

A Technical Note

Refining of a Lead-Acid Battery Grid Alloy

Dj. I. MILOSAVLJEVIĆ and I. D. DOROSLOVAČKI

Institute for Chemical Power Sources, IHTM, Beograd (Yugoslavia)

(Received March 10, 1978; in revised form June 20, 1978)

Summary

In the course of searching for new possibilities for improving the properties of a lead alloy for starting battery grids, the effect of ammonium chloride has been studied. It has been found that treating the melt with small quantities of NH_4Cl (0.05 wt.%) reduces the melting losses of antimony and arsenic, refines the structure, and improves the resistance of the alloy, particularly to localized corrosion.

Introduction

The simple binary lead-antimony alloy with a high percentage of antimony is not able to meet all the requirements for behaviour in production and use in starting battery grids. The possibility of improving grid alloys based on the Pb-Sb system is not great and is limited by: (a) the parameters of the existing grid casting technology which require, in order to make full use of the casting machines, an alloy of precisely defined castability at pouring and mould temperatures chosen in advance; (b) the negative effect of antimony on battery self-discharge; (c) the unstable price of antimony on the world market.

The first requirement could be met by increasing the antimony content of the alloy, up to, say, the eutectic composition, but this would be in conflict with the other two factors which require the antimony content to be as low as possible. To solve this problem multicomponent alloys have been developed in which antimony remains as the main alloying addition with arsenic, copper and tin as the other alloying elements. Sometimes, for grain refining purposes, selenium or sulphur are added [1], but these and some of the other favourable additions may give rise to problems in the processing of scrap batteries [2]. It therefore appears that the possibility of improving the

*Based on an unpublished paper presented at the 3rd International Symposium on Electrochemische Stromquellen, Technical University of Dresden, G.D.R., April 25 - 28, 1978.

properties of the multicomponent alloys, now widely used, by additional alloying is rather restricted. Consequently, it would be recommended that other ways of achieving this should be tried. Our attention was thus drawn to the fact that treating baths of lead, zinc, tin and their alloys with 0.1 - 0.2 wt.% of NH_4Cl removes non-metallic inclusions from the melt [3]. As we did not find any data in the literature on the use of such treatment with grid alloys we were led to undertake the experiments described in this work.

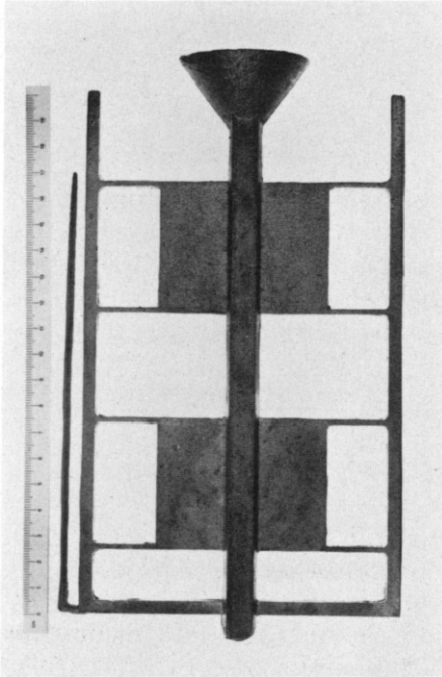


Fig. 1. Casting.

Experimental

Method

The experimental procedure was as follows: ammonium chloride tablets, in the quantity of 0.05, 0.10, 0.15 and 0.20% of the charge weight, were plunged into, and held within the melt by a perforated steel bell. After the reaction of NH_4Cl with the bath was completed, the specimens for further examination were cast. Parameters of melting and casting were kept constant. The properties of the treated specimens were compared with the properties of the untreated specimens.

Materials

The alloy used in this work was obtained from a Yugoslav lead-acid battery producer. Its chemical composition was: 5.23% Sb, 0.25% As, 0.05%

Cu, 0.02% Sn, 0.002% Bi, 0.001% Ag, Pb — remainder. This alloy is used for starting battery grids and we shall refer to it as the "S" alloy.

Ammonium chloride was of p.a. purity and in the form of 1 and 2 g tablets.

Melting and casting

In the preheated crucible of a resistance furnace, a quantity of the "S"-alloy (4000 g) was charged, melted, covered with a layer of dry charcoal and overheated to 400 ± 5 °C. After treatment with NH_4Cl , the melt was poured through the crucible bottom into the split-mould, temperature 150 ± 5 °C. The inner surface of the mould was previously coated in the same manner as the grid moulds in regular production, *i.e.* with a water suspension of cork flour to which carboxymethylcellulose is added as a binder.

