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Review of cast-on-strap joints and strap alloys for lead–acid batteries

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Abstract

This review examines the influence of the various parameters involved in the cast-on-strap (COS) process on the quality of the resulting lug–strap joints. In addition, it provides the findings of an investigation on the macroscopic and microscopic features of COS joints in commercial lead–acid batteries. Some examples of the most common defects that can affect the performance and life of batteries are presented. The nature of the fusion at the lug–strap interface for the various lugs and strap alloy compositions used in conventional, hybrid and valve-regulated lead–acid batteries are also discussed.

Keywords: Cast-on-strap; Defects; Fusion; Lug–strap interface; Strap alloys; Valve-regulated lead–acid batteries

1. Introduction

The cast-on-strap (COS) process is a widely applied method for grouping plates of the same polarity in each cell of a lead–acid battery. This process brings about the joining or soldering of the grid lugs with the strap, to form a 'COS joint'. The joints provide structural integrity to the cell and act as electrical connections between the individual grids and, subsequently, between the cells via the inter-cell welds. Therefore, it is important that these COS joints be mechanically strong, bonded well to the grid lugs, possess good corrosion resistance, and offer low electrical resistance.

In recent years, many COS machines have become available with improved technology and high production rates. Nevertheless, due to the complex heat-transfer conditions involved, the quality of the resulting joint is highly sensitive to each of the process parameters. The effects of some of these parameters on the quality of the joints have been reported elsewhere [1,2].

Tear-down analyses of commercial batteries have been carried out at Pasminco and it has been found that the COS joints in many of the batteries exhibit various physical (macroscopic) defects which could affect the performance and/or life of the batteries. There are also some reports of the failure of negative plates in valve-regulated lead–acid (VRLA) batteries due to corrosive attack at the lug/top-bar area [3,4]. It can therefore be deduced that COS joints are still an area of concern that needs more attention and improvement.

In this paper, the parameters involved in the COS process and their effects on the quality of the joints are reviewed. The nature of fusion at the lug–strap interface for various lug and strap alloy compositions used in commercial batteries is discussed.

2. Cast-on-strap process

2.1. Joining / fusion process

The COS process basically involves immersion of the cleaned (brushed) and stacked plate lugs into a preheated mould cavity filled with molten lead (strap) alloy, followed by cooling of the strap. The joining occurs by partial melting of the lug surface which then wets and fuses with the strap alloy in the liquid state. This fused lug–strap interface solidifies at a rapid rate and, thereby, creates a bond between the lug and the strap.

During the solidification process of the strap and the lug–strap interface, unless favourable heat transfer conditions exist, the joint can exhibit several casting defects (e.g., shrinkage porosity) as well as lack of fusion. As the sizes of grids and straps vary from battery to battery, the cooling/heat-extraction conditions required to produce a

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defect-free COS joint demand careful design of the strap mould and control of the process variables.

Some of the important COS operating conditions which demand careful attention are:

- grid lug and strap composition;
- strap alloy pour temperature;
- strap mould temperature;
- flux composition;
- lug cleanliness;
- grid lug thickness and spacing;
- lug immersion time;
- lug penetration depth;
- strap thickness.

It is to be noted that the heat-transfer conditions for each battery design change significantly because of the difference in the relative mass of the strap and the grids of each cell. This necessitates the implementation of appropriate parameters for each battery design in order to obtain joints of good quality.

2.2. Macroscopic features of cast-on-strap joints

The quality of the COS joints can be assessed by observing the macroscopic features of the cross-sections of the lug–strap joints. The main features to be noted are described below. The parameters of the process that affect these features will become clearer from further discussions and specific examples given in the following sections.

Meniscus — The meniscus represents the integrity of the joint, and describes the contact angle between the strap alloy and the lug surface. A positive meniscus indicates that the strap alloy has completely wet the lug surface to form an obtuse angle, and vice versa; this is shown schematically in Fig. 1. A negative meniscus indicates the reverse and can increase corrosion at the lug–strap interface by holding electrolyte in the crevice between the lug and the strap.

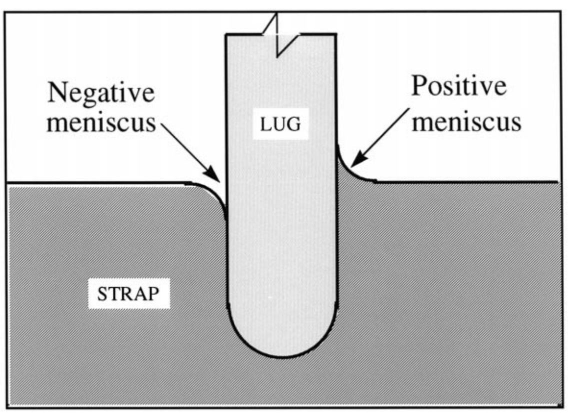

Fig. 1. Schematic diagram of types of meniscus that can form in a COS joint.

Extent of fusion — This represents the percentage of the lug immersed below the strap surface that shows intimate joining with the strap alloy. The extent of fusion is important in terms of both the electrical and physical properties of the joint. Poor fusion indicates a reduced area of interface across which the current can pass in the cell, thus weakening the joint as well as decreasing the electrical conductivity of the joint.

Gas and shrinkage porosity — Gas porosity occurs at the lug–strap interface when the gas formed by vaporization of the flux cannot escape to the strap surface because the mobility of gas bubbles in the melt has been lowered. Porosity is also caused by shrinkage of grains during solidification and usually occurs more readily in alloy systems with a wide freezing range. This phenomenon also reduces the area of conduction and the strength of the joint but is, in turn, less severe than gas porosity and lack of fusion.

