

Age-hardening of grid alloys and its effect on battery manufacturing processes

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Abstract

The age-hardening behaviour of three generic classes of lead–antimony grid alloys commonly used in the lead/acid battery manufacturing industry were studied. The effects on age-hardening behaviour of several heat treatments devised to simulate downstream processing of battery grids in the manufacturing process were investigated together with the effect of varying cooling rate following casting. Rapid cooling (water quenching) resulted in a general acceleration and enhancement of the age-hardening behaviour of all alloys, whilst heat treatment following casting generally gave rise to a reduction in peak hardness.

Introduction

The origin of the work on age-hardening reported here lay in the persistent requests by customers of the authors' company for assistance in overcoming problems associated with (a) materials handling and (b) high grid inventories/work-in-progress (WIP). These requests have been usually associated with the use of low-antimony alloys and the need for higher production rates. A significant confounding variable in this situation is the range of process or manufacturing equipment used throughout the Asian region. Many problems have developed with some of the older, modified equipment still in use. In particular, the softness of the grids has caused high levels of internal scrap during plate-making operations such as pasting. It has also been observed that other processes (e.g., flash drying, curing) often aggravated this softness problem. There has been considerable confusion over the time that cast grids should be left prior to further processing. This confusion has resulted in high grid inventories or WIP, with associated increases in the cost of manufacture.

An examination of the literature revealed only limited data on the age-hardening characteristics of the alloy types presently in use. Furthermore, it was difficult to predict exactly how the various heat-treatment practices would effect the mechanical properties of these alloys. Consequently, processes such as flash drying and curing have been considered as forms of heat treatment and the effects on a range of generic battery alloys have been examined.

Alloys under investigation

The alloys listed in Table 1 represent three generic classes of antimonial alloy that are commonly used in the industry. Alloys containing grain refiners have been chosen both because of the obvious interest in these throughout the Asian region, and because there are almost no published data of the type presented here.

TABLE 1

Composition (wt.%) of alloys under examination

Element	Alloy 1	Alloy 2	Alloy 3
Sb	2.8–3.2	1.5–1.7	0.75–0.85
Sn	0.15–0.25	0.2–0.3	0.25–0.35
As	0.1–0.2	0.15–0.25	0.20–0.25
Se	0.02–0.03	0.02–0.03	0.025–0.030
Cu	0.03–0.05	0.03–0.05	0.03–0.05
S	0.002–0.004	0.002–0.004	0.002–0.004

TABLE 2

Heat-treatment regimes

Regime	Temperature (°C)			
	80	150	200	70
1	3 min			
2		3 min		
3			3 min	
4	3 min			36 h
5		3 min		36 h
6			3 min	36 h

Experimental

Sample casting

Samples were gravity cast into plain carbon steel moulds of 100 mm in length and 6.5 mm in diameter. The pour temperature was 470 °C and the mould temperature 200 °C. Rapidly-cooled samples were obtained by quenching the samples in iced water immediately after casting. Slow cooling was achieved by allowing the samples to cool naturally in air at room temperature.

Heat treatment

A number of heat-treatment regimes, listed in Table 2, were devised with the aim of simulating the heating effects of the flash-drying and curing processes used in the manufacture of lead/acid batteries. All alloys under investigation, both slow-, and rapidly-cooled samples were subjected to each of these regimes 24 h after casting. Samples which were aged naturally at room temperature were used as controls.

Hardness measurement

Hardnesses of all samples were determined using a Brinell tester with a non-standard 2 mm ball indenter. A load of 4 kgf was applied for a period of 5 s. The data are expressed in terms of the Brinell number (HB).

Brief outline of the theory of age-hardening

The first observation of age-hardening was made by Wilm, cited in ref. 1; who, in 1906, discovered that when commercial aluminium alloyed with copper was quenched

from a high temperature an increase in hardness developed on standing at room temperature. This phenomenon occurs in many other alloy systems, including lead–antimony.

The primary requirement for an alloy system to age-harden is a reduction in the solid solubility of solute atoms with temperature. Figure 1 shows the lead-rich region of the lead–antimony equilibrium diagram. The solvus line AB, which represents the change in the solubility limit of antimony in lead with temperature, demonstrates that the solubility of antimony falls from 3.45 wt.% at 252 °C to 0.3 wt.% at 50 °C. Thus, the necessary condition for age-hardening, namely, that solid solubility decreases with temperature, is satisfied.

