

PATENT SPECIFICATION

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(54) ANTIMONY LEAD ALLOYS

(71) We, VARTA AKTIENGESellschaft, a Company organised under the Laws of Germany, of Neue Mainzer Strasse 54, 6000- Frankfurt am Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a low-antimony lead alloy suitable for the manufacture of accumulator grids.

As is known, lead accumulator grids are usually made from a Pb-Sb alloy containing 15 6-11% antimony. The antimony gives the required strength and casting properties to lead which, when pure, is very soft and unsuitable for manufacturing accumulator grids. The antimony in the alloys is expensive and considerably increases the cost of manufacturing the grids. Self-discharging of the accumulator and gas formation increase with increasing antimony content, and antimony ions migrate to the negative electrode of the accumulator and poison it during operation.

Attempts have therefore been made to reduce to a minimum the antimony content of grids for lead accumulators.

30 Although the required strength can easily be obtained, it is impossible to manufacture satisfactory accumulator grids containing lead and 1.0-3.5% antimony only, since they are brittle and tend to crack, apparently as a result of coarse dendritic solidification and the resulting flaws in casting (such as cavities and microporosity).

As an example of an attempt to reduce the antimony content to a minimum, U.S. Patent Specification No. 2,148,741 discloses an alloy containing Sb, Sn and As or Cu or Se. However, an alloy containing e.g. only As and Cu has a considerable tendency to cracking and brittleness, whereas Se admixtures cannot give the necessary hardness

[Price 33p]

unless the antimony content is higher than 6%.

British Patent Specification No. 622,512 proposes to construct positive grids for lead accumulators from a lead alloy containing 50 1.0-5% Sb and an admixture of 0.005 to 0.5% Se. The purpose of adding selenium is to reduce or suppress the tendency to crack when the grids cool after casting.

It has been shown that such low-antimony 55 alloys containing from 1-3.5% antimony do not crack after casting, but the grids are too soft to be used in the manufacture of accumulator plates. If the grids are hardened by subsequent heat-treatment, e.g. 60 by solution heat treatment and subsequent precipitation or aging, there is a decrease in toughness and the grids become brittle and break under mechanical stress.

Consequently, alloys according to the 65 said British Patent Specification are too soft and, more particularly, take an excessive time to harden and become too brittle if heat-treated in order to obtain the required strength.

70 British Patent Specification No. 1,105,548 describes antimony-free alloys for lead accumulator grids, the alloys comprising Pb, Te, Ag and As. These alloys are, however, usually too soft and have therefore not been 75 used in the manufacture of accumulators.

It is an object of the invention to provide a low-antimony Pb, Sb alloy suitable for casting into accumulator grids which can be given an appropriate hardness, tensile 80 strength and toughness merely by cooling the cast grids in air or by cooling them with a water spray, and without the use of an additional solution heat treatment. Such additional heat treatment, while it will improve hardness upon aging has the disadvantage that a reduction in toughness occurs.

It is a further object of the invention to provide a low-antimony Pb, Sb alloy which 90

SPECIFICATION AMENDED - SEE ATTACHED SLIP

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retains its casting properties and casting performance even in the production of thin accumulator grids, e.g. for starter batteries, and which gives grids having high resistance to corrosion when subjected to severe electrochemical stress.

According to the invention, the alloy comprises 1.0-3.5% especially 1.5-3.5% Sb, 0.025-0.2% As, 0.005-0.1% Se, and 0.01-0.5% Sn, the remainder being Pb and impurities.

It will be understood that the alloy according to the invention may be given a heat treatment subsequent to casting whenever such heat treatment is found to be desirable or necessary.

In the case of alloys for positive grids of industrial accumulators and thin positive starter grids, from 0.025-0.1% Ag may with particular advantage be added to the alloy. The silver stabilises the structure of the alloy, increases resistance to corrosion, suppresses the formation of coarse grains during any heat treatment to which the alloy may be subjected and suppresses discontinuous precipitation which would otherwise result in a reduction in toughness.

Good results, in the case of severely-stressed industrial and starter grids, have been obtained with alloys comprising 1.5-2.8% e.g. 2.2-2.8% Sb, 0.03-0.06% As, 0.01-0.1% e.g. 0.01-0.04% Se, and 0.015-0.03% Sn, the remainder being lead. As before Ag may advantageously be added, preferably in an amount of 0.03-0.06%.

In order to be suitable for lead accumulator grids, the alloys need a minimum hardness on the Brinell Hardness Test Specified in British Standard Specification No. 240: Part 1: 1962 using 25 "Kiloponds" (Kilogram force) with a 5 mm diameter ball for 30 seconds, of 11-13 kg/mm². Pb-Sb alloys need to contain at least 6.5% Sb if the natural hardness of the grids is to be greater than the required hardness. The term "natural hardness" denotes the hardness of the cast grid when not subjected to heat treatment after casting. In the case of known alloys containing between 1.5 and 6.5% antimony, the difference between the natural and the required hardness has to be made up by heat treatment.

Thus, in the known low-antimony Pb, Sb alloys, the difference between the natural and the required hardness can be compensated by a heat treatment including a solution treatment, that is by heating at temperatures above 225°C, followed by aging for a suitable time, e.g. approximately 1 week. The solution treatment is e.g. carried out at 225-250°C for 30-60 minutes in order to obtain the required hardness during the subsequent aging.

The selenium added to the alloy of the present invention decreases cracking but

has hardly any effect on the strength. The arsenic obviates the need for subsequent heat treatment, which may reduce toughness. The tin considerably improves the casting properties and casting performance, and the silver stabilises the structure, increases the toughness and improves the resistance to corrosion.

