

The Spreadability of Automotive Solders

Partially molten solders do not spread well if the matrix grains are too large. Large initial grains, high heating temperatures, long heating times and compositional variations may all contribute to poor spreadability

BY H. W. KERR

ABSTRACT. The spreadability of Pb-Sb-Sn-As automotive solders has been examined using a simple test. Solders do not spread well if the matrix grain size is too large. Several factors have been shown to be important in retaining a small grain size including composition, initial grain size and thermal treatment. Alloys containing two solid phases in the partially molten state ripen more slowly than alloys containing only one solid phase. Different compositions also have different amounts of macrosegregation in cast ingots, because of a change in the solidification morphology from single phase dendrites to two phase duplex dendrites.

Introduction

Solders are used to fill certain crevices remaining on automobile bodies after initial welding assembly. Most North American automobiles require from six to eight pounds of these alloys and the industry uses over 50 million pounds of "body" solder per year. Despite this wide usage, considerable intermittent difficulties are encountered with the alloys now in use.

The application of body solders involves heating the alloy to a partially molten state and then using a trowel to apply and spread it over the area of interest while occasionally heating the solder with a large torch when it becomes too cold to work. A common difficulty is that certain batches of solder do not spread easily; instead of spreading like soft butter they are "sugary" or "grainy" and cannot be applied evenly. Besides slowing down the soldering process on the assembly line, poor spreadability results in more pores in the alloy after the solder is subsequently ground to fit the smooth

lines of the automobile, and these pores often remain even after the area is painted.

This paper reports the results of an investigation designed to pinpoint the variables which can lead to poor spreadability. The study centered around an alloy commonly used for this purpose which contains about 92% lead, 5% antimony, 2.5% tin and 0.5% arsenic. Although the results are only immediately useful for this particular alloy, similar characteristics are almost certainly found for other soldering or brazing alloys which are only partially melted.

The Pb-Sb-Sn-As alloy was originally developed empirically for use as a body solder.¹ In order to understand the effects of small compositional changes, an initial investigation of alloys containing 5.4% antimony, 2.25–3.0% tin and 0.2–0.6% arsenic was undertaken. These results have been reported in detail elsewhere² but certain conclusions are summarized here in order to explain the approach used in the spreadability investigation.

For alloys made up from 99.999%

purity elements a minimum in the upper liquidus temperature was found for all tin concentrations investigated at about 0.40–0.45% arsenic. Lower arsenic concentrations resulted in the initial solidification of large lead dendrites, with the subsequent solidification of three other phases; tin arsenide, tin antimonide and antimony. Alloys with arsenic concentrations of about 0.45% and above exhibited primary tin arsenide needles at the top surfaces of the small ingots but most of the volume of these ingots was dominated by duplex dendrites formed by the simultaneous solidification of lead and tin arsenide.

The addition of impurities, either by using 99.9% purity lead or by intentional additions of 0.03–0.04% sulphur, raised the nucleation temperature of the tin arsenide phase. In the range 0.4 to 0.5% arsenic such impurities resulted in shorter tin arsenide plates in more equiaxed lead grains. In all cases solidification was completed by the growth of tin antimonide and antimony.

Since the constitution and micro-

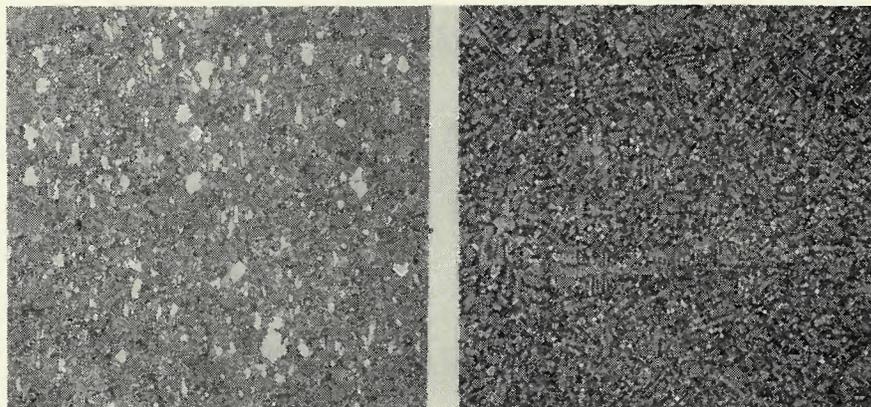


Fig. 1—Sections of commercial body solders (left) as-received virgin solder (right) as-received reclaimed solder; X200. Note that the virgin solder contains larger non-matrix phase particles

but the matrix grain size is too small to be seen, whereas the lead dendrites are easily visible in the reclaimed solder but the particles of the other phases are very small.