When an alloy containing 3 wt.% antimony is cast and cooled very slowly, there is an initial formation of crystals of lead containing antimony in solid solution. As the temperature passes through the solvus line, however, the antimony begins to precipitate out as large particles until finally, at room temperature, there is only 0.3 wt.% of antimony remaining in the solid solution. By contrast, if the alloy is cooled extremely quickly after casting (for instance by quenching in water), the antimony atoms would be denied the opportunity to precipitate out of the solid solution. The resulting structure is known as a supersaturated solid solution because there is considerably more antimony in solution than would normally be the case under equilibrium conditions. This condition is described as being meta-stable and it is this partial stability that provides the driving force for the age-hardening process.

In order to achieve the equilibrium state, the solute antimony atoms will be rejected from the solid solution and will tend to form extremely small precipitates. It is the formation of the latter that causes hardening of the alloy. In simple terms, as these precipitates grow, the hardness of the alloy will increase until a critical size is achieved after which partial softening, or over-ageing, will take place. The extent and speed with which this precipitation hardening occurs is dependent upon: (i) the energy available to drive the process, which is derived from the degree of supersaturation; (ii) the energy available for solute atom diffusion, which is derived from the temperature of the alloy [1].

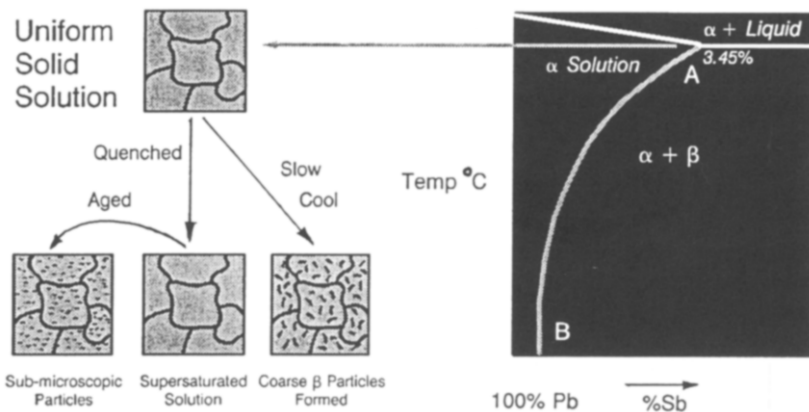


Fig. 1. Solubility of antimony in lead.

Results

Alloy 1: Pb-2.8 to 3.2wt.%Sb

Slow cooling

The age-hardening behaviour of alloy 1, following casting and air cooling, is given by curve 1, Fig. 2. It indicates the presence of two contributing processes: the first appears to give rise to a rapid increase in hardness that results in a peak of 22.5 HB at 14 days after which over-ageing occurs; the second produces a slow, but steady, increase in hardness which is still increasing at 150 days after casting.

Heat treatments aimed at simulating the effect of flash drying resulted in a suppression of both hardening processes, see curve 2, Fig. 2. This caused a softening of the order of 3 to 5 HB. Furthermore, it was found that the degree of softening increased with increase in the simulated flash-drying temperature.

The heat treatments designed to simulate flash drying followed immediately by curing resulted in complete suppression of the hardening process and an accompanying reduction in hardness of between 3 and 4 HB, see curve 4, Fig. 3.

Rapid cooling

The age-hardening of cast and quenched samples of alloy 1 is represented by the curves in Fig. 2. Comparison with the ageing curve for the air-cooled sample shows clearly that the hardening process has been both enhanced and accelerated by rapid cooling of the cast sample. As with the slowly-cooled samples, two hardening processes are present, the first of which results, in this case, in a peak hardness of 32 HB at 7 days. Softening as a result of over-ageing then occurs until the second process becomes dominant giving rise to a steady rise in hardness which is still increasing after 150 days.

