

Short Communication

Transmission electron microscopic observation of precipitates in an aged Pb–0.1wt.%Ca–0.3wt.%Sn alloy

L. Muras^{a,1}, P.R. Munroe^b, S. Blairs^b, P. Krauklis^b, Z.W. Chen^{c,2}, J.B. See^{d,*}

^a Bradken Consolidated Ltd., PO Box 105, Waratah, NSW 2298, Australia

^b School of Materials Science and Engineering, University of NSW, Sydney, NSW 2052, Australia

^c CSIRO Division of Manufacturing Technology, Brisbane Laboratory, PO BOX 883, Kenmore, Qld. 4096, Australia

^d Pasmenco Research Centre, Boolaroo, NSW 2284, Australia

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Abstract

Samples of a Pb–0.1wt.%Ca–0.3wt.%Sn alloy were cast and either air-cooled or ice-water-quenched. They were then age-hardened for 400 days at ambient temperature and examined by thin foil transmission electron microscopy. In the air-cooled and aged condition, the alloy exhibits a sluggish ageing response, while a rapid ageing response occurs in the water-quenched and aged samples. In both types of sample, precipitate dispersions were observed. These are tentatively identified as Pb₃Ca with an ordered L₁₂ crystal structure. In the air-cooled and aged condition, the particles were about 100 nm in diameter and occurred in planar arrays consistent with precipitation on migrating grain boundaries. In the water-quenched and aged samples, the particles were about 10 nm in diameter and uniformly distributed with a smaller interparticle spacing, which is probably due to nucleation on tangle dislocations. The more rapid ageing kinetics in the water-quenched and aged condition are attributed to the excess vacancy concentration produced by quenching.

Keywords: Lead alloys; Calcium; Tin

1. Introduction

The use of lead–antimony grid alloys causes loss of electrolyte from lead/acid batteries and, as a consequence, lead–calcium grid alloys are preferred when low-maintenance or maintenance-free performance is required. Considerable effort is currently being devoted to the development of an advanced lead/acid battery system for zero-emission electric vehicles [1]. Because an essential requirement of such advanced batteries is that they should be maintenance-free, it is anticipated that lead–calcium alloys will be utilised in the advanced lead/acid battery system.

Due to the intrinsic softness of lead alloys, knowledge of the age-hardening behaviour of these alloys is im-

portant to eliminate problems in battery manufacture. In a recent investigation, Chen et al. [2] studied the age-hardening of a Pb–0.1wt.%Ca–0.3wt.%Sn alloy and the effects of heat exposure on this process. This alloy is widely used in the manufacture of lead/acid batteries. According to Bouriden et al. [3], processes associated with hardening of Pb–Ca–Sn alloys with Sn/Ca < 1 include: (i) fast discontinuous transformation without precipitation; (ii) slow discontinuous transformation without precipitation, and (iii) precipitation. In this case, discontinuous transformation refers to the movement of grain boundaries.

In the recent investigation [2], it was found that for the Pb–0.1wt.%Ca–0.3wt.%Sn alloy, samples quenched in ice water, immediately after solidification, harden and over-age very rapidly (Fig. 1). By contrast, air-cooled samples harden slowly over a considerably longer period and also reach a slightly higher peak hardness. Metallographic observation suggests that the high rate of hardening of the quenched samples, compared with the air-cooled samples, may result from a decrease in

* Corresponding author.

¹ Formerly student at School of Materials Science and Engineering, University of NSW, Sydney, NSW 2052, Australia.

² Formerly with Pasmenco Research Centre, Boolaroo, NSW 2284, Australia.

