intergranular penetration and etching of the substrate that can be seen in the photomicrographs. The microprobe composites show that the penetrant is entirely zinc. The bismuth is associated with the lead in the bulk solder. The microprobe composite for Fig. 15 (flux A) shows the antimony associated with the zinc as bright spots along the interface. The same feature occurs in Fig. 16 (flux B) and Fig. 17 (flux C). The tin is associated with the lead in Fig. 15 and does not

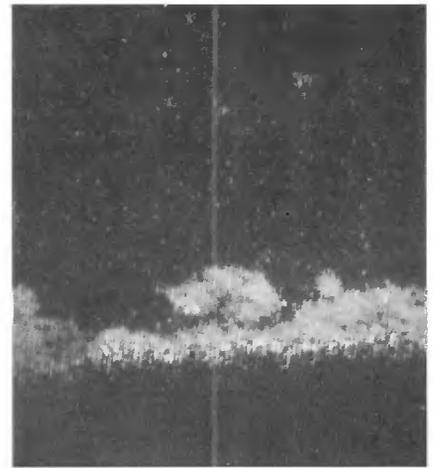
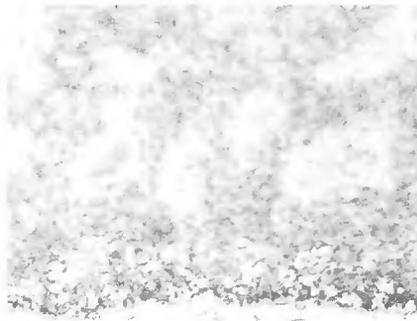


Fig. 14 — Solder 3 (79.7Pb-0.6Sn-18.5Bi-1.2Ag) with flux D. (Left) photomicrograph (x500); (right) x-ray microprobe composite (X1,000)

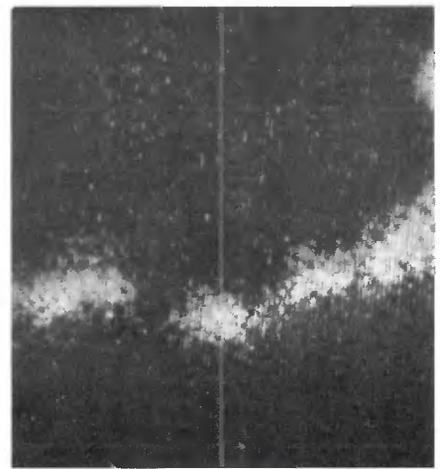
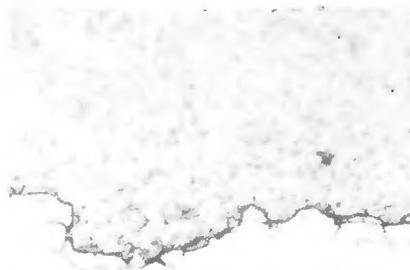


Fig. 15 — Solder 4 (90Pb-9Bi-1Sb) with flux A. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X2,000)

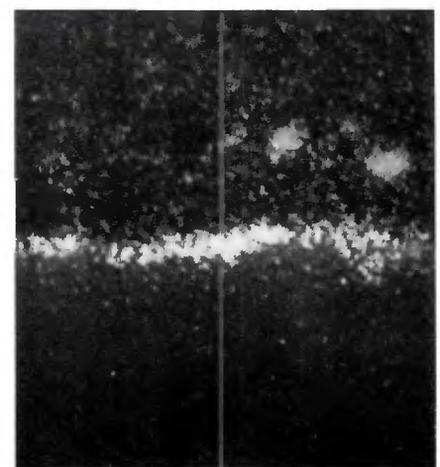


Fig. 16 — Solder 4 (90Pb-9Bi-1Sb) with flux B. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X2,000)

appear at the interface.

The darker centers of the small round spots in the microprobe composite for Fig. 17 are concentrations

of antimony, surrounded by a mixture of antimony with zinc. The light streaks at the bases of these small round spots represent a mixture of

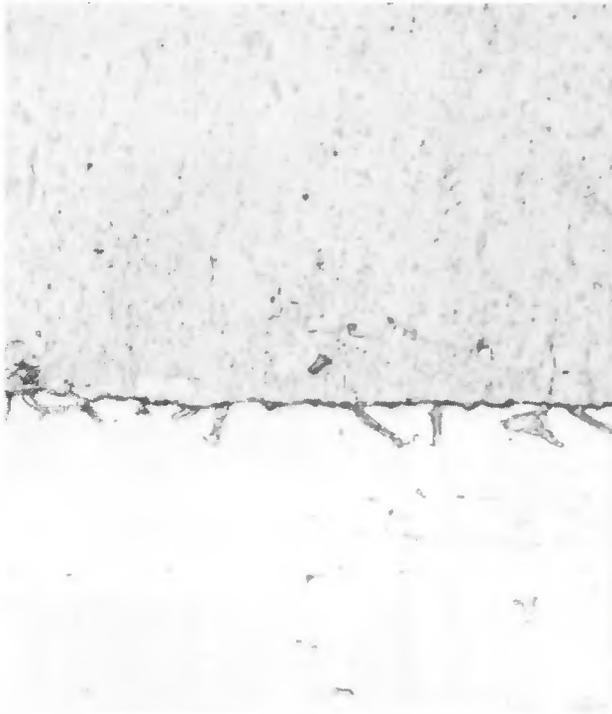


Fig. 17 — Solder 4 (90Pb-9Bi-1Sb) with flux C. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X900)