Curve 4 of Fig. 2 demonstrates that the flash-drying treatments conducted at 80 and 150 °C result in an increased peak hardness, although a slight reduction in long-term hardness is observed. By contrast, flash drying at 200 °C (curve 5, Fig. 2) causes

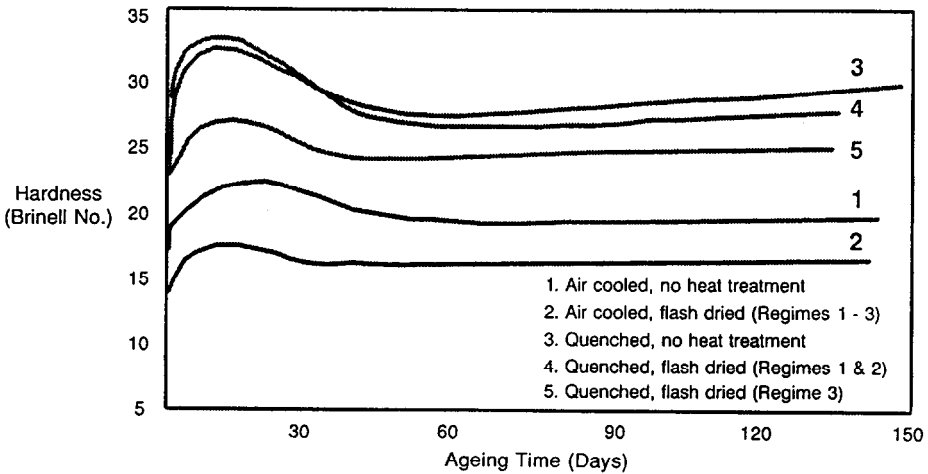


Fig. 2. Effect of cooling rate and subsequent heat treatment (regimes 1-3) on the age-hardening behaviour of alloy 1.

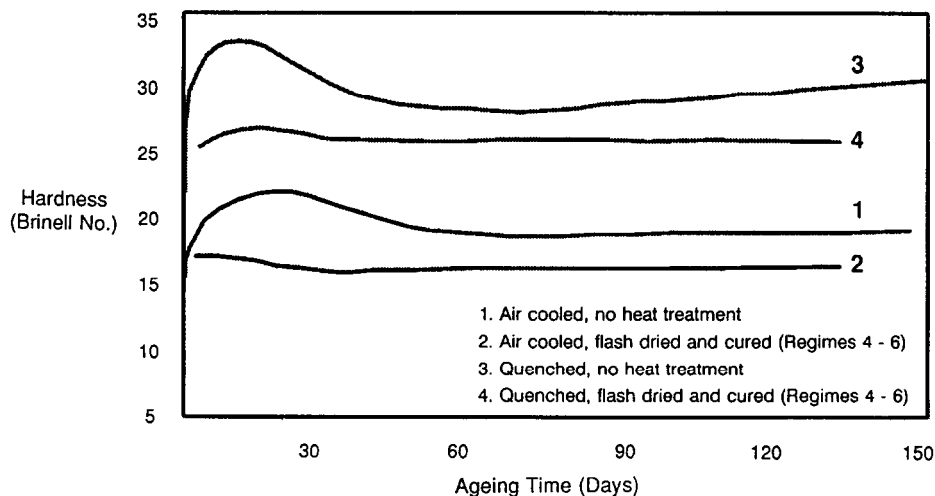


Fig. 3. Effect of cooling rate and subsequent heat treatment (regimes 4–6) on the age-hardening behaviour of alloy 1.

a significant suppression of the hardening curve and this gives rise to a reduction in both the peak and long-term hardnesses.

As was the case with the above slowly-cooled samples, heat treatments aimed at simulating flash drying followed immediately by curing resulted in near complete suppression of the hardening process, curve 4, Fig. 3 and an accompanying reduction in peak hardness of between 4 and 7 HB.

Alloy 2: Pb–1.5 to 1.7wt.%Sb

Slow cooling

The age-hardening performance of slowly-cooled, cast samples of alloy 2 is represented by curve 1, Fig. 4. It is evident that there is only one hardening process present and that this results in a peak hardness of 16 HB at 30 days. The alloy then begins to soften slightly as a consequence of over-ageing.

The data of curve 2 in Fig. 4 show that all the flash-drying treatments result in a decrease in both the initial and the long-term hardness. The extent of this effect increases with increasing flash-drying temperature.