Specimens

From each charge six castings (Fig. 1) have been cast, each consisting of the stem, four plates of dimensions $50 \times 25 \times 2.2$ mm, plate holders and the triangular section rod (the castability probe). The stem has been used for chemical analysis; the plates for metallography and mechanical testing, and plates with their holders for corrosion tests.

Results

Castability and mechanical properties

Treatment of the "S"-alloy melt with NH_4Cl has not shown a significant effect upon castability, hardness and tensile strength. For example, adding 0.05% NH_4Cl to the melt improved castability by 6%, hardness by 2% and tensile strength by 4%, approximately.

Chemical composition

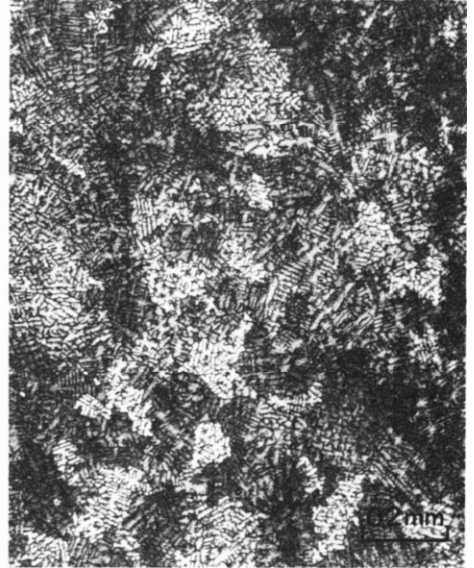
As has been stated, the initial values of the Sb and As contents in the "S"-alloy were 5.23% and 0.25% respectively. In the untreated specimens, they dropped to 5.00% and 0.17%, due to melting losses. However, treatment with 0.05% NH_4Cl already prevents any loss of Sb and As and the original content values are retained. Further increase in the NH_4Cl content during treatment of the melt has not shown any additional effect on the change of the Sb and As contents in the "S"-alloy, compared with the effect of 0.05% NH_4Cl .

Structure

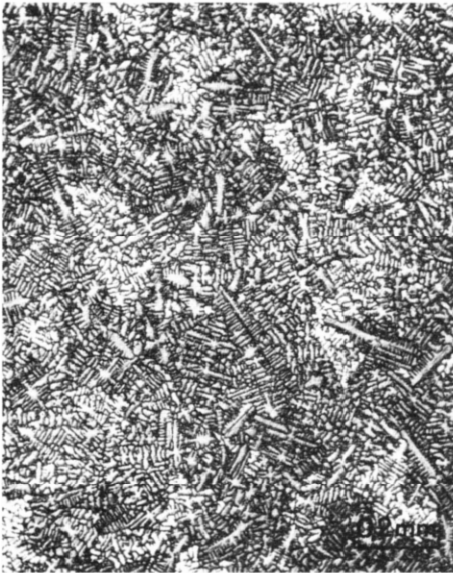
Treatment of the melt with NH_4Cl shows a strong effect upon the structure. Generally speaking, it results in structure refining, as can be seen in Fig. 2. The structure of a non-treated specimen (Fig. 2a) has large grains with the boundaries underlined by block orientation of the dendrites in the separate grains. Dendrite cells are not uniform in size and, as a consequence,



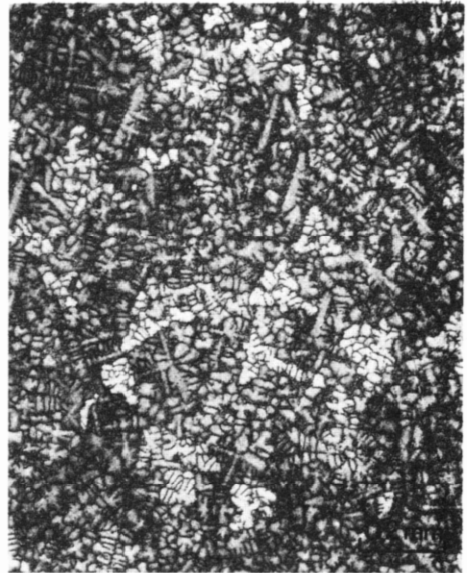
(a)



(b)



(c)



(d)

Fig. 2. Microstructure of the specimens; (a) non-treated with NH_4Cl ; (b) treated with 0.05% NH_4Cl ; (c) treated with 0.10% NH_4Cl ; (d) treated with 0.20% NH_4Cl .