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This investigation was carried out while on leave at the Ford Scientific Research Staff Laboratories, Dearborn, Michigan.

Table 1—Chemical Analyses of Commercial Body Solders

Body solder	Composition, wt %				
	Antimony	Tin	Arsenic	Sulphur	Lead
Virgin	5.28	2.62	0.41	0.0025	bal
Reclaim A	5.50	2.72	0.42	0.0025	bal
Reclaim B	5.26	1.55	0.42	0.0025*	bal

* Estimated

structure of Pb-Sb-Sn-As alloys are very sensitive to the exact arsenic and impurity contents, the spreadability might conceivably be affected by small compositional changes. This possibility was investigated using the simple spreadability test described below on various alloys. The effects of other variables such as the initial grain size and the thermal treatment of the solder were also tested.

Alloys

Both commercial and simulated body solders were investigated. The commercial alloys were either as-received (virgin) solder or reclaimed solder which had been remelted and rapidly solidified. A typical analysis of a virgin solder is given in Table 1 along with the analyses for two reclaimed solders. The microstructures of the virgin and reclaimed solders were very different (Fig. 1). The virgin solder contained relatively large non-matrix particles in a lead matrix whose grain size could not be detected but was presumably very small since recrystallization would have occurred during the production of the alloy, but grain growth would be restricted by the other phases. In contrast, lead dendrites can be seen in the reclaimed solders, surrounded by small particles of the other phases.

Three 1000 gm ingots of simulated solders with nominal compositions of 2.5% tin, 5.4% antimony and 0.3, 0.5 and 0.7% arsenic were cast into glass tubes, quickly cooled to room temperature, and then swaged from 19 mm diameter to 7.2 mm diameter. Commercial purity (99.9%) lead was used in these ingots to simulate the impurity contents of commercial body solders. The same weight of virgin commercial solder was subjected to the same procedure as a standard. The chemical analysis of specimens from the top and bottom of each ingot is given in Table 2. A typical microstructure of these swaged simulated solders is shown in Fig. 2; the grain size of the lead matrix is presumably very small because of the swaging operation and the particles of non-matrix phases are generally somewhat smaller than in virgin solders.

Spreadability Test

The assembly line soldering oper-

ation was simulated using a very simple technique. Specimens weighing about 250 gm were placed on a steel sheet and heated with a gas torch while being mixed with a trowel. When the alloy was in a uniform, partially molten state an attempt was made to smooth its surface with the trowel, and the solder was then allowed to solidify. Since it was found that the temperature to which the solder was heated was important in determining spreadability, an effort was made to keep this temperature approximately constant and especially not to overheat any regions of the specimen.

Two features could be used to qualitatively assess the spreadability. First, some solders were obviously easier to spread. Second, the consistencies of the solders were reflected in their surface quality, for good solders had smooth shiny surfaces and poor solders had rough dull surfaces. Photographs of the surfaces were taken, and sections of the specimens were examined metallographically to relate the spreadability to the microstructure.

Results and Discussion

Results of the spreadability tests are

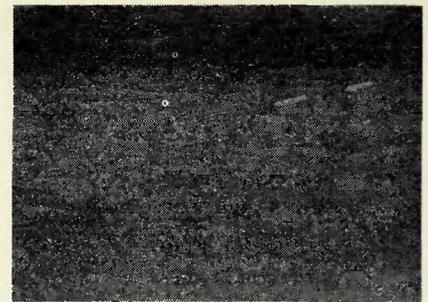


Fig. 2—A typical microstructure of the swaged simulated body solders; X200. Compare with Figure 1.

summarized in Table 3. The description of the spreadability is related to both the ease with which the alloy could be spread and the smoothness of the resulting surface. The extremes of resulting surface quality are illustrated in Fig. 3. Virgin solder had a smooth and, in places, shiny surface while the same solder spread after being held for 20 hours at 260°C had a very rough and dull surface. The ridges in Fig. 3 (left) are an artifact produced by grooves on the trowel used to spread the alloy.

