

## Short Communication

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### The Problem of Maintaining Ca Concentration in Pb-Ca Alloys for Grid Casting

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Manufacturers of lead-acid batteries are showing a growing interest in Pb-Ca alloys for grids. These alloys possess remarkable age-hardening properties so that very small amounts of Ca are sufficient to confer mechanical strengths comparable to those shown by Pb-Sb alloys, the traditional material for acid battery grid manufacture. The substitution of Ca for Sb reduces self-discharge and gassing. All these advantages are, nevertheless, offset by the tendency of Ca to oxidize preferentially during cast grid manufacture, concentrating it in the slag and being lost as an alloying element. Such a phenomenon is particularly serious if one bears in mind the low Ca content in the alloy, often less than 0.1%.

A knowledge of the factors involved in the kinetics of this preferential oxidation of Ca is necessary in order to avoid the problem. With this aim, an investigation was made by González *et al.* [1] on the influence of the temperature of the molten alloy and the composition of the atmosphere on the stability of Pb-Ca alloys. An interesting conclusion from such work was that if the temperature is not too high, the oxidation rate of the molten Pb-Ca alloys is very slow, even less than that for pure lead. It is only at high temperatures, of the order of 700 °C, that the harmful influence of Ca on the oxidation rate of dilute Pb-Ca alloys in air becomes evident. Therefore, it is clear that some other primary factor has to exist to account for the important Ca losses detected in practice when casting Pb-Ca alloy grids.

Feliu *et al.* [2] faced this problem in attempting to produce in the laboratory Pb-Ca cast grids of perfectly controlled composition. It was found that the main decreases in Ca content took place just during meltdown and whenever the alloy was remelted after solidification and cooling down in the crucible for a prolonged time. Other authors report similar difficulties [3, 4].

### Experimental

Part of the tests were performed with a stainless-steel crucible especially designed to provide the desired atmosphere at the head space over the molten

alloy. A 4 kg alloy charge was put into this crucible. A plug cock in its lower part permitted successive samples of the alloy to be cast without breaking up the continuity of the molten surface.

In the tests carried out under argon, passage of this gas over the alloy in the crucible was started one hour prior to its heating up. Once the alloy was molten and at the casting temperature, another hour was allowed to elapse before the first sample was cast. One and 2 hours from then, subsequent samples were obtained, and the alloy in the crucible was left to solidify. At the end of a further 3 hours as a minimum, and sometimes of one full day, the alloy was remelted, and using the same procedure as previously three more samples were taken.

In another part of the research the weight variation of the molten alloy was determined by means of an accurate balance. In this case the metal sample, weighing only about 15 g, was contained in a small alumina crucible inside a controlled-atmosphere tubular furnace.

## Results and Discussion

Figure 1 shows the typical compositional changes which occur in Pb-Ca alloys during melting and holding at casting temperature. It will be seen that the highest Ca losses take place during meltdown instead of occurring throughout the whole time the alloy remains molten.

In preliminary tests an attempt was made to assess whether the high oxidation rates during melting might stem from the fact that the protective oxide film over the melt which stifles further attack had not yet been formed. With this in mind the scale (or film) which grows with time over the molten alloy was repeatedly disturbed by breaking it up mechanically. The parallelism in the behaviour of thus-treated and untreated Pb-Ca alloys (Figs. 2 and 3) seems to preclude the opinion that a temporary failure of the protective cover could be the real cause of the discussed phenomenon.

As the main Ca losses take place upon the melting of alloys that have been kept at room temperature for a certain time, there was also the suspicion that air moisture condensation on the solidified alloy at low temperature might play a role in the effect. Figure 3 corroborates this possibility since if the temperature of the solidified alloy is kept at 150 °C, the Ca losses in the subsequent remelts in contact with air are greatly reduced as compared to those of the material cooled down to room temperature (Fig. 2).