Lug melting — This describes the extent and position of macroscopic melting of the lug surface due to excessive heat in the joining system. While lug melting below the strap surface is not in itself a problem, it usually indicates a poorly controlled joining process. Excessive lug melting right up to the strap surface would, however, significantly reduce the strength of a COS joint.

2.3. Requisites of strap alloy

Among the various parameters (listed in Section 2.1) which affect the COS process, the first and foremost is the selection of an appropriate strap alloy compatible with the grid lug composition. With the latest developments in low-maintenance and maintenance-free batteries, various alloys (lead–calcium, lead–tin) are used for making battery grids. This has led to the need of appropriate strap alloys which suit a particular grid alloy.

The strap alloys must satisfy the following basic requirements:

- form good bonding with the grid alloy;
- possess good corrosion resistance to the internal conditions of the battery (exposure to high temperatures, acid/alkaline conditions, etc.);
- possess high mechanical strength;
- offer low electrical resistance.

Furthermore, in terms of fusion, the strap alloy must also meet the following three criteria.

(1) In order to ensure proper fusion, the molten strap alloy must transfer heat effectively to the immersed lug, and thus allow the surface of the lug to melt. Entrained air and gases produced by flux vaporization at the lug–strap interface present a barrier to heat transfer. To minimize the effect of these barriers, the strap alloy must have

Table 1
Generally recommended strap alloy compositions (wt.%)

Battery and grid alloy	Strap alloy	Reference
Low-maintenance battery with low-antimony grids	2.75–4.5 wt.% Sb (with grain refiners 0.07 wt.% Cu, 0.003 wt.% S or 0.02 wt.% Se)	[2,5]
Very-low-maintenance/hybrid battery with Pb–Ca and Pb–Sb grids	(a) 2.75–4.5 wt.% Sb (with grain refiners 0.07 wt.% Cu,0.003 wt.% S or 0.02 wt.% Se);	[2,5]
	(b) 3.5–3.6 wt.% Sb (with no Sn and 0.020–0.023 wt.% As)	[7]
Battery with pure-lead grids	Pure lead	[5]
VRLA gel batteries with Pb–Ca–Sn grids	(a) Pb–2 wt.% Sn; (b) Pb–2 wt.% Sn with 0.03 wt.% As	[6]
VRLA AGM batteries with Pb–Ca–Sn/Pb–Sn grids	(a) Pb–0.8–2.5 wt.% Sn (Sb, As < 0.002 wt.%, Ni, Te < 0.0005 wt.%); (b) Pb–2 to 3 wt.% Sn; (c) Pure lead	[2,7]

high fluidity to allow the escape of the entrapped gases to the melt surface and high wettability with the lug alloy to promote bonding between the two alloys. Good wetting results in a positive meniscus.

(2) For fusion to occur, there must be a sufficient heating period in which both the lug and strap remain at least partially molten at the interface. During the COS process, the strap temperature falls soon after filling of the mould due to heat loss through the mould walls and into the lug. On the other hand, the temperature of the lug surface increases due to the incoming heat from the melt. At some time after immersion, the lug surface in contact with the melt strap reaches a transient peak temperature. Thus, it is important that the transient peak temperature is at least just above the final solidification temperatures of both alloy systems.

(3) In order that inter-cell welding be carried out efficiently during assembly of the batteries, the solidified strap alloy must be fine grained and ductile, and there must be minimum age-hardening between casting and inter-cell welding [5].

Table 1 lists the strap alloys which are currently being used, as well as those suggested for particular applications [2,5–7]. The macroscopic and microscopic features of the joints, as observed in some commercial batteries, are also discussed below.

3. Lug–strap interface

3.1. Lead–antimony strap alloys

The main characteristic of the lead–antimony alloy that makes it suitable for use in straps and through-the-partition welds is that it has a wide freezing range with a moderate amount of eutectic [2]. In most automotive battery applications, antimony levels of 2.75–4.5 wt.% are preferred, as sufficient eutectic is necessary to fuse completely with the lug. At levels of antimony below 2.75 wt.% in the strap, it is not possible to attain sufficient eutectic by segregation at the interface and, therefore, this leads to lack of fusion.

A typical COS joint between a Pb–1.7 wt.% Sb lug and Pb–2.7 wt.% Sb strap is shown in Fig. 2. The extra eutectic at the convex, positive type of meniscus has aided the bonding process to get better fusion. The interface region of a Pb–1.7 wt.% Sb lug and Pb–3.5 wt.% Sb strap joint that exhibits gas porosity and shrinkage porosity is shown in Fig. 3. This porosity could be due to both the fluxing operation and the presence of grain refiners in the strap alloy.

In the case of hybrid batteries, lead–calcium alloys for negative grids have a high melting point (327°C) compared with antimony alloys (250°C for Sb contents of 1 wt.% and above). Furthermore, lead–calcium alloys have no eutectic to melt partially at the surface and bond with the strap

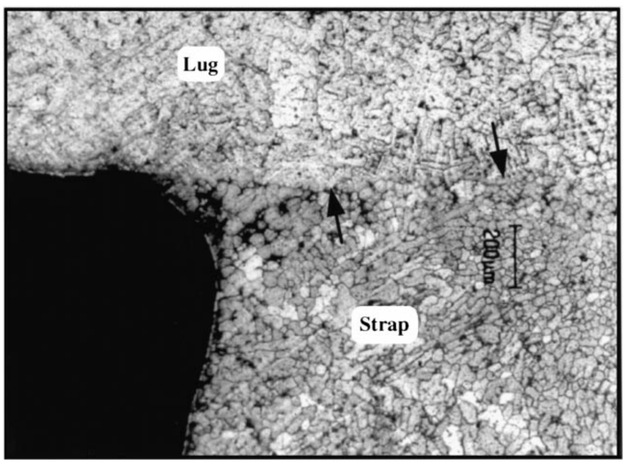

Fig. 2. Pb–1.7 wt.% Sb lug/Pb–2.7 wt.% Sb strap interface. Note excellent fusion at the interface (indicated by arrows).

