

Age hardening of a Pb-0.1wt.%Ca-0.3wt.%Sn alloy and the effects of heat during battery manufacturing on this process

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Abstract

Age hardening, and the effects of heat exposure on this process, are studied for a cast Pb-0.1wt.%Ca-0.3wt.%Sn alloy. Although the alloy is age hardenable, samples quenched immediately after solidification harden and start overageing very quickly. By contrast, air-cooled samples harden slowly over a considerably longer period and reach a higher peak hardness. The high rate of hardening of quenched samples compared with air-cooled samples may result from a decrease in the degree of the slow grain boundary movement and an increase in the rate of precipitation. Exposure to heat does not decrease the hardness and the grain morphologies remain unchanged. Hardness is increased significantly by exposure to heat, particularly at 70 °C for a long time and also at 200 °C for a short time.

Introduction

The use of low-antimony and Pb-Ca-Sn alloys has become increasingly important as the demand escalates for low-maintenance and maintenance-free batteries. Compared with traditional lead-antimony alloys (> 4 wt.% Sb), however, low-antimony and Pb-Ca-Sn alloys may have lower castabilities and a reduced ability to age harden. This can cause problems in handling and increase the reject rate of grids during manufacturing.

Although there have been many studies on the metallurgical properties of low-antimony and Pb-Ca-Sn alloys, there is a lack of detailed information that assists with the efficient manufacture of battery grids. As a consequence, the Pasminco Research Centre has recently completed a study to generate a complete set of data on the castability and age hardening of low-antimony and Pb-Ca-Sn alloys. This has been achieved by using experimental conditions that simulate those encountered during battery manufacture.

For the range of low-antimony alloys, results on castability and preliminary data on age hardening have been given elsewhere [1, 2]. This paper describes results for the age hardening of a Pb-Ca-Sn alloy with composition Pb-0.10wt.%Ca-

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0.29wt.%Sn-0.014wt.%Al-0.022wt.%Bi. This type of Pb-Ca-Sn alloy is currently used widely in the manufacture of low-maintenance and maintenance-free batteries.

Experimental

Casting

The casting facility and casting procedure were the same as those used for the castability study [1], except for differences in the size and shape of the cast cavity. The dimensions of a cast sample were 6.5 mm×6.5 mm×~100 mm.

For each casting, the mould was immediately opened after pouring. The cast samples were quickly taken from the mould and either cooled in air or quenched in ice water. When a cast sample was taken from the mould, the gate head in the sample was immediately cut off. This is an important part of the procedure as the gate head acts as a heat source and results in slower cooling near the top end of the sample, particularly for air-cooled samples.

The melt was poured at a temperature of 500 °C into a mould maintained at 300 °C. Thermal histories of cast samples were determined by a K-type thermocouple (1 mm diameter) that was placed at the centre of the cast cavity with the tip in contact with the mould. The output of the thermocouple was transferred to an Osborne SX-16 computer with a PCL-818-CS data acquisition system. Two readings were recorded every second. Typical thermal characteristics of both air-cooled and quenched samples are shown in Fig. 1(a). More details of the temperature change in the first few seconds after the samples taken from the mould are shown in Fig. 1(b). In this Fig., a line with a slope of -40 °C/s is also drawn and this line will later be used in the Discussion as a comparison.

Heat exposure

The regimes of heat exposure for the cast alloys are listed in Table 1. Heat exposure at 80, 150 and 200 °C for 3 min simulates flash-drying after pasting of the battery grids, whilst exposure at 70 °C for 36 h simulates high-temperature curing.