This idea is confirmed by the results of later tests directly planned to investigate the effect of air moisture. Small Pb-Ca alloy samples, hanging in the previously mentioned tubular furnace, were heated from room temperature to 500 °C in contact with air. The alloy, which melted in just about 1 min, was kept for 15 min at 500 °C. This cycle was repeated four times, cooling down to room temperature and weighing after each cycle. Between two successive cycles the sample was exposed for 2 hours at least (in a desiccator over  $\text{CaCl}_2$  or water) to dry or wet air. Figure 4 illustrates the

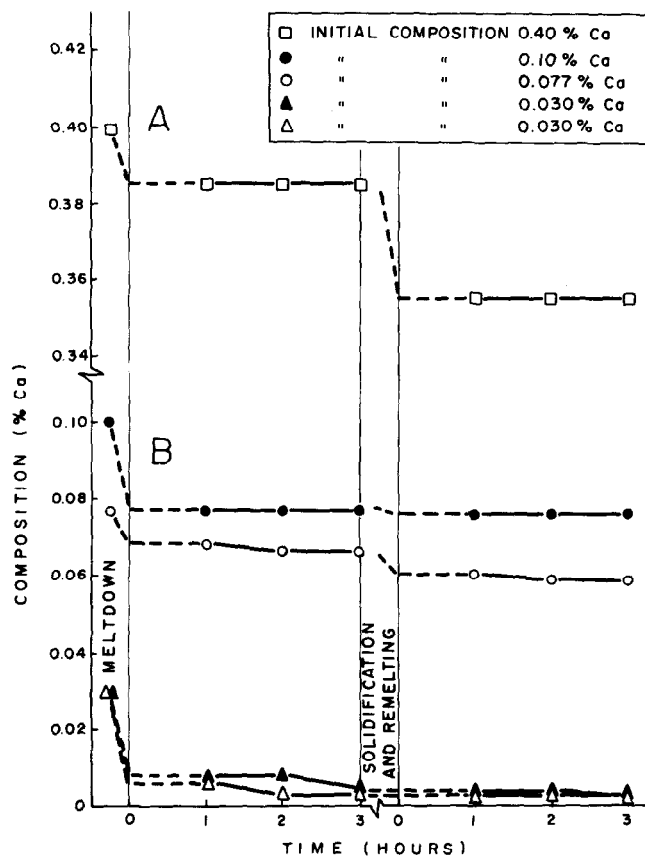


Fig. 1. Compositional changes occurring in the Pb-Ca alloys during melting and exposure at 500 °C. A, In contact with air; B, under argon atmosphere.

marked effect of wet air at room temperature on the subsequent oxidation of Pb-Ca alloys at high temperature and, in contrast, its slight influence on the oxidation of unalloyed Pb. It may be that the film of moisture on the sample surface during storing in wet air at room temperature promotes a slight aqueous electrochemical reaction, and the oxygenated corrosion products arising from it themselves react with the Ca at high temperature and/or obstruct, by an as yet unexplained mechanism, the subsequent formation of protective scale over the molten alloy. It should be pointed out that other experiments, not described here, have demonstrated that the effect of moisture in the air during the heating period was not harmful.

The experimental observation [5] that it is possible to counteract to a great extent the severe oxidation of the molten Pb-Ca alloy, which has been previously exposed to a moist atmosphere at room temperature, by a chemical cleaning of its surface (in a mixture of 3 parts glacial acetic acid and 1 part 30% hydrogen peroxide) before heating it up, adds considerable support

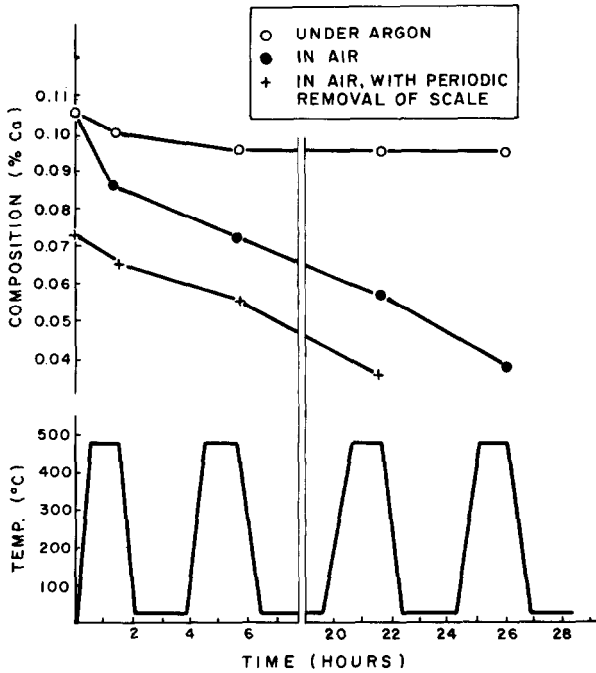


Fig. 2. (Top) Changes in Ca content of the melt upon subjecting the alloy to thermal cycles between 500 °C and room temperature. (Bottom) Chronological sequence of the experimental conditions.