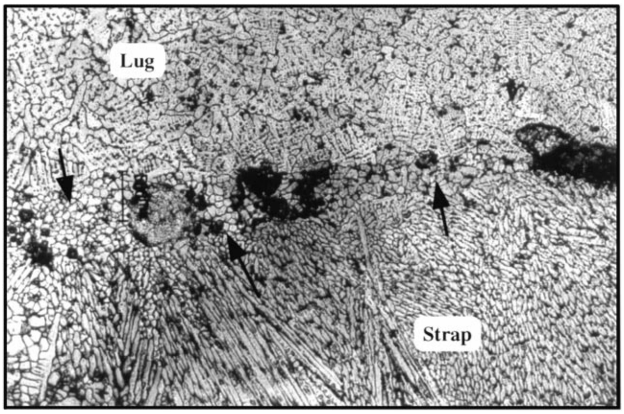

Fig. 3. Pb–1.7 wt.% Sb lug/Pb–3.5 wt.% Sb strap interface. Note gas porosity and shrinkage porosity (on right) at interface (indicated by arrows).

alloy. Due to this fact, it is impossible to fuse a Pb–Ca grid to an antimonial strap by a hand-burning operation, as it cannot provide sufficient heat to melt Pb–Ca lugs. But, in the COS operation, the ability of the bonding process is enhanced by brushing/cleaning the lugs and treating the surface with a flux, and maintaining the molten strap alloy sufficiently hot. The cleaning and fluxing operations remove and reduce any oxides at the surface of the lugs and, thereby, favour melting of the lug surface. The eutectic liquid in the strap permits the gases from the fluxing operation to escape before solidification takes place.

The good wetting and fusion that can be achieved for a Pb–0.1 wt.% Ca-0.3 wt.%–Sn lug and a Pb–3.5 wt.% Sb strap are shown in Fig. 4. Again, a higher proportion of eutectic is seen in the meniscus region.

The grain refiners in the antimonial strap alloy also provide a fine grain structure in the solidified strap and thus aid the inter-cell welding process. Excessive grain refiners can, however, cause problems with porosity by coming out of the solution (as dross particles) and collecting at the interfaces of entrained gas bubbles. This prevents the bubbles from escaping to the melt surface as it solidifies. It has been reported [2] that in strap alloys (used for Pb–Ca–Sn–Al grid alloys) containing too much sulphur, compounds such as aluminium or calcium sulphide can form at the interface and, thereby, inhibit bonding and cause premature corrosion of the interface.

The lug–strap interface for a lead–calcium lug of a rolled and expanded grid is shown in Fig. 5. These micrographs portray heat transfer and solidification phenomena that occur during the fusion process. During solidification, the initial steep temperature gradient set at the lug–strap interface falls gradually due to rapid extraction of heat from the lug surface. Hence, the solidification front at the lug surface initiated as a heterogeneously nucleated chill zone proceeds further as columnar/dendritic grains into

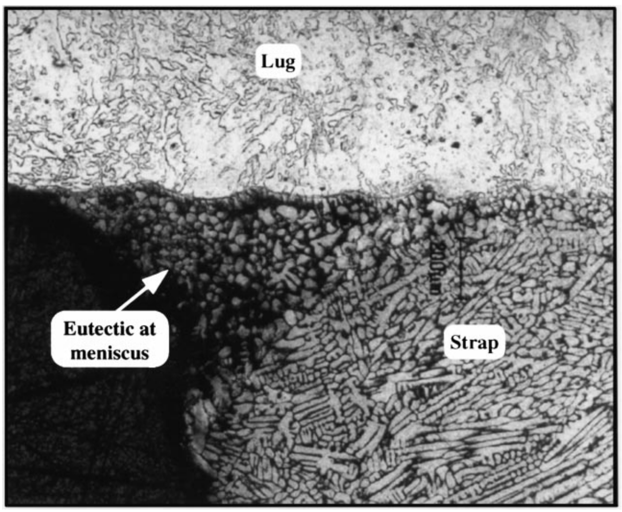

Fig. 4. Pb–0.1 wt.% Ca lug/Pb–3.5 wt.% Sb strap interface. Note excellent fusion and extra eutectic at meniscus.