Heat exposure at temperatures of 150 and 200 °C for a short time was carried out in the melting furnace described previously [1]. A LABELC drying oven was used for short heat-exposure times at 80 °C, as well as for long heat-exposure times. During

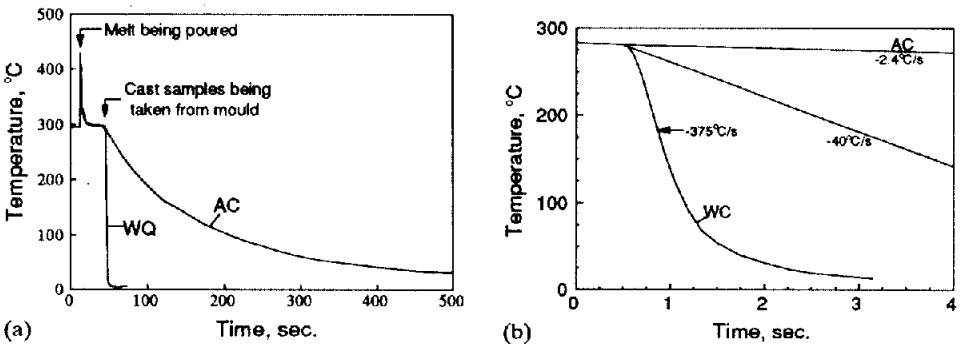


Fig. 1. Thermal cycles of cast samples, AC: air cooled; WQ: ice water quenched. (a) full thermal cycles; (b) initial cooling after being taken from mould. (A reference line with a slope of -40 °C/s has been drawn in (b).)

TABLE 1

Heat-exposure conditions for Pb-Ca-Sn alloy

Condition	Time at given temperature				
	Room temperature (days)	80 °C (min)	150 °C (min)	200 °C (min)	70 °C (h)
Regime 0			no heat exposure		
Regime 1	1	3			
Regime 2	1		3		
Regime 3	1			3	
Regime 4	10	3			
Regime 5	10		3		
Regime 6	10			3	
Regime 7	1	3			36
Regime 8	1		3		36
Regime 9	1			3	36
Regime 10	10	3			36
Regime 11	10		3		36
Regime 12	10			3	36

the opening of the furnace or oven for transfer of the samples, the internal temperature dropped by ~ 5 °C. After closing the furnace or the oven, the temperatures returned to the set point within ~ 1 min.

Hardness measurement

Hardness testing used a DVK-2 Hardness Tester in the Brinell mode. A nonstandard indenter (2 mm diameter ball) was used with a load time of 5 s and a loading speed of 300 $\mu\text{m/s}$. A loading of 4 kgf was applied to maintain the load/diameter ratio of $P/D^2 = 1.0$; this is the lowest ratio specified in ASTM E 10 for a Brinell hardness test for soft materials [3].

Metallography

Limited metallography was carried out on some typical samples to examine the effects on microstructure of cooling rate and heat exposure after casting. Metallographic samples were cut with water running onto the samples. They were then cold mounted using Struers Epofix which takes 24 h to set. The mounted samples were polished to 4000 μm using SiC papers. Samples were then chemically polished using a mixture of acetic acid and hydrogen peroxide, and etched using a mixture of ammonium molybdate, citric acid and water. The microstructures were examined by optical microscopy.

Results

Hardness versus time

Hardness data obtained over a period of 400 days at room temperature (~ 22 °C) are plotted in Fig. 2(a) for samples that were not exposed to heat after

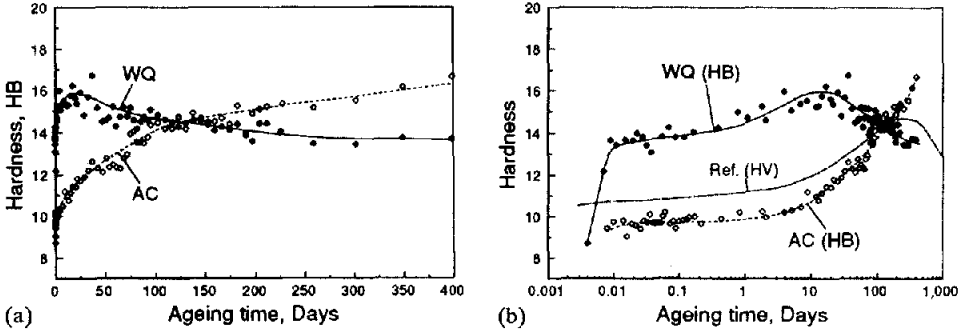


Fig. 2. Hardness curves for Pb-Ca-Sn alloy cast and aged naturally, AC: air cooled; WQ: ice water quenched. (a) linear time scale; (b) log time scale. In (b), a reference line (Ref.) is drawn to schematically represent the age-hardening curve of a cast Pb-0.12wt.%Ca-0.24wt.%Sn alloy from Bourirden *et al.* [4] who used Vickers hardness tests instead of Brinell hardness tests.