The influence of the flash-drying treatment followed immediately by the curing treatment is demonstrated by curve 2 in Fig. 5. Clearly, the hardening process is accelerated by this treatment resulting in an immediate increase in hardness of the order of 4 HB which represents a rise of approximately 35%. The long-term hardness is, however, reduced.

Rapid cooling

The age-hardening behaviour of cast and quenched samples of alloy 2 is represented by curve 3, Fig. 4. The two processes associated with the hardening behaviour of both the slowly- and rapidly-cooled samples of alloy 1 are again present. It is also clear that rapid cooling has resulted in an increase in peak hardness and an acceleration of the hardening process. A peak hardness of 23 HB is achieved at 25 days. A slight reduction in hardness then follows due to over-ageing at the alloy. After 100 days,

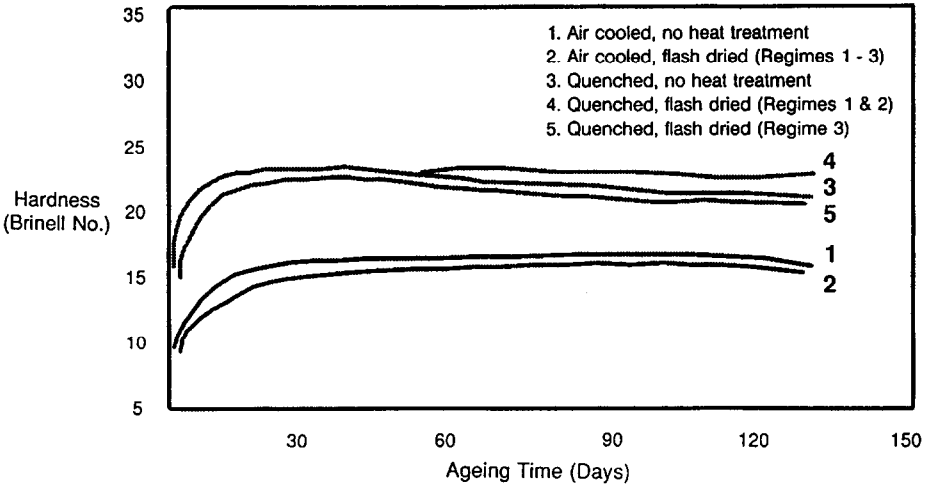


Fig. 4. Effect of cooling rate and subsequent heat treatment (regimes 1–3) on the age-hardening behaviour of alloy 2.

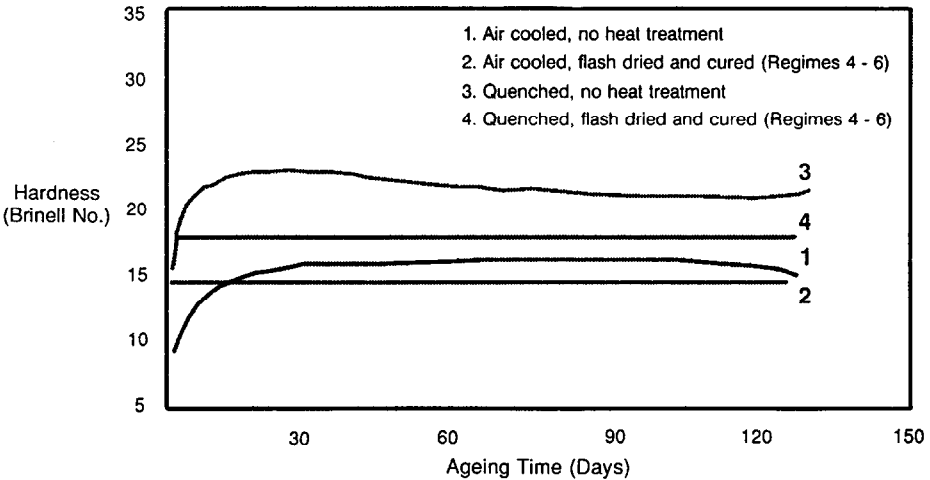


Fig. 5. Effect of cooling rate and subsequent heat treatment (regimes 4–6) on the age-hardening behaviour of alloy 2.

the second process begins to predominate and this results in a gradual rise in hardness that is still occurring after 130 days.