The differences in spreadability could be explained by examination of the microstructures of the alloys, some of which are shown in Fig. 4. In all cases alloys which retained a small grain size spread well, whereas alloys having large grains of the lead matrix spread poorly. This is shown clearly by comparison of Fig. 4(a) with Figs. 4(b), 4(d) and 4(e); only the alloy shown in Fig. 4(a) spread well. Fig. 4(c), which shows a region of swaged Ingot 1 (0.30% arsenic) illustrates

Table 2—Chemical Analyses of Swaged Simulated Body Solders (in weight per cent)

Ingot number	Section	Composition, wt %			
		Arsenic content		Tin	Antimony
		(nominal)	(actual)		
1	top	0.30	0.18	1.79	4.0
	bottom	0.30	0.36	2.84	5.95
2	top	0.50	0.50	2.31	5.10
	bottom	0.50	0.53	2.52	5.40
3	top	0.70	0.68	2.45	5.34
	bottom	0.70	0.71	2.43	5.22
4	top	virgin	0.48	2.79	5.66
	bottom	virgin	0.48	2.80	5.87

Table 3—Summary of Spreadability Tests on Commercial and Simulated Body Solders

Alloy*	Prespread condition	Spreadability	Comments
Virgin	as received	good	
Reclaim A	as received	good-mediocre	
Reclaim B	as received	mediocre-poor	low tin content
Ingot 1	swaged	good	occasional large grains
Ingot 2	melted and solidified	poor	
	swaged	good	
Ingot 3	melted and solidified	poor	
	swaged	good	
Ingot 4	melted and solidified	poor	
	swaged	good	
Virgin	ripened 20 hours at 260°C	very poor	very large grains

* Analysis given in Table 1 or 2

that occasional large grains did result in this alloy during spreading, but most of the specimen contained smaller grains and it spread well. (Note the difference in magnification for this figure). At least three variables are important in determining the matrix grain size; composition, initial grain size and thermal treatment during processing.

Composition

The spread specimens of virgin solder Fig. 4(a), showed that many grain boundaries of the lead matrix contained large particles of non-matrix phases comparable in size to the large non-matrix particles in the as-received virgin solder, Fig. 1(a). From the constitutional investigation² it is known that heating these alloys to temperatures above 247°C (freezing range is 240-280°C, approximately) should completely melt the antimony and tin antimonide phases, but melting of the tin arsenide phase will depend on the exact arsenic content of the alloy. Since the size of the large non-matrix particles suggest that they were at least partially solid during the spreading operation, these particles are almost certainly tin arsenide. Their presence at the lead grain boundaries implies that they somehow impede grain coarsening of the lead matrix. Hence if the composition were such that this phase were not present the matrix grains might coarsen more rapidly.

It is believed that Reclaim B solder does show the effects of the absence of the tin arsenide phase, which could not be detected either by cooling curve or metallographic studies in this solder, presumably because of the low tin content. This has resulted in a larger grain size and poorer spreadability than in Reclaim A solder, even though the initial dendrite size was comparable in the two reclaimed solders.

The effects of composition were found to be less serious than expected in the swaged simulated solders, however. That is, alloys having average nominal arsenic compositions of 0.3, 0.5 and 0.7% all spread well if they were first swaged, even though the liquidus temperature of the tin arsenide phase would vary by about 20°C for this composition range in pure quaternary alloys.² This apparent lack of composition sensitivity may be due to at least two factors. First, the use of commercial purity lead in these simulated solders would increase the nucleation temperature of the tin arsenide phase because of the presence of impurities, thus decreasing the range of liquidus temperatures of this