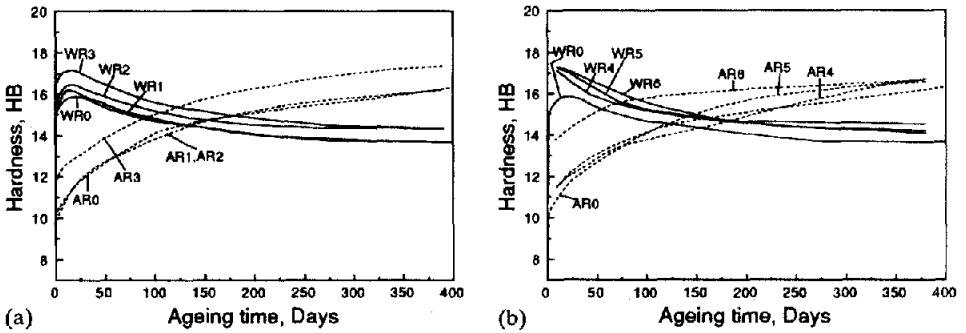


Fig. 3. Hardness curves for Pb-Ca-Sn alloy after casting and heat exposure for a short time, A: air cooled; W: ice water quenched. (a) heat exposure regimes 0, 1, 2 and 3; (b) heat exposure regimes 0, 4, 5 and 6. R0, RX, etc. correspond to heat-exposure regimes given in Table 1. Solid curves are for quenched samples, dashed curves are for air-cooled samples.

casting. Each plotted value is an average of three hardness measurements at a particular time. The curves have been traced based on the data as plotted. Data and curves in Fig. 2(a) have been replotted using a log scale in Fig. 2(b) to give more detail for the early stages of age hardening. In Fig. 2(b), a curve that schematically represents the results from a recent study from Bourirden *et al.* [4] is also given as a reference curve.

Quenched samples harden very quickly reaching 13 HB from less than 9 HB in about 1 h. After this initial period, the samples continue to harden at a decreasing rate to a maximum of ~16 HB at ~20 days. Hardness decreases slowly thereafter to less than 14 HB by the end of the 400-day period. On the other hand, air-cooled samples harden at a considerably slower rate. The peak hardness of ~16.5 HB within the test period, which is the final hardness for the air-cooled samples, is slightly higher than the peak hardness of quenched samples. Figure 2 shows that the hardness of the air-cooled samples is still increasing at the end of the 400-day period.

Figure 3 gives age-hardening curves for the samples with heat exposures after casting for 3 min at 80, 150 and 200 °C, whilst Fig. 4 presents curves for the samples

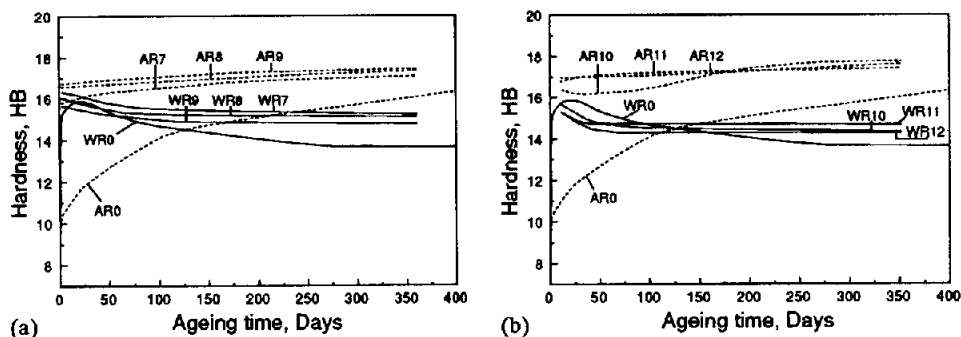


Fig. 4. Hardness curves for Pb-Ca-Sn alloy after casting and heat exposure for a long time; A: air cooled; W: ice water quenched. (a) heat exposure regimes 0, 7, 8 and 9; (b) heat exposure regimes 0, 10, 11 and 12. R0, RX, etc. correspond to heat-exposure regimes given in Table 1. Solid curves are for quenched samples, dashed curves are for air-cooled samples.

with further heat exposure for 36 h at 70 °C. For comparison, Figs. 3 and 4 also contain the age-hardening curves for samples that have not had heat exposure after casting.