Treatments simulating flash drying at temperatures of 80 and 150 °C have little effect on the initial age-hardening behaviour of quenched alloy 2 but do cause a slight increase (~4%) in long-term hardness, see curve 4, Fig. 4. Flash drying at 200 °C results in an initial drop in hardness of ~12% and a long-term decrease of ~2%, curve 5, Fig. 4.

All flash-dry/cure heat-treatments resulted in rapid completion of the age-hardening process, as demonstrated by the flatness of curve 4 in Fig. 5. The resultant

hardness of the quenched samples of alloy 2 treated in this manner ranged from 17 to 19 HB.

Alloy 3: Pb-0.75 to 0.85wt.%Sb

Slow cooling

Curve 1 in Fig. 6 represents the age-hardening of cast and air-cooled samples of alloy 3. It is evident that there is only one hardening process in operation and that the hardness is still rising at 100 days after casting, at which stage the hardness is 11 HB.

Flash-drying heat treatments conducted at 80, 150 and 200 °C have little effect on the hardness of slowly-cooled samples of alloy 3 in the short term, but do result in a long-term reduction of ~7%, see curve 2, Fig.6.

Finally, heat treatments simulating flash drying followed immediately by curing result in no initial change in hardness, see curve 2, Fig. 7. The long-term hardness is significantly reduced, however, due to the accelerated completion of the hardening process at an elevated temperature and the early onset of over-ageing.

Rapid cooling

The age-hardening character of cast and quenched samples of alloy 3 is given by curve 3 in Fig. 6. Again, it is apparent that rapid cooling has increased both the rate of hardening and the hardness of the alloy. Only one hardening process occurs and 100 days after commencement of the test the hardness is still increasing. At this stage, the hardnesses of the samples are ~14 HB.

It can also be seen from curve 4 of Fig. 6 that the 80 °C flash-drying treatment marginally increased the long-term hardness of the alloy, whilst treatment conducted at 150 and 200 °C (curve 5) resulted in an initial drop in hardness of approximately 1 HB and a long-term reduction of approximately 2 HB.

The effect of the flash drying/curing cycle on the rapidly cooled samples of alloy 3 (see curve 4, Fig. 7) was similar to that experienced with slowly cooled samples

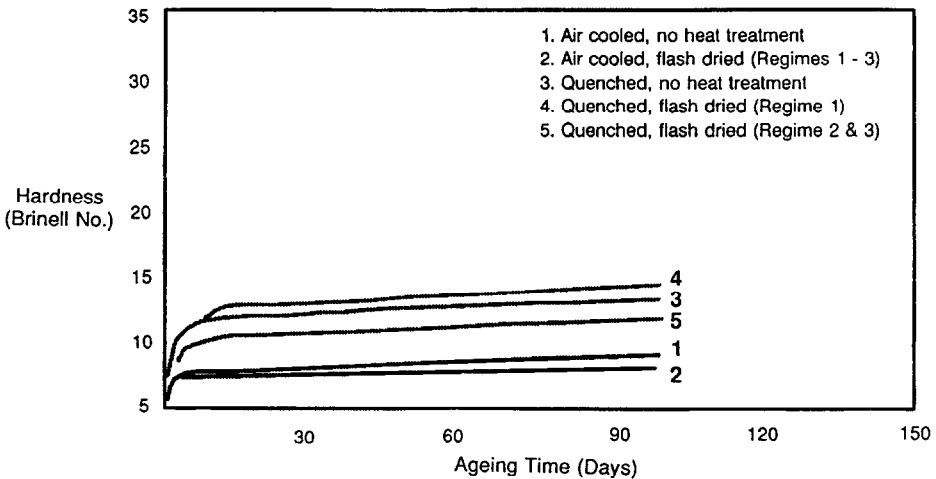


Fig. 6. Effect of cooling rate and subsequent heat treatment (regimes 1-3) on the age-hardening behaviour of alloy 3.