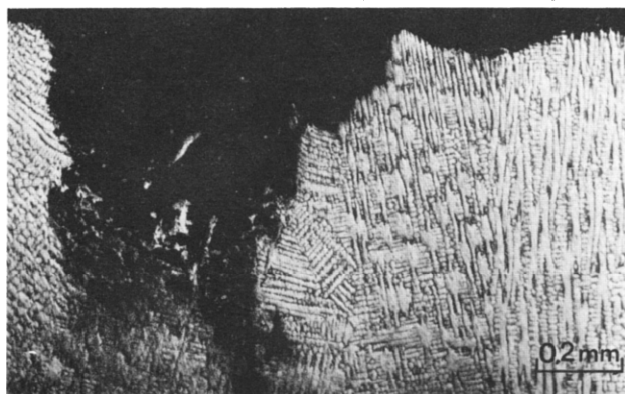
there is pronounced microsegregation of antimony. Treatment of the “S”-alloy melt with 0.05% NH_4Cl (Fig. 2b) causes the grains to become rounded and their size is reduced more than ten times. Dendrites are finer, shorter, and more randomly oriented. Their block orientation has disappeared.

Increase of the NH_4Cl content up to 0.10% (Fig. 2c) does not change qualitatively the main structural features, seen in Fig. 2b, but the structure becomes a little coarser. Treatment of the melt with 0.15% and 0.20% NH_4Cl (Fig. 2d) results in further coarsening of the structure.

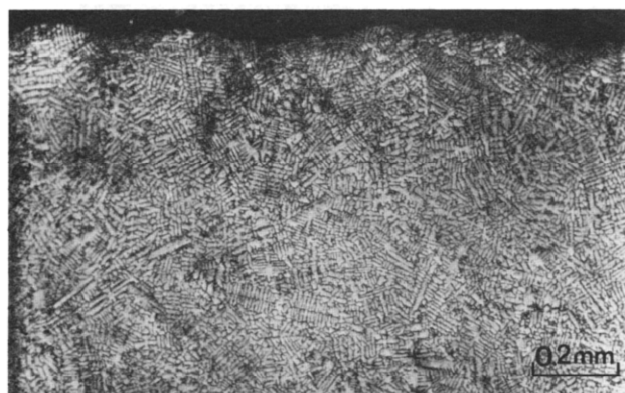
Corrosion test

Resistance to anodic corrosion was analyzed using the NIAI method [4], which consists of exposing the specimens to anodic polarization under the following conditions: solution: sulphuric acid of 1.26 g/cm^3 density; current density: 10 mA/cm^2 ; temperature: $20 - 22 \text{ }^\circ\text{C}$; time: 30 days.

Resistance to uniform corrosion is very slightly improved by treating the bath with ammonium chloride. On the other hand, we have noticed strong local corrosion of the untreated specimens which was apparent as small pits (up to 1 mm diameter, and up to 1 mm deep, to the extent of 2 - 4 pits per cm^2). Treating the melt with NH_4Cl , even with 0.05% NH_4Cl , prevents this type of corrosion. Cross-sections of the corroded specimens, non-treated and treated, are presented in Fig. 3.



(a)



(b)

Fig. 3. Cross-section of the corroded specimens; (a) non-treated with NH_4Cl ; (b) treated with 0.05% NH_4Cl .

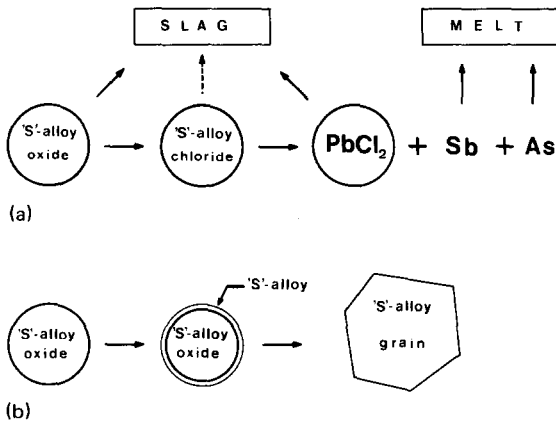


Fig. 4. The proposed mechanisms of the NH_4Cl reaction with the non-metallic inclusions (the "S"-alloy oxide particles); (a) prolonged treatment ($\% \text{NH}_4\text{Cl} = 0.1 - 0.2$); (b) shortened treatment ($\% \text{NH}_4\text{Cl} = 0.05$).