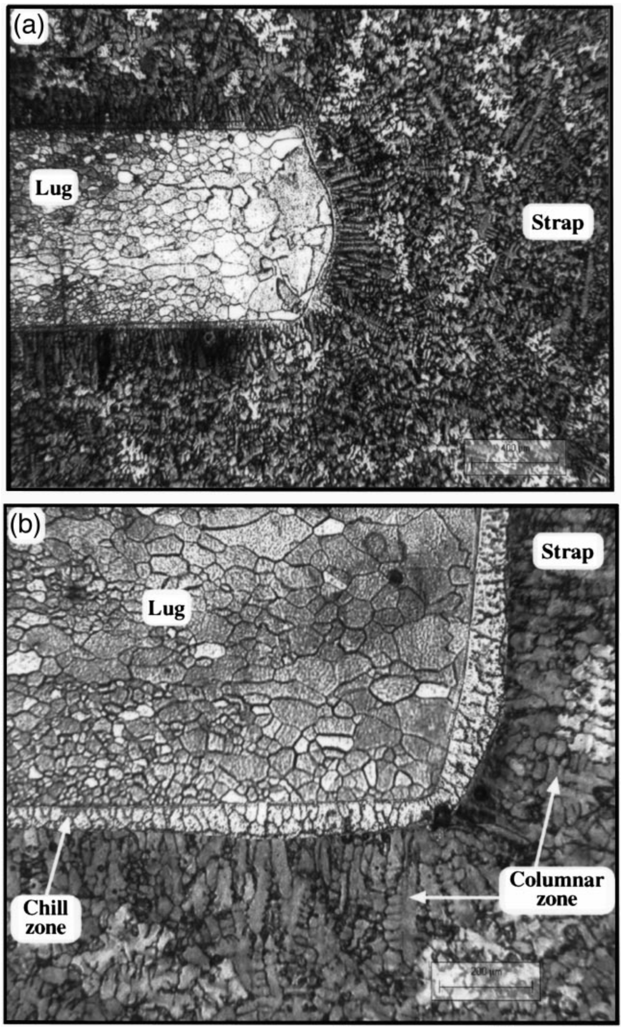

Fig. 5. Lug–strap interfaces for lead–calcium lugs of rolled and expanded grids: (a) note chilled and columnar grains at edge of lugs and randomly oriented grains of strap away from lug (×50); (b) higher magnification (×200) of another joint showing distinct chill zone and columnar grains at interface.

the strap, opposite to the direction of heat extraction. At the same time, rapid heat extraction from the bottom of the strap mould results in randomly oriented dendritic grains and completes the fusion process.

The heat transferred to the lugs during the solidification (or fusion) process results in heat treatment of the lugs. This brings about some changes to the microstructure of the lugs in the regions within and close to the strap. These changes are more pronounced for mechanically rolled grids/lugs (Fig. 6a) than for conventionally cast grids. Thus, the microstructures shown in Fig. 5 represent a thermograph which indicates the direction and amount of heat flux that is flowing through the lug and strap regions during the COS process. The highly textured grains in the lug (prior to immersion in the strap alloy) have recrystallized and grown into bigger grains. The amount and size of recrystallized grains in the lug have varied with the amount and direction of the heat flux. In the lug region outside the strap (Fig. 6b), the recrystallization has occurred only partially and has resulted in fairly small grains which still exhibit the directionality of rolling.

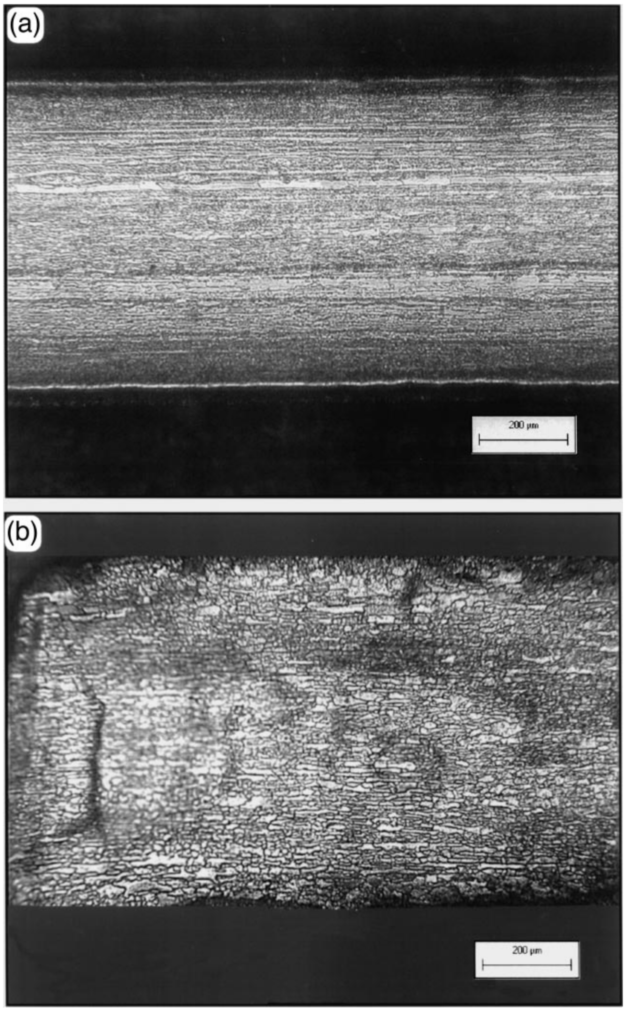

Fig. 6. Micrographs of rolled and expanded lug (a) prior to immersion and (b) after immersion, outside strap region.

Despite the fact that antimonial alloys provide excellent fusion with lead–calcium grid alloys, it is well known that antimony has the deleterious effect of increasing evolution of hydrogen gas at the negative. Hence, in VRLA batteries where any gassing is critical, it is impractical to use an antimonial alloy even in the strap.

3.2. Lead–tin strap alloys

As noted in Table 1, VRLA batteries generally utilize lead–calcium–tin alloys for the grids and lead–tin (2–3 wt.%) alloys for the straps. In contrast to the antimonial strap alloy, lead–2 wt.% Sn alloy has a very small freezing range, no eutectic liquid, and a melting point near to that of the grid alloy (320°C). All of these alloy characteristics render the fusion process more difficult. In practice, however, this problem is overcome by pretreating the lugs (i.e., by cleaning, fluxing and tinning) prior to immersion into the molten strap. Preheating the lugs may also prevent chilling and, thereby, enhance the bonding.

Tinning is carried out by dipping the lugs in either pure tin (which melts at 232°C) or 63 wt.% Sn–37 wt.% Pb eutectic alloy (which melts at 173°C) [2,8]. Tinning creates additional eutectic liquid at the lug–strap interface to allow a positive meniscus and complete fusion. Also, the lower melting point alloy allows longer time for the fusion/soldering action. A recent Pasminco survey of alloys used in VRLA batteries has indicated that tinning is being adapted by some battery manufacturers, based on the fact that minor amounts of lead–tin eutectic are observed in the interface regions of some of the lug–strap cross-sections.