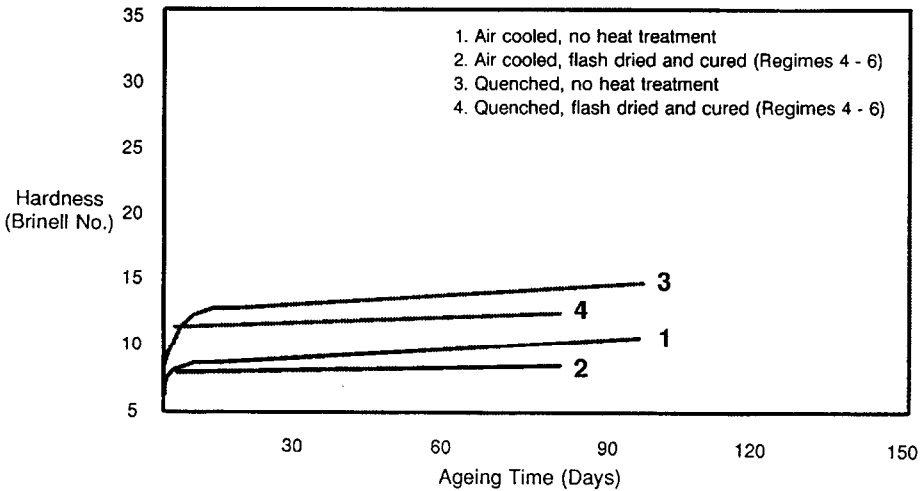


Fig. 7. Effect of cooling rate and subsequent heat treatment (regimes 4–6) on the age-hardening behaviour of alloy 3.

TABLE 3

Peak hardnesses, and time taken to reach peak hardness, for low-antimony alloys

Alloy type (%Sb)	Peak hardness of air-cooled sample (HB)	Days taken by air-cooled sample to achieve peak hardness	Days taken by quenched sample to achieve air-cooled peak hardness
2.8–3.2	22.5	14	0.2
1.5–1.7	16	30	0.2
0.75–0.85 ^a	11	100	0.8

^aThis alloy was still hardening after 100 days.

in that no initial change was recorded. Nevertheless, the long-term hardness was influenced significantly due to over-ageing.

Discussion

Table 3 lists the peak hardnesses obtained by each of the naturally aged samples of air-cooled antimony alloy, as well as the time taken to achieve these hardnesses for both the air-cooled samples and the quenched samples. As would be expected, an increasing antimony content gives rise to a significant rise in hardness. It is also clear that by rapidly cooling of all three alloys it is possible to both enhance and accelerate the hardening process.

Examination of the data in Figs. 2–7 reveals that, for all low-antimony alloys, all heat treatments carried out 24 h after casting and air cooling of the samples result generally in either no change, or a reduction, in the alloy hardness. The one exception

is alloy 2 for which the flash-dry/curing regimes gave rise to accelerated ageing, but not over-ageing, of the samples. Despite the fact that this regime produced an immediate rise in hardness (Fig. 5), it was noted that there was a reduction in the long-term hardness.

Similarly, for all but a few low-temperature flash-drying simulations, heat treatments of cast and quenched low-antimony alloys promoted hardness reductions. Despite this, it is interesting to note that the enhancement of the hardening process achieved by the quenching of low-antimony alloys immediately after casting is retained throughout all subsequent heat treatments. Thus, it can be concluded that permanent improvements in the mechanical properties of all three alloys can be achieved simply by increasing the cooling rate of the alloy following casting.

Manufacturing implications

The above work has highlighted the following important aspects in terms of battery-grid manufacture.

(i) The only way to improve the hardness of grids made from the above generic alloys is to introduce some form of rapid cooling. This could be carried out by a cold water spray, a cool air blower, or a water-cooled transfer block.

(ii) Flash-drying temperatures and processes that are set at values of 180 °C or higher will aggravate the softening problem. Obviously, the time that plates are exposed to these temperatures is critical.

(iii) Dry-charging processes that require the use of high temperature will almost certainly lead to significant softening of plates.

(iv) Curing, which tends to be carried out under 100 °C, appears to have the effect of suppression of the hardening process. One exception appears to be alloy 2 in the 'as-cast' condition, in which an initial improvement was observed.

(v) Despite the fact that peak hardness takes many days to be achieved in all the alloys examined, the most significant rate of change in hardness occurs within hours of casting. Therefore, there would be little benefit in ageing grids beyond a day; in the case of the quenched grid, no delay at all is required.

References

- 1 E. C. Rollason, *Metallurgy for Engineers*, Arnold, London, 4th edn., 1980, pp. 96–101.