Discussion

Treating the melt with small quantities of ammonium chloride, just before casting of the starting battery grid alloy, has several effects upon its properties — significant for the production and exploitation of the grids. These effects are: preventing the melting losses of antimony and arsenic, decreasing pitting corrosion, and structure refining. In order to explain them, one has to take into account the fact that NH_4Cl decomposes at the melt temperature into ammonia and hydrogen chloride. Both of these are gaseous and cause vigorous stirring of the bath, which could result in: preventing gravity segregation, more uniform distribution of the existing crystallization centres throughout the melt, and faster floating upward of inclusions and their adhesion to the slag. In other words, due to this mechanical influence on the bath, the number of possible local corrosion centres (the coarser non-metallic inclusions) will be decreased and accordingly the resistance to pitting corrosion improved. Also, better distribution of the crystallization centres present would contribute to a finer structure.

It is rather unlikely to expect a chemical reaction of NH_3 with the components of the bath. Therefore, the only effect which we would ascribe to ammonia is mixing of the bath. On the other hand, a strong chemical reaction of hydrogen chloride with the oxides is to be expected. This means that hydrogen chloride will react with the non-metallic inclusions in the melt and with the slag as well, thus forming the chlorides. The chlorides of Sb and As are unstable in the bath of Pb-Sb alloy, and as their oxides both of them are replaced by lead, and returned back into the melt.

In the reaction of hydrogen chloride with the oxides water vapour develops and intensifies the mixing of the bath. Increasing the NH_4Cl content from 0.05% up to 0.20% resulted in coarsening of the "S"-alloy

structure. Prolonged treatment of the melt with the increased quantity of NH_4Cl would "clean" the non-metallic inclusions more thoroughly from the melt. Then, the finest non-metallic inclusions (the oxide particles), *i.e.* the potential crystallization centres are either transferred to the slag or converted into the chlorides. The structure then becomes coarser. On the other hand, treating the "S"-alloy bath with 0.05% NH_4Cl is of short duration and the possible crystallization centres remain in the bath with the surface activated by hydrogen chloride. Therefore, one can say that refining of the structure with 0.05% NH_4Cl is the result of the activation of the crystallization centres, already present in the bath. These proposed mechanisms are schematically presented in Fig. 4.

The structure obtained by treating the melt with 0.05% NH_4Cl consists of fine grains and fine randomly oriented cellular dendrites. The grain boundaries are not underlined by the dendrite blocks, which could contribute to their decreased sensitivity to corrosion. Adding to this a uniform distribution of antimony, this structure (Fig. 2b) could be considered as the closest to the concept of "optimum structure" for this alloy.

In spite of the fact that the effect of NH_4Cl treatment on the probability of the occurrence of hot-tearing has not been studied in this work, one could say, according to published data [5], that resistance to hot-tearing should be increased due to the grain refining obtained by treatment of the "S"-alloy bath with ammonium chloride.

The favourable effect of NH_4Cl upon properties could be expected in the other grid alloys based on the Pb-Sb system. Therefore, treatment of the alloy bath with small quantities of NH_4Cl in the kettle of a grid casting machine has to be considered.

The other practical use of treating the melt of a grid alloy with NH_4Cl could be raising the casting temperature, let us say by $20^\circ - 40^\circ \text{C}$, to cast thinner grids and probably save a few per cent of the alloy, expecting that the structure of these grids will be as fine as the structure of the ordinary cast grids.

Conclusions

Treatment of the bath of the starting battery grid alloy (5.23% Sb, 0.25% As, 0.05% Cu, 0.02% Sn, 0.002% Bi, 0.001% Ag, Pb — remainder) with a small quantity of ammonium chloride has the following consequences: (a) melting loss of antimony and arsenic is prevented; (b) refining of the structure; (c) increased resistance to pitting corrosion; and probably (d) reduced possibility of hot-tearing.

In order to achieve these advantages, it is sufficient to plunge into the melt 0.05% (of the charge weight) of NH_4Cl in the form of tablets in a perforated bell before casting the alloy.

The effect of NH_4Cl can be explained by the cooperative influence of ammonia and hydrogen chloride on the non-metallic inclusions in the melt.

Acknowledgement

The authors gratefully acknowledge the sponsorship of the Research Fund of the SR Serbia.

References

- 1 U. Heubner and A. Überschaer, Proc. 5th Int. Lead Conf., Metall. Bull., London, 1976, p. 59.
- 2 D. Van Doorn, Proc. Int. Conf. Lead and Zinc into the 80's, Zinc Development Association, London, 1977, p. 16.
- 3 A. V. Kurdyumov *et al.*, Liteinoe proizvodstvo tsvetnih i redkih metallov, Metallurgiya, Moscow, 1972, p. 233.
- 4 J. A. Aguf and M. A. Dasoyan, Vestn. Elektropromsti., 29 (1958) 56.
- 5 U. Heubner and A. Überschaer, Z. Metallkd., 66 (1975) 74.