Typical features observed for lead–calcium lug and lead–tin strap joints are shown in Figs. 7–9 In these joints, although the extent of fusion is found to be generally good in the lug tip regions, adhesion at the sides of the lugs is quite poor and the meniscus is of a negative type (Figs. 7 and 9). The presence of a small percentage of porosity is also quite common. More importantly, in a number of cases, the point of fusion of the lug with the strap (i.e., the lug–strap interface at the lug tip) occurs quite close to the strap surface, and even outside the top level of the strap (Fig. 7). This could be due to a shallow penetration depth set for the lugs in the COS process. It is also possible that extensive lug melting at the tip could have occurred, thereby shifting the interface towards the strap surface. If the point of fusion occurs closer to the top surface of the strap, then the mechanical strength of the joint decreases.

The micrograph shown in Fig. 8 suggests that the lead–tin (2–3 wt.%) alloy has good fusing properties with lead–calcium grids. The strap alloy exhibits a cellular substructure of segregated tin. But the lack of fusion at the

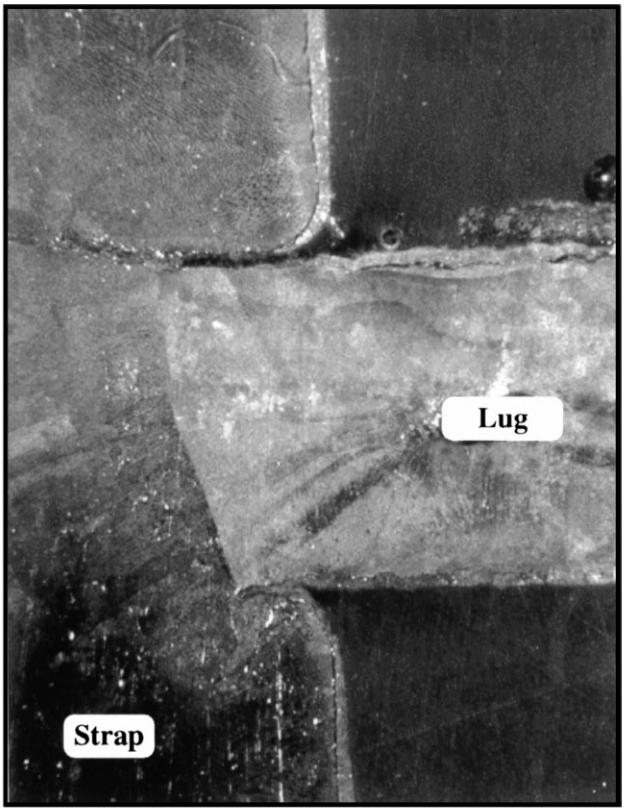

Fig. 7. Macrograph showing common defects found in lead–calcium lug/lead–tin strap joints. Note negative meniscus and lack of fusion along sides of lug.

sides of the lug can only be due to the insufficient heat applied to bond the lug to the strap. This means that either the strap metal/mould temperature was too low, or the lugs were too cold to melt at the surface before bonding. It is also possible that the time interval between the dipping of lugs in the strap and the freezing of the strap was insufficient for bonding to occur at the sides which are relatively cooler than the lug tip. As the lug tip touches the main pool of the molten strap and reaches fairly high temperatures, fusion can take place quite easily.

In one of the VRLA batteries, a polymeric layer was found around the COS joint, and is shown in Fig. 9. The macrograph suggests that the COS joint was subsequently dipped in a polymeric resin. Also, the lug has formed a positive meniscus with the polymer. Despite the presence of porosity and the lack of fusion, the polymer prevents the exposure of the joint to the corrosive environment within the battery and also improves its mechanical property.

Lead–2 wt.% tin strap alloys have been found to form good quality joints with lead–tin lugs that exhibit positive meniscus and good fusion. Micrographs of the interfaces of lead–0.6 wt.% tin lug/lead–2 wt.% tin strap, with excessive tinning, are given in Fig. 10. The tin layer is quite uneven and varies in thickness from 0–0.2 mm around the lug. Excessive tinning has led to tin segregation within the strap (dark regions in the lower regions of the

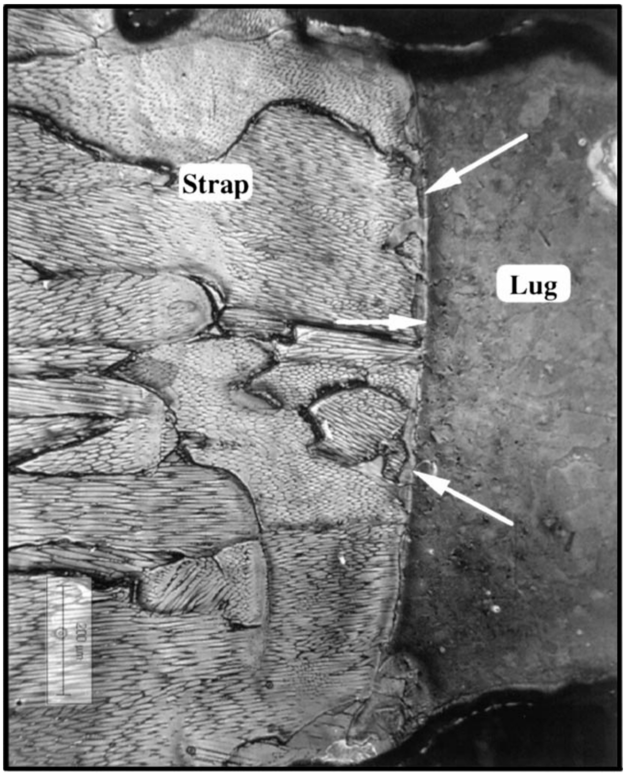

Fig. 8. Micrograph of lead–calcium–tin lug/lead–tin strap interface. Arrows indicate interface. Note excellent fusion at interface.

micrograph in Fig. 10a). It is important, however, to note that too much tin at the interface can make the COS joint more susceptible to corrosion, if gassing occurs [2,8,9].