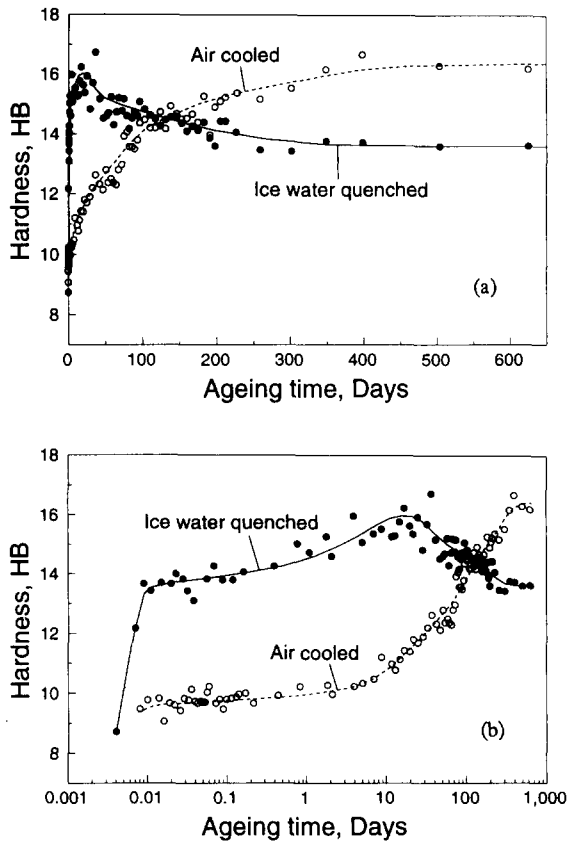


Fig. 1. Hardness curves for Pb-0.1wt.%Ca-0.3wt.%Sn alloy cast and aged naturally. Note: data presented here are more complete than those previously given in Ref. [2]. (a) Linear time scale, and (b) log time scale.

the degree of the slow grain-boundary movement and an increase in the rate of precipitation [2].

It was shown that ageing at elevated temperatures will accelerate the hardening process and increase the hardness of the air-cooled sample [2]. To obtain alloy grids with higher strength (hardness) without decreasing the production rate of batteries, further knowledge about precipitation in the alloy is necessary to optimise the post-casting cooling rate and heat treatment. In this study, transmission electron microscopy (TEM) was used to observe aspects of precipitation in the cast Pb-0.1wt.%Ca-0.3wt.%Sn alloy.

2. Experimental

Samples of a Pb-0.1wt.%Ca-0.3wt.%Sn alloy were cast, and either air-cooled or ice-water quenched, and then aged at room temperature as described in Ref. [2], which gives details of the casting procedure and thermal histories. At the time of the TEM investigation, the samples had been ageing naturally for about 400 days. From Fig. 1, at the ageing time of 400 days, it is clear that the hardness of both samples had stabilised.

Thin foil samples were prepared for TEM examination by cutting 3 mm diameter discs from 1 to 2 mm thick sections of the alloys by spark erosion, and then thinning the discs to perforation using an ion mill. The ion mill was fitted with a cryostage, which allows the samples to be cooled to liquid-nitrogen temperature (77 K) during milling. This minimises any unwanted phase transformations that may occur as a result of the heat generated during the milling process.

The thin foils were examined in a JEOL 2000FX TEM that was operated at 200 kV. This instrument is furnished with an energy dispersive X-ray spectrometer (EDS). To prevent unwanted transformations from occurring due to interaction with the incident electron beam, the samples were cooled to a temperature of 120 K, using a cryostage.

3. Results and discussion

TEM of the air-cooled sample revealed the presence of fine particles (about 100 nm in diameter) that were heterogeneously distributed throughout the microstructure. The particles were arranged in small groups, often linearly (Fig. 2), which suggests that they had nucleated on prior grain boundaries, before subsequent boundary migration occurred.

EDS analysis of these particles revealed that they were richer in calcium than the surrounding matrix. Their small size prevented unambiguous microchemical analysis being performed. Selected area diffraction patterns, obtained from regions of the microstructure containing these particles, revealed the very faint presence of superlattice reflections, in addition to the fundamental reflections arising from the presence of the lead matrix. These superlattice reflections were



Fig. 2. Thin foil transmission electron micrograph of precipitates in cast Pb-0.1wt.%Ca-0.3wt.%Sn alloy, air-cooled and aged for 400 days.

consistent with an ordered face-centred cubic (or $L1_2$) crystal structure. It is believed that these particles are $L1_2$ -structured Pb_3Ca .