Figure 3(a) shows that, one day after casting, a short heat exposure of 3 min at 80 and 150 °C (AR1 and AR2) does not seem to affect the hardening process for air-cooled samples. At 200 °C (AR3), however, this heat exposure period of 3 min shifts the hardness curve upward by slightly higher than 1 HB. A similar short-term heat exposure applied 10 days after casting at 80 and 150 °C does not affect significantly the hardness of the air-cooled samples, although a slight increase in hardness is noticed in the later stage. A significant increase in short-term hardness is observed for samples after heat exposure at 200 °C.

For quenched samples, short exposure times generally give a slight increase in hardness, particularly for short-term hardness (Fig. 3). An exception is the sample exposed at 80 °C for one day after casting for which little increase in hardness is observed.

Figure 4 shows that exposure for a long time at 70 °C increases slightly the long-term hardness of the quenched samples. For air-cooled samples, the hardness increased significantly and remained at a high value for the whole test period.

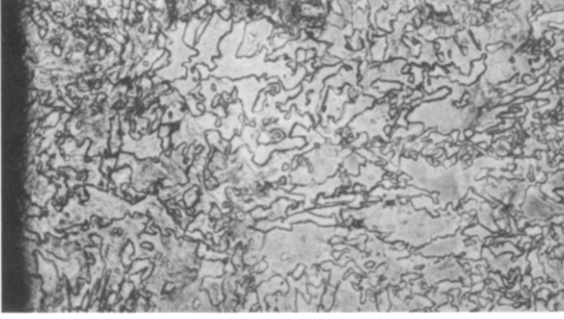
Metallography

The microstructures of typical air-cooled and quenched cast samples are shown in Figs. 5 and 6, respectively. The grain morphology of the air-cooled samples is typical of those noted frequently in the literature; a recent example can be found in a paper by Prengaman [5]. Quenched samples (Fig. 6) have similar grain morphologies to those of air-cooled samples, except that the grain sizes of the quenched samples are apparently larger. In quenched samples, however, some grain boundaries similar to those described by Bourden *et al.* [4] as rectilinear fronts have been observed and they are indicated by arrows in Fig. 6.

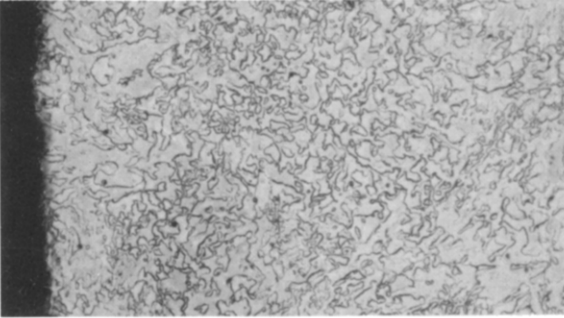
Discussion

Effects of cooling rate after solidification

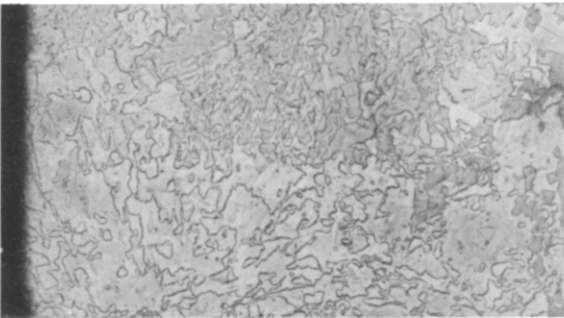
Figure 2 shows that the Pb-Ca-Sn alloy is age hardenable. Quenched samples harden very quickly immediately after casting, but the peak hardnesses are lower than



(a)