3.2.1. Effect of increased tin in strap alloy without tinning

Attempts to join Pb–3.1 wt.% Sb lugs and Pb–Ca lugs to Pb–2% Sn strap were made by means of an automated, bench-scale COS apparatus at Pasminco [1], by fluxing

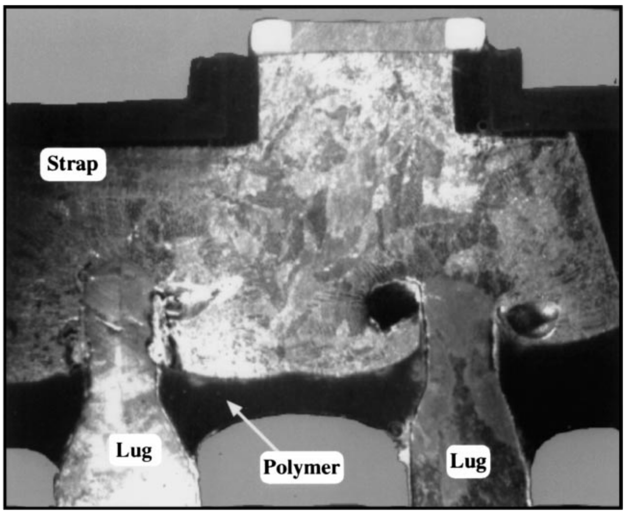

Fig. 9. Positive strap of a VRLA AGM battery (Pb–0.06 wt.% Ca–1.7 wt.% Sn grid and Pb–3 wt.% Sn strap) showing presence of porosity, negative meniscus and crevice at lug–strap interface. Note polymer layer (black region) that surrounds joint.

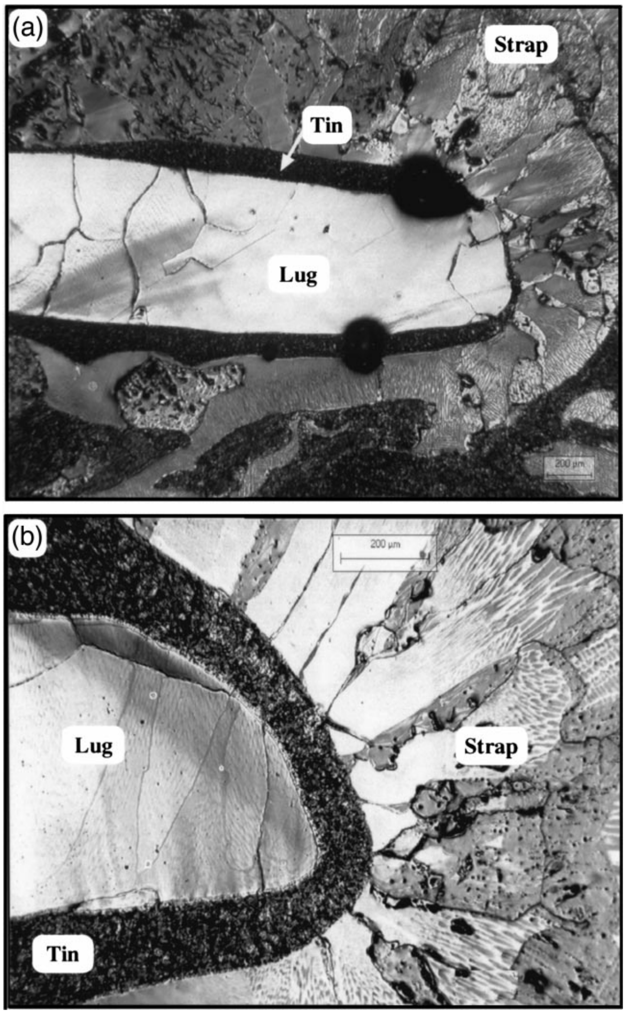

Fig. 10. Micrographs of lead–tin lug and lead–tin strap joints made by tinning: (a) ×50; (b) ×100. Note pores and uneven layer of tin at lug–strap interface. Tin segregation within strap is evident in lower half of (a).

(but without any tinning) the lugs prior to dipping in the strap. The joints with antimonial lugs displayed poor fusion, similar to the observations noted above for lead–calcium lugs. For lead–calcium alloy lugs [1], strap alloys with tin contents of up to 4.25 wt.% resulted in better fusion at the sides and tips of the lugs, and no porosity at or near the interface, but still exhibited negative menisci, irrespective of the lug thickness, as shown in Fig. 11. Also, excessive lug melting had occurred. This suggests that proper tinning of the lugs followed by the use of lead–2 to 3 wt.% Sn provides a better quality joint than the use of any higher level of tin in the strap with no tinning operation.

3.3. Pure-lead straps

Although pure lead is not widely known as a strap material, some manufacturers have chosen to use it in VRLA (AGM) batteries, for lead–calcium–tin grids. It is believed that, due to its fairly low melting point, pure lead has been considered for straps. It should be emphasized, however, that pure lead has an inherently low creep resis-

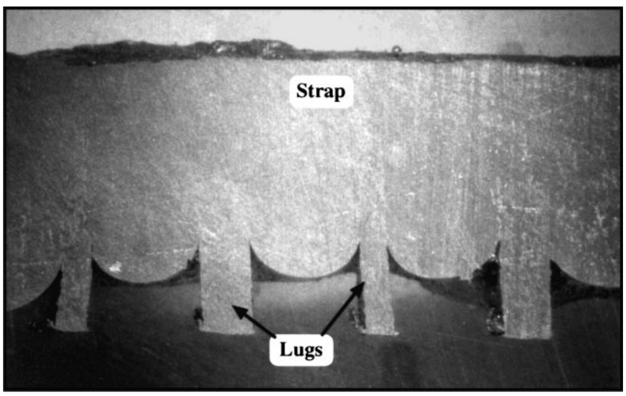

Fig. 11. Macrograph of lead–calcium lug/Pb–4 wt.% Sn joint. Note negative meniscus.