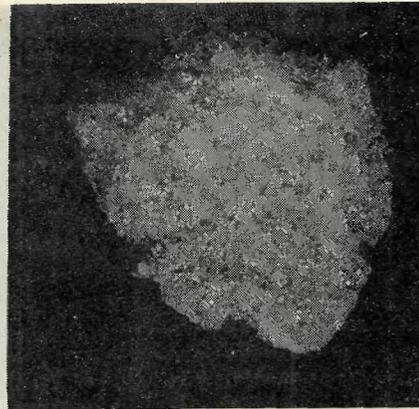
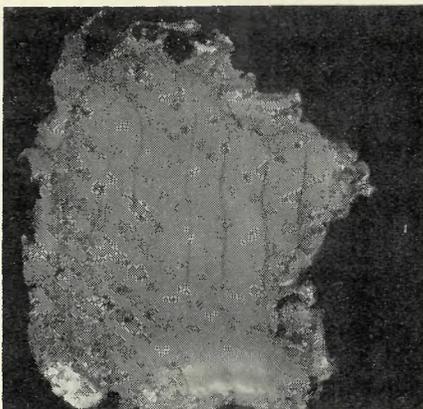


Fig. 3—Surfaces after the spreadability test on (left) as-received virgin solder and (right) virgin solder first annealed

20 hours at 260°C. (X $\frac{1}{4}$). These specimens show the extremes of good and very poor surface quality and spreadability.

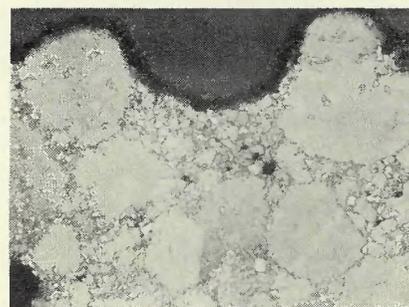
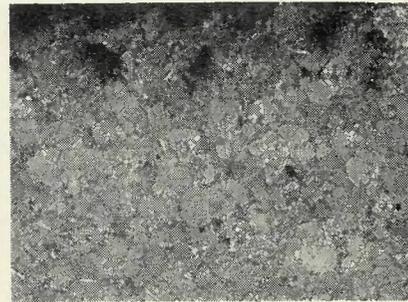
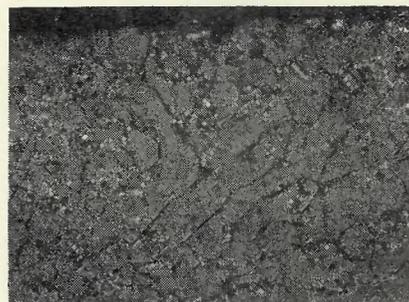
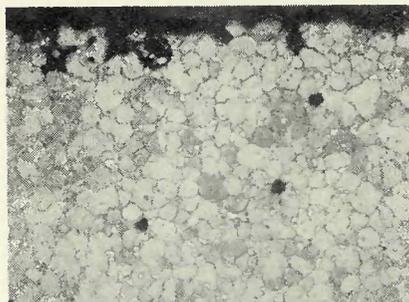


Fig. 4—The microstructures near the surfaces of spread specimens of (a) as-received virgin solder (X100); (b) as-received Reclaim B solder (X100); (c) swaged Ingot 1 (X200); (d) melted and solidified Ingot 2 (X100); (e) virgin solder annealed 20 hours at 260°C (X100). Photos are in order, top to bottom. See Table 3 and the text for a description and discussion of the spreadability of these specimens.

phase for the arsenic compositions studied. Second, since considerable macrosegregation was found in the swaged Ingot 1, some regions of the spread alloy might have higher arsenic contents if complete mixing did not occur during the heating and spreading of the alloy. Since some regions would remain low in arsenic, these would ripen preferentially, as illustrated in Fig. 4(c), but the alloy still spread well because in most areas the grain size remained small.

The macrosegregation found at the low arsenic content (Table 2) is an important result which is related to the solidification microstructure of the alloy. In this alloy the lead phase freezes first as large dendrites in the colder part of the ingot, rejecting the other elements into the remaining liquid. At high enough arsenic contents, however, the lead and tin arsenide phases freeze simultaneously with fewer side branches and a smaller grain size.² This change in morpholo-

gy allows the other phases, antimony and tin antimonide, to freeze in between the primary phases and thus reduce the macrosegregation considerably. The commercial solder alloy which was cast and swaged as a standard (Ingot 4) had no detectable macrosegregation. This slight improvement from the simulated solders with high arsenic concentrations is presumably the result of the nucleation effects of unknown impurities in the commercial solder. In summary, the investigation showed that even if high (0.45–0.50%) arsenic contents are not necessary for good spreadability, it would be difficult to produce large ingots of a lower arsenic content with a uniform composition.