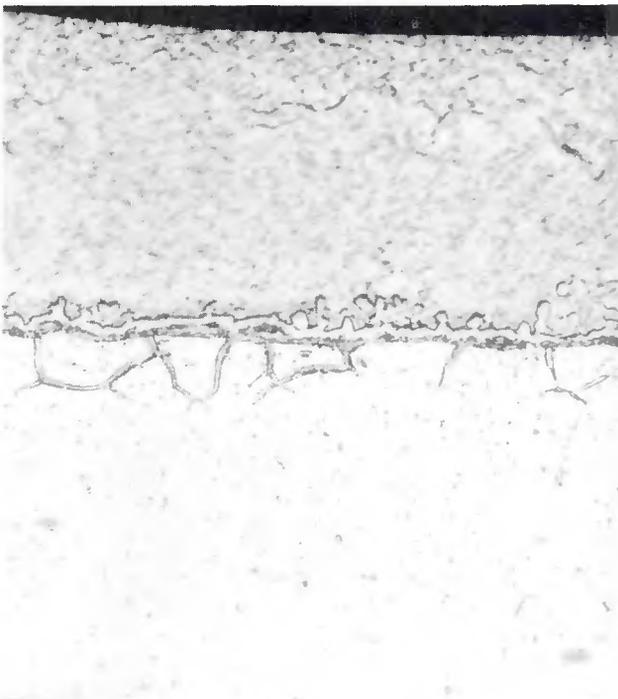


Fig. 18 — Solder 4 (90Pb-9Bi-1Sb) with flux D. (Left) photomicrograph (X500); (right) x-ray microprobe composite (X2,000)

aluminum, zinc, and antimony.

Figure 18 (flux D) is of special interest due to the presence of cadmium in the flux. Both the photomicrograph and the microprobe composite show that the cadmium laid down by the flux separated from the substrate and allowed lead and bismuth to penetrate below. This effect contrasts with the information given in the *Aluminum Soldering Handbook* (Ref. 1). The upper light streak in the

microprobe composite is a layer of cadmium with zinc at its lower edge. To the right edge of the composite, the dark area below the cadmium and zinc is lead and bismuth. The lower streak across at the true interface is a mixture of zinc, aluminum, and a small amount of tin. The streak extending down into the substrate below is primarily zinc. This represents the intergranular penetration easily seen in the photomicrograph.

Conclusions

Several general observations can be made on the basis of the evidence shown. In every case there is little, if any, alloying with the solid substrate. The presence of zinc in all the fluxes is usually the alloying agent when alloying occurs, but excessive zinc leads to intergranular penetration. Silver in the solder is a beneficial, but expensive, alloying agent. The com-

bination of silver and zinc produces an alloy interface, but this interface is always sharply defined from the aluminum substrate. This is in sharp contrast with ordinary tin-lead solders on copper or brass, the ideal solder system, where up to five different alloys have been identified in the interface with no definite dividing lines between the substrate and the solder (Ref. 2). In some cases with these aluminum solders and fluxes, the band of alloying has a tendency to break away and float upward into the bulk of the solder. This is probably related to the amount of time at melting temperatures. If the flux contains cadmium, this is found with the silver at the interface, or slightly removed from the interface. The zinc from the flux often penetrates through the surface layers of silver and cadmium to diffuse into the aluminum along the grain boundaries. Thus the statement that the solder does not contact the

aluminum, but instead wets and adheres to the plated layer formed on top of the aluminum by metals from the flux (Ref. 1), is not entirely correct.

Tin seems to add little to the effectiveness of the solder-aluminum bond, and as humidity corrosion tests have shown, tin at the interface accelerates detachment of the solder from the aluminum. Three of the four fluxes contain tin ions, but the microprobe composites of fluxes and of the wetting tests show that the tin does not form a uniform band at the interface. Instead, the tin seems to be associated with either the zinc or the silver. It does not alloy extensively with the substrate.

The key to even a partial answer to the problems of soldering aluminum revolves around the interfacial compositions. If a component, or a combination of components, could be developed to produce a graded, dif-

fused interface, alloying with both the solder and the substrate, an aluminum solder would be practical.

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WRC Bulletin No. 194 May 1974

"Fatigue Behavior of Pressure-Vessel Steels"

by J. M. Barsom

The regulations governing the design of pressure vessels are based on experience gained over many operational years and have evolved, primarily, to prevent failure under static load conditions. This design philosophy has been successful in ensuring adequate service behavior because pressure vessels are not usually subjected to large numbers of load fluctuations during their expected service life. However, the need to effectively utilize materials and to provide the utmost in safety and reliability has made it imperative to determine the fatigue behavior of these structures.

The fatigue life of structural components is determined by the initiation of cracks and their propagation to critical dimensions. This report presents fatigue-crack-initiation and fatigue-crack-propagation data for pressure-vessel steels operating in a benign environment and at temperatures below the creep region.

Data obtained by testing pressure vessels and pressure-vessel components, and the results of surveys of pressure-vessel failures are discussed. It is concluded that the probability of fatigue failure of properly designed and fabricated pressure vessels is very low and that the most effective approach to keep this probability low is to minimize the magnitude of the stress (strain) concentration factors. This can be accomplished through proper design of details and through proper fabrication.

This paper was prepared for the Pressure Vessel Research Committee of the Welding Research Council. The price of WRC Bulletin 194 is \$4.50. Orders should be sent to the Welding Research Council, 345 East 47th Street, New York, N.Y. 10017