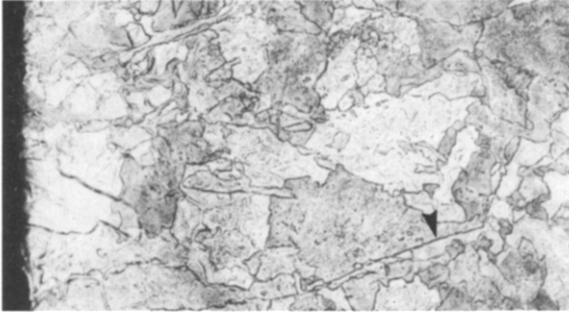
(b)



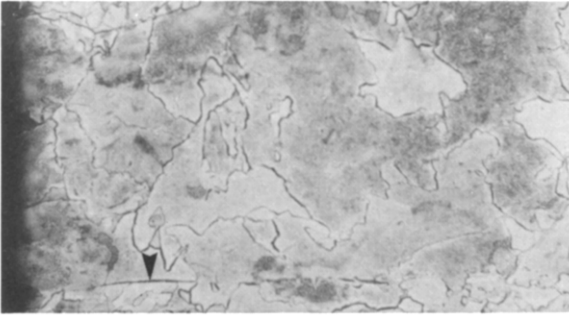
(c)

Fig. 5. Microstructures of cast and air-cooled samples showing the common irregular grain morphology, $\times 100$; (a) air-cooled R0 sample, 175 days after casting; (b) air-cooled R6 sample, 155 days after casting; (c) air-cooled R12 sample, 128 days after casting.

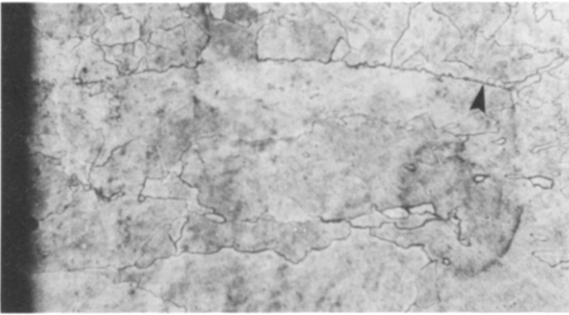
those of air-cooled samples. The hardening behaviour described here for the Pb-Ca-Sn alloy is considerably different from that of low-antimony alloys [2]. With the latter alloys, the general trends in the hardening curves are the same for both quenched and air-cooled samples, but the higher rate of cooling by quenching results in a slightly higher hardening rate and considerably higher peak and final hardnesses.



(a)



(b)



(c)

Fig. 6. Microstructures of cast and quenched samples showing the common irregular grain morphology, $\times 100$: (a) quenched R0 sample, 175 days after casting; (b) quenched R6 sample, 155 days after casting; (c) quenched R12 sample, 128 days after casting. Rectilinear boundaries are indicated by arrows.

In a recently comprehensive study of hardening processes in Pb–Ca and Pb–Ca–Sn alloys Bourden *et al.* [4] described the transformation processes that contribute to the hardening of Pb–Ca–Sn alloys with $\text{Sn}/\text{Ca} < 1$ as:

- fast grain boundary movement without precipitation: the front of the reaction in each grain is rectilinear; contribution to hardness is high

- slow grain boundary movement without precipitation: the front of the reaction becomes very irregular, like a jigsaw puzzle; contribution to hardness is medium-high
- precipitation: the reaction commences in the vicinity of the grain boundaries; this generates thin zones of lamellar precipitates of intermetallic compounds Pb_3Ca ; contribution to hardness is medium

In this investigation, quenched samples (Fig. 6(a)) have similar grain morphologies to those of air-cooled samples (Fig. 5(a)), except that the grain sizes of the quenched samples are apparently larger. It can hence be assumed that the extent of the slow grain boundary movement as described by Bouirden *et al.* [4] is much greater for the air-cooled samples than for the quenched samples. This assumption is supported by the grain boundary appearance of quenched samples such as the one identified by an arrow in Fig. 6(a); these boundaries are most probably the rectilinear fronts of reaction after the first fast grain boundary movement. This type of grain boundary is not seen in the air-cooled samples and suggests that the slow grain boundary movement has been completed in the air-cooled samples.