Initial Grain Size

Since body solders do not spread well if the grain size is too large, the initial grain size must be small for good spreadability. This was shown clearly by the alloys which were first melted and solidified before being reheated and spread. The large grains in these alloys, Fig. 4(d), resulted in poor spreadability, whereas swaged specimens of the same compositions spread well.

The best method to produce a fine grain size is cold working. Small grains are also produced by rapid solidification, but the grains are somewhat larger than in worked specimens

(Fig. 1) and are dendritic. Hence even after rapid solidification the solder should be cold worked for best spreadability as noted elsewhere.¹ This solidified microstructure leads to coarser grains and poorer spreadability, and solders reclaimed in this way are therefore not so acceptable as virgin solder.

Thermal Treatment

Even if the starting grain size is small, large grains will result if the solder is either overheated and completely melted or held at an intermediate temperature for a long time because of the normal grain ripening process.¹ The extreme case of holding a virgin solder for 20 hours at 260°C coarsened the grains so much that individual grains protruded from the spread surface, Fig. 4(3).

The application of solder to an automobile body will therefore only be successful if the operator is skilled enough not to work the solder too long or overheat the solder.

Conclusions

1. Partially molten solders do not spread well if the matrix grains are too large. Large initial grains, high heating temperatures, long heating times and compositional variations may all contribute to poor spreadability.

2. Alloys which contain two solid phases when in the partially molten

state coarsen more slowly than alloys which contain only one solid phase. In Pb-Sb-Sn-As alloys containing about 5% antimony, 2.5% tin and 0.5% arsenic the two "high temperature" phases are the lead matrix and tin arsenide.

3. In Pb-Sb-Sn-As alloys containing about 5% antimony and 2.5% tin, arsenic contents of about 0.3% exhibit considerable macrosegregation in cast ingots, but the macrosegregation is essentially eliminated in alloys containing 0.5 and 0.7% arsenic. This has been related to a change in the solidification morphology from single phase dendrites to more equiaxed duplex dendrites as the arsenic content is increased.

Acknowledgements

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References

1. D. J. Harvey; U.S. Patent 3, 197, 862, (1965).
2. H. W. Kerr; J. Inst. Metals, 99 (1971) 238.

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"Elastic-Plastic Deformations in Pressure Vessel Heads"

By F. A. Simonen and D. T. Hunter

This publication presents the results of an investigation of the elastic-plastic behavior of pressure vessel heads under internal pressure. The work was sponsored over a two-year period by the Pressure Vessel Research Committee, with the first year being devoted to ellipsoidal heads and the second year to torispherical heads. Battell's computer program, NONLEP, developed for elastic-plastic analysis of thin shells of revolution, was applied to a set of typical head geometries subjected to internal pressure. This program includes effects of large deformations and strain hardening and thus it was possible to predict the additional pressure-carrying capability of heads beyond the collapse pressure predicted by limit analyses. Curves giving details of the numerical results are organized as appendices, with the main body of the publication devoted to discussion of the analyses.

"Summary Report on Plastic Limit Analysis of Hemispherical- and Toriconical-Head Pressure Vessels"

By J. C. Gerdeen and D. N. Hutula

The Subcommittee on Shells of the PVRC has been sponsoring a design study for the purpose of formulating design criteria for pressure vessels operating at temperatures below the creep range. Various design criteria have been considered, including elastic stresses, elastic-plastic stresses, buckling, and plastic collapse (limit analysis).

It was noted that both elastic and plastic analyses had been conducted for torispherical- and ellipsoidal-head vessels. For hemispherical-head vessels, only an elastic analysis had been conducted. It was desirable that a plastic analysis also be conducted for these heads. For toriconical heads, detailed analyses of any kind were lacking. Results of plastic limit analysis for torispherical heads had been applied as an approximation to toriconical heads, but the accuracy of this approximation was questionable.

This report describes the proposed work which now has been completed.

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