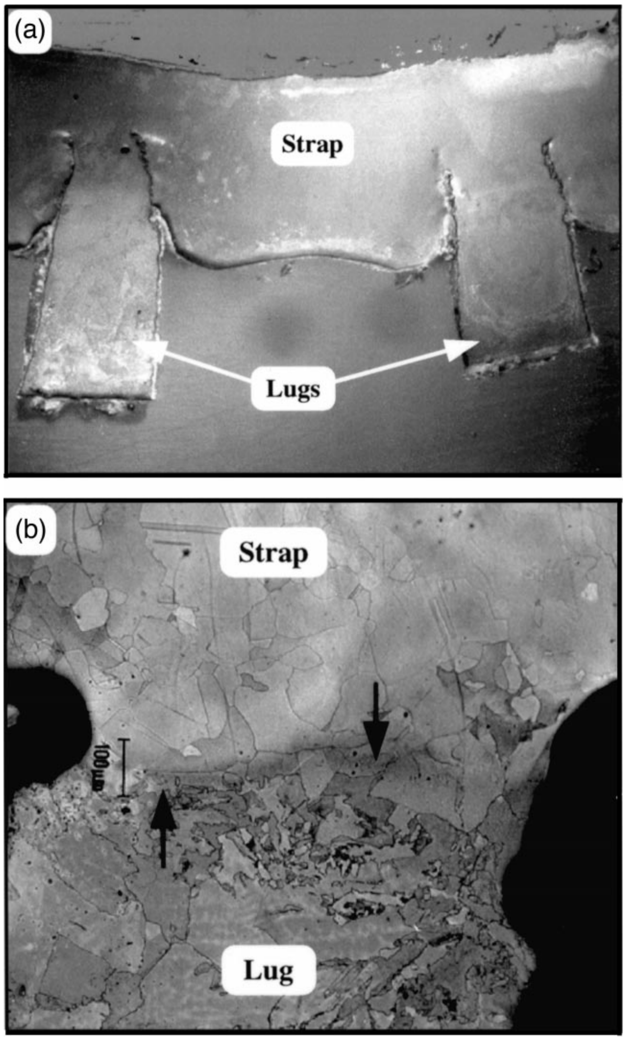

Fig. 12. (a) Macrograph of Pb–Ca lug and pure-lead strap joint (×4). (b) Micrograph of lug–strap interface (indicated by arrow) (×50).

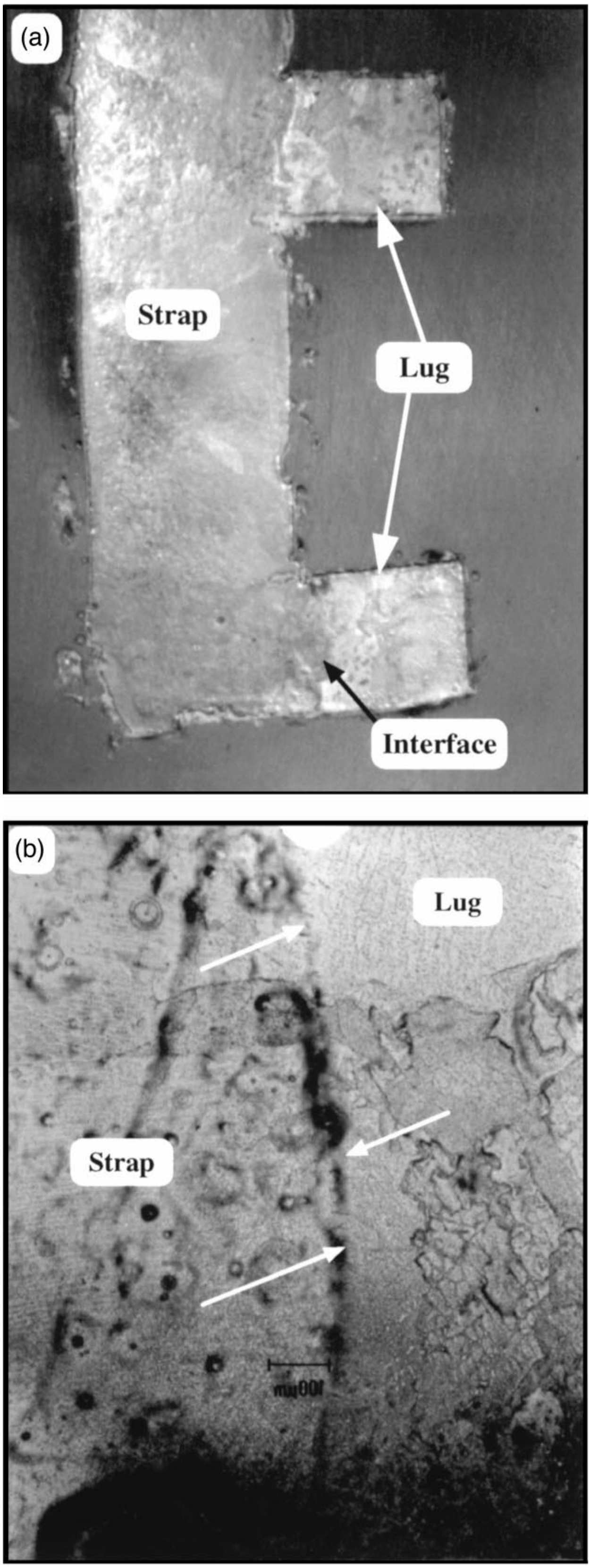

Fig. 13. (a) Macrograph of Pb–Ca lug/pure-lead strap joint. Note position of interface and meniscus angle. (b) Micrograph showing interface region.

tance and this may lead to mechanical problems, especially when the temperature of the battery gets higher.