Bouirden *et al.* [4] used an alloy with the composition $Pb-0.12wt.\%Ca-0.24wt.\%Sn$. This is similar to that of the alloy used here. Three of the thermal histories for the alloy used in the work of Bouirden *et al.* [4] were: (i) cooled at $40\text{ }^\circ\text{C/s}$ immediately after solidification; (ii) rehomogenised for 1 h at $310\text{ }^\circ\text{C}$ and then air cooled; (iii) rehomogenised for 1 h at $310\text{ }^\circ\text{C}$ and then quenched in water.

As noted above, the high cooling rate in quenching from this investigation results in rapid hardening compared with the relatively slow hardening rate of air-cooled samples. The cooling characteristics of air-cooled and water-quenched samples in the first moments after the samples taken from the mould are illustrated in Fig. 1(b). A line with a slope of $-40\text{ }^\circ\text{C/s}$, as experienced for the as-cast samples of Bouirden *et al.* [4], has been plotted for comparison. The cooling rate of these authors' as-cast samples is much higher than the cooling rate experienced for the air-cooled samples reported here. It would therefore be expected that the as-cast samples of Bouirden *et al.* [4] should harden more quickly than our air-cooled samples. The hardening rate of the as-cast samples from Bouirden *et al.* [4] is seen, however, to be very similar to that of the air-cooled samples in this investigation (Fig. 1(b)).

The alloy used by Bouirden *et al.* [4] has a slightly higher calcium content (*viz.*, 0.02 wt.\%). According to the $Pb-Ca$ phase diagram [6], alloys with calcium contents above about 0.08 wt.\% will solidify with Pb_3Ca as the first phase to form. Indeed, Prengaman [5] noted that $Pb-Ca$ alloys with $Ca > 0.12\text{ wt.\%}$ usually contain small amounts of the Pb_3Ca primary particles in the structure.

Precise details of the solidification structures of $Pb-Ca$ alloys for $Ca > 0.08\text{ wt.\%}$ are relatively scarce in the literature. The slightly higher calcium content which increases the amount of the primary particles may, or may not, result in a finer cast structure. This does not explain, however, the similarity in hardening rate between our air-cooled samples and the as-cast types of Bouirden *et al.* [4], given the large differences in cooling rates.

Our alloy has a slightly higher tin level (0.05 wt.\%) and, according to Bouirden *et al.* [4], this may give a slightly reduced rate of slow grain boundary movement. The presence of 0.02 wt.\% bismuth may increase marginally the rate of all the transformation processes [4], and hence the hardening rate [4, 7]. In addition, the aluminium content of $> 0.01\text{ wt.\%}$ acts as a grain refiner during solidification [4, 5], and hence the number of discontinuous transformation sites is increased [4], resulting in a higher rate of hardening. Considering the possible slightly lowered rate due to the slightly higher tin content and the possible slightly higher rate due to the presence of small amounts

of aluminium and bismuth, the overall small differences in composition are not expected to have a marked effect on the hardening rate.

Since the slight differences in composition do not appear to account for the coincidence of the hardening rate for both our air-cooled samples and the as-cast samples of Bouirden *et al.* [4], given the difference in cooling rates, it is assumed that this particular difference in cooling rate ($-40\text{ }^{\circ}\text{C/s}$ and $-2.4\text{ }^{\circ}\text{C/s}$) does not have a significant effect. At this point, it is worthwhile emphasizing once again that the cooling rate exerts a great influence on the hardening rate according to Fig. 2. Based on the above discussion, it is not unreasonable to suggest that there may be a critical cooling rate after solidification. Above this critical cooling rate, the transformation processes of slower cooling as described above are altered and, hence, the hardening process is also altered.

It can further be assumed that a cooling rate as high as that experienced in quenched samples after solidification results in a lower degree of completion of the slow grain boundary movement. This may, in turn, act as the basis for a higher rate of precipitation and, hence, a higher rate of hardening. The observed decrease in hardness after ~ 20 days also seems to be reasonable due to the 'overgrowth' of precipitates. On the other hand, precipitation does not seem to proceed as fast in air-cooled samples as in quenched samples, and results in a long period of higher hardness. Hence, by the end of the 400-day period, there is still no sign of overageing for the air-cooled samples.