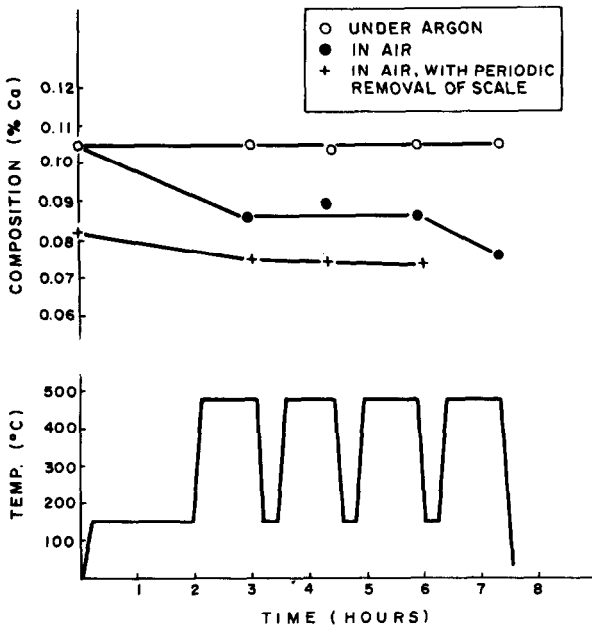


Fig. 3. (Top) Changes in Ca content of the melt upon subjecting the alloy to thermal cycles between 500 and 150 °C. (Bottom) Chronological sequence of the experimental conditions.

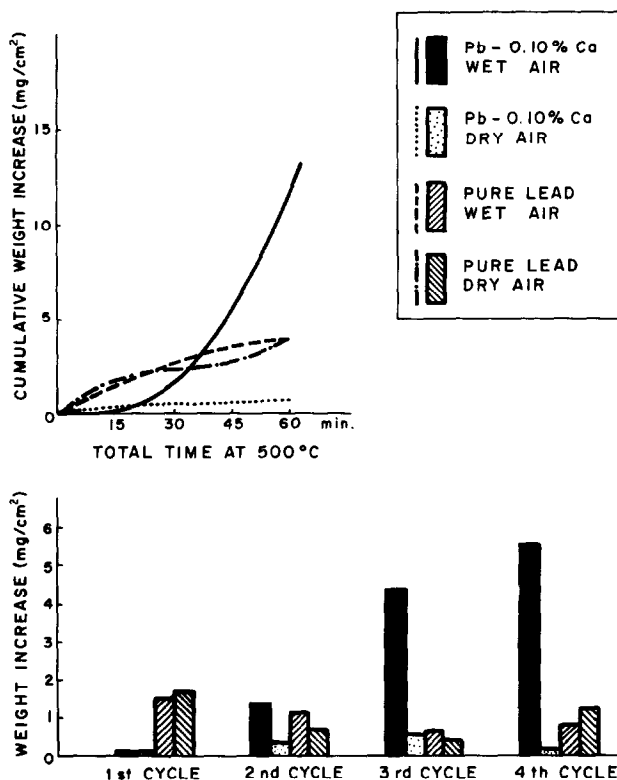


Fig. 4. Effect of storing in wet or dry air at room temperature on the subsequent oxidation of molten Pb-0.10% Ca alloy and pure lead at high temperature, when these materials are subjected to the thermal cycles described in the text.

to the foregoing interpretation. As would be expected the oxidizibility of pure lead is not affected by a similar surface cleaning.

To summarize, it seems likely that a number of practical problems encountered in maintaining the Ca concentration in Pb-Ca alloys have their origin at low temperature due to the effect of air moisture. Therefore, all possibility of water condensation on the solidified alloy in the shop should be avoided. Even the disparity of results obtained in some fundamental laboratory studies on the oxidizibility of these alloys [5] may be related to this interference of moisture, depending on the particular experimental method used in each instance.

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