An example of a joint between a lead–calcium–tin lug and a pure-lead strap is illustrated in Fig. 12. It is seen that a lack of fusion between the lug and the strap has occurred at the sides of the lug within the strap, rather than at the lug tip. Although the exact parameters used during the COS process of these joints are not known to the author, the cross-sections of the joints suggest that the strap mould temperature was not held sufficiently high to bring about the fusion process. It appears that a gap has formed due to uneven cooling or heat extraction from the grid during fusion.

It is noteworthy that some battery manufacturers are utilizing optimized conditions in the production of these joints, as shown in Fig. 13, to produce a joint with complete fusion and no porosity. Nevertheless, the position of the interface (Fig. 13a) is very close to the surface of the strap. The heat-transfer conditions have been such that the cooling has occurred quite uniformly at the junction to give a meniscus which is neither positive nor negative. Thus, it is seen that it is possible to obtain a sound joint for the same set of lug–strap alloys, provided the heat-transfer

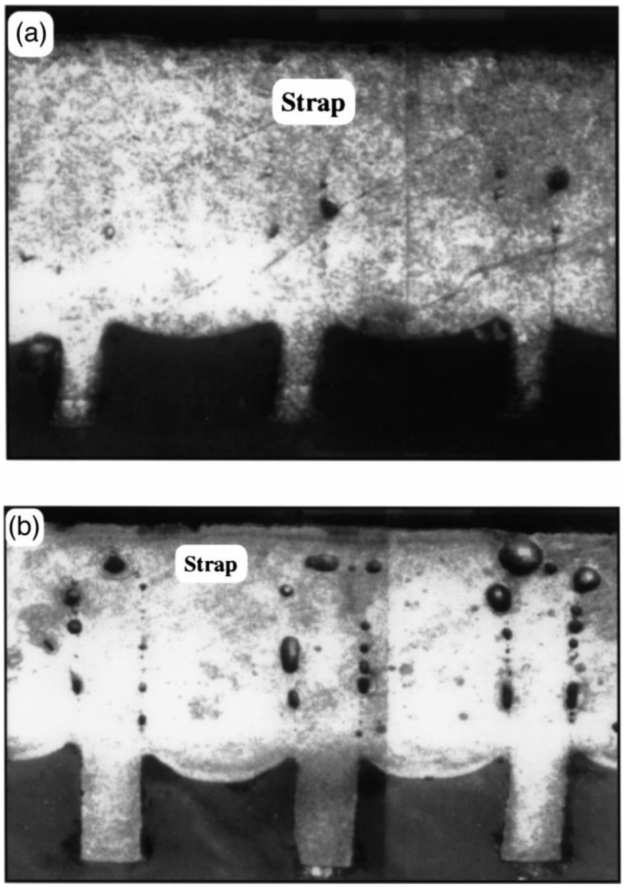

Fig. 14. Macrographs of antimony/antimony joints: (a) thin lugs; (b) thick lugs.

Table 2
Effects of various parameters in COS process on quality of joints [1,2,8]

COS parameter	Effect on joint quality
Excessive nucleants	Results in entrapped gases at lug–strap interface.
Strap metal/mould temperature	Insufficient heating of strap mould and hence strap alloy leads to lack of positive meniscus, appearance of porosity, and lack of fusion. Excess heating of strap mould/alloy leads to extensive melting of lugs.
Lug thickness	Affects size and distribution of porosity. Thin lugs form better joints than thick lugs.
Lug cleanliness and fluxing	Proper fluxing enhances fusion. Poor fluxing results in lack of positive meniscus.
Pre-tinning	Aids to form a positive meniscus and good fusion.

conditions and other parameters employed in the process are optimized.

3.4. Lug thickness parameter

A systematic study of the effects of lug thickness and lug penetration depth was conducted using custom-made COS apparatus [1] for antimony/antimony and calcium/antimony lug/strap joints [1], by keeping all other process parameters the same. It was found that the same general principles applied for both lug alloys. As illustrated in Fig. 14a and b, for the same lug penetration depth, the level of porosity is much higher for thick (1.7 mm) lugs than for thin (0.9 mm) lugs. The faster cooling rate of the strap in the case of thick lugs would inhibit the escape of gases created during the fluxing reactions, leading to excessive porosity on solidification. Furthermore, the better fusion found with thinner lugs is probably due to the less heat from the surrounding strap required to initiate the fusion process and the less time required to form the joint. The above results demonstrate that even geometrical parameters, such as lug thickness, can exert a profound effect on the resulting joint.

4. Conclusions

The major effects of some of the process variables on the fusion process and the quality of the joint discussed in this review are listed in Table 2. The various effects illustrate the importance of each parameter.

Due to the complex interrelated nature of the fusion/joining occurring in the COS process, it is clear that the quality of the COS joint is quite difficult to control, unless carefully monitored. In practice, it appears that such control requires improvement, as evident from the examination of several COS joints. It is imperative that complete control of an appropriate strap mould design which suits the grid size and shape, proper surface preparation of the lugs, as well as optimization of the strap metal/mould temperature and the lug temperature are all essential for the manufacture of sound COS joints.

Among the different strap alloys, lead–antimony (2.75–4.5 wt.%) appears to be the only alloy that easily produces COS joints with better integrity than those of lead–tin or pure lead. As antimony is an undesirable element, especially for VRLA batteries, there is wide scope for the development of suitable strap alloys.

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