Another point to note in Fig. 2 is that the maximum hardness obtainable for air-cooled samples must be significantly higher than that for quenched samples. An explanation for this can also be the significantly higher rate of growth of precipitates in the quenched samples. This not only results in a considerably earlier 'overgrowth', but also fewer precipitates that lead to a lower obtainable maximum hardness.

Given the differences between the hardening behaviour of the air-cooled and quenched samples as described above, it is unexpected that, in the study by Bouirden *et al.* [4], there is essentially no difference in hardening behaviour for the rehomogenized/air-cooled and rehomogenized/quenched samples, apart from the very early stage. The implication of this is that the cooling rate only significantly influences the hardening process for a cast structure.

Effects of heat exposure

Figure 3 shows that no decrease in hardness is observed due to heat exposure for a short time; this behaviour is again totally different from that observed for antimonial lead alloys [2].

For air-cooled samples, Fig. 3(a) (AR3) and Fig. 3(b) (AR6) clearly illustrate that there is an increase in hardness for samples after short-term exposure at $200\text{ }^{\circ}\text{C}$. This increase is particularly noticeable for the short term, especially for AR6.

From Fig. 4(a) and (b), the three curves for each group of conditions such as R7, R8 and R9 or R10, R11 and R12 for both air-cooled and quenched samples form a set of curves that have similar hardening behaviour. Given the experimental error, each set of curves does not clearly show whether 80, 150 or $200\text{ }^{\circ}\text{C}$ has the most significant effect. This indicates that the difference in the temperature to which a sample is exposed for a short time before exposure for 36 h at $70\text{ }^{\circ}\text{C}$ does not have a marked effect on the subsequent age hardening.

Figure 4(a) and (b) (solid curves) demonstrate that the 36 h exposure at $70\text{ }^{\circ}\text{C}$ modifies the age hardening of the quenched samples in that long-term hardness is

slightly increased. This is more apparent from the group of curves WR7, WR8 and WR9.

A significant increase in the hardness of air-cooled samples after 36 h exposure at 70 °C is clearly shown in Fig. 4(a) and (b). The hardnesses are relatively constant with time, although slight increases do occur. This suggests that the structure of the samples, after the transformation and/or precipitation during the heat exposure, is very stable at room temperature. The results in this investigation indirectly agree well with the data of Bouirden *et al.* [4] which show that increasing the ageing temperature up to 100 °C not only increases considerably the hardening rate of the as-cast samples, but also increases slightly the peak hardness. Our data for the air-cooled samples, however, show that there is no overageing at room temperature, at least for times up to 400 days.

As discussed before, the slower rate of hardening for air-cooled samples is probably due to the high degree of completion of the secondary grain boundary movement and the delay in the onset of precipitation. The increases in the hardnesses of air-cooled samples after short times of exposure at 200 °C, or long times of exposure at 70 °C, most likely result from the significant increases in the rate of nucleation of the precipitates and, hence, the hardening rate. An increased rate of precipitation does not seem to result in an increased rate of overgrowth of precipitates (overageing). The net result is that hardness remains high.

The data described in this paper for the age hardening of the Pb–Ca–Sn alloy, which has been air cooled after solidification, give a high degree of certainty that a significant increase in hardness can be achieved by a simple heat treatment.

Conclusions

1. The cast Pb–0.1wt.%Ca–0.3wt.%Sn alloy is age hardenable. Samples quenched immediately after solidification harden and start overageing very quickly, whilst air-cooled samples harden slowly over a period of long time.
2. Quenching may decrease the extent of the slow grain boundary movement and increase the rate of precipitation. This results in an overall higher rate of hardening.
3. Exposure to temperatures similar to those encountered during battery manufacturing does not result in a decrease in hardness for either air-cooled or quenched samples.
4. Heat exposure at 200 °C for 3 min or at 70 °C for 36 h yields moderate and significant increases, respectively, in the hardnesses of the air-cooled samples. This may be the result of a significant increase in nucleation rate, but not of the growth rate of precipitates due to the heat exposure.

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