In contrast, the water-quenched samples exhibited two distinct microstructures. In some areas, lamellae of a second phase were observed, with a thickness of about 50 nm and a spacing of about 200 nm (Fig. 3). EDS analyses from these lamellae indicated enrichment with calcium, and this phase is also believed to be Pb_3Ca . When the lamellae were examined under strong diffraction conditions, bundles of dislocations were seen tangled around the calcium-rich particles. Elsewhere in the water-quenched sample, very fine particles, about 10 nm in diameter, were observed to be homogeneously distributed throughout the microstructure (Fig. 4). Comparison of this micrograph with Fig. 2 for the air-cooled



Fig. 3. Thin foil transmission electron micrograph of lamellar structure in cast Pb–0.1wt.%Ca–0.3wt.%Sn alloy, ice-water-quenched and aged for 400 days.



Fig. 4. Thin foil transmission electron micrograph showing dislocation tangles associated with precipitates in cast Pb–0.1wt.%Ca–0.3wt.%Sn alloy, ice-water-quenched and aged for 400 days.

sample shows that the interparticles spacing was significantly smaller in the water-quenched alloy. Again, dislocation contrast was observed to be associated with these particles under strong diffraction conditions. It is possible that the dislocations may have acted as preferential sites for nucleation of the particles. Furthermore, strain contrast was also seen around these particles, suggesting that they were still partially coherent with the lead matrix.

In both the air-cooled and water-quenched samples, a small number of fine particles (about 1 μm in diameter) were also observed (Fig. 5). EDS analyses of these particles revealed only the presence of aluminium. Electron diffraction patterns were also consistent with the presence of aluminium. Since aluminium is insoluble in lead, the presence of these particles is not surprising.

As shown in Fig. 1, the air-cooled samples have only reached the peak hardness for ageing times of up to 400 days at room temperature. The fact that no fine precipitates were observed in the air-cooled samples indicates that the rate of formation of Guinier–Preston (GP) zones is low. This would give rise to the low hardening rate. On the other hand, the water-quenched samples were found to reach peak hardness very rapidly and showed significant overageing under the same conditions, indicating that the precipitates observed have coarsened significantly. The higher rate of precipitation in the water-quenched alloy is consistent with enhanced diffusion rates that are produced by a significant excess vacancy concentration due to rapid cooling. The excess vacancy concentration in this case could also be expected to produce a higher concentration of GP zones prior to precipitation, which act as nuclei for subsequent precipitation and thus explain the observed fine particle dispersion in the as-quenched case.

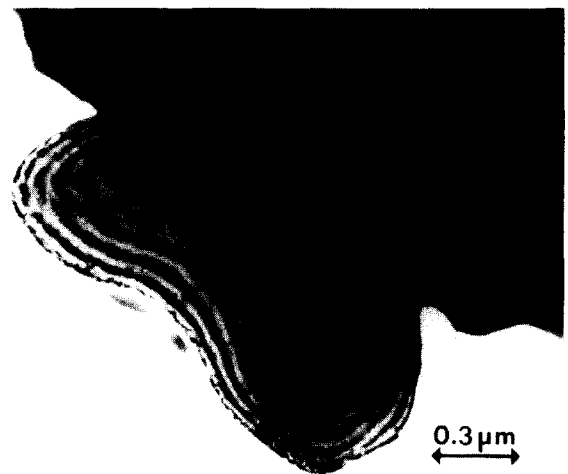


Fig. 5. Thin foil transmission electron micrograph of an aluminium-rich particle in cast Pb–0.1wt.%Ca–0.3wt.%Sn alloy, ice-water-quenched and aged for 400 days.

4. Conclusions

1. The Pb–0.1wt.%Ca–0.3wt.%Sn alloy in the cast and air-cooled condition aged at room temperature for 400 days was found to have a dispersion of particles approximately 100 μm in diameter. These particles are probably Pb_3Ca with an $L1_2$ -ordered crystal structure.

2. The Pb_3Ca particles occur in planar arrays, consistent with precipitation on migrating grain boundaries.

3. Water-quenching immediately after casting and then ageing under the same conditions causes some of the Pb_3Ca to form as part of a lamellar structure, and the remainder to precipitate in a fine (about 10 nm in diameter) and homogeneous dispersion during ageing.

4. The water-quenched and aged Pb_3Ca particles were observed to be associated with tangle dislocations, which may be preferred nucleation sites for precipi-

tation. The more rapid ageing kinetics in this case may be attributed to a significant excess vacancy concentration produced by quenching.

Acknowledgement

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