In order to ensure that the accumulator grids are manufactured in an efficient manner, they have to be given the required strength in a short time. An admixture of about 0.05% arsenic has an excellent effect in increasing the speed and extent of age hardening. This is because the aforementioned proportion of approximately 0.05% is the maximum solubility of arsenic in the lead crystal lattice, which has an excellent effect during age hardening. If the proportion of arsenic is much higher than 0.05% it is retained as a heterogeneous phase, which interferes with the age hardening, thus reducing the resulting increase in strength.

The optimum proportion of tin is 0.02%. If the tin content is between 0.01 and 0.03%, the fluidity and the casting performance are considerably improved. If the proportion is less than 0.01%, the tin no longer has a good effect, whereas a proportion of more than 0.03% results in an alloy which is too fluid during casting and in the formation of fibre-like structures in the alloy.

As already mentioned, the arsenic increases the rate and degree of age hardening. In the case of alloys not containing arsenic, the required temperature of the heat treatment for obtaining the required hardness is 225°C, whereas in the case of alloys containing arsenic according to the invention, the required hardness is obtained by carrying out a solution treatment at a temperature of 200°C. Since the grids have a temperature of 200-225°C on leaving the casting mould, the reduction in the hardening temperature to 200°C has considerable economic advantages, since an additional subsequent heat treatment can thus be omitted. Consequently, alloys containing arsenic can be given the required hardness in a reasonable aging time. If the grids are sprayed with water immediately after removal from the mould, the extent and speed of hardening can be further improved, or the antimony content can be further reduced, within the range 1-3.5%. Grids containing arsenic and selenium and up to approx. 2% antimony can be given the required hardness by aging at room temperature after casting, and grids containing up to 1.5% antimony can be given the required hardness by spraying with water after casting and subsequent aging at room temperature. The aging time required to

produce the desired level of alloy hardness is moderate, being approximately 1 week. The tin also improves the casting properties and increases the casting performance. The silver, when present, stabilises the structure, increases the toughness (ductility) and improves the resistance to corrosion.

The combination of Pb, Sb, As, Se, Sn and Ag can increase the strength of low-antimony alloys without impairing the ductility by more than 5%, and without impairing the toughness. There is also a considerable improvement in the casting properties and casting performance, and an increase in the resistance to corrosion. A hardness of up to approximately 28 kg/mm² can be obtained by solution treatment subsequent to casting, for 15-60 minutes at 200-245°C followed by spraying or quenching the grids with water, and aging at room temperature.

The higher temperature and longer duration of heat treatment during such subsequent solution treatment, followed by aging at room temperature, reduce the ductility and toughness of the low-antimony Pb-Sb alloys containing As, Se and Sn admixtures. The reduction in ductility is due to the formation of coarse grains during the solution treatment, and to discontinuous precipitation during aging. By using the alloy according to the invention the speed of migration of grain boundaries during solution heat treatment is reduced as is the speed of discontinuous precipitation during aging is reduced. The decrease in the migration of grain boundaries limits the formation of coarse grains. Since the rate of discontinuous precipitation is reduced, continuous precipitation usually anticipates and consequently prevents discontinuous precipitation. Discontinuous precipitation can also be appreciably reduced by aging at relatively high temperatures, e.g. up to 100°C, even in the case of alloys not containing silver. If no silver is added, however,

coarse grains are still formed during heat treatment.

WHAT WE CLAIM IS:—

1. An antimony lead alloy which comprises 1.0-3.5% Sb, 0.025-0.2% As, 0.005-0.1% Se, 0.01-0.5% Sn, the remainder being lead and impurities.

2. An antimony lead alloy which comprises 1.5-3.5% Sb, 0.025-0.2% As, 0.005-0.1% Se, 0.01-0.5% Sn, the remainder being lead and impurities.

3. An antimony lead alloy according to Claim 1 or Claim 2 in which the selenium content is 0.01-0.1%.

4. An antimony lead alloy as claimed in Claim 1 or Claim 2 or Claim 3 which includes 0.025-0.1% Ag.

5. An antimony lead alloy as claimed in Claim 1 which comprises 2.2-2.8% Sb, 0.03-0.06% As, 0.01-0.04% Se, and 0.015-0.03% Sn, the remainder being lead and impurities.

6. An antimony lead alloy as claimed in Claim 1 which comprises 2.2-2.8% Sb, 0.03-0.06% As, 0.01-0.04% Se, and 0.015-0.03% Sn, the remainder being lead and impurities.

7. A low-antimony lead alloy as claimed in Claim 4 which comprises 1.5-2.8% Sb, 0.03-0.06% As, 0.01-0.04% Se, 0.015-0.03% Sn and 0.03-0.06% Ag, the remainder being lead and impurities.

8. A low-antimony lead alloy as claimed in Claim 4, which comprises 2.2-2.8% Sb, 0.03-0.06% As, 0.01-0.04% Se, 0.015-0.03% Sn and 0.03-0.06% Ag, the remainder being lead and impurities.

9. An accumulator grid when made from an alloy as claimed in any one of Claims 1 to 7.

10. A lead acid battery in which the grids are as claimed in Claim 9.

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The combination of Pb, Sb, As, Se, Sn and Ag can increase the strength of low-antimony alloys without impairing the ductility by more than 5%, and without impairing the toughness. There is also a considerable improvement in the casting properties and casting performance, and an increase in the resistance to corrosion. A hardness of up to approximately 28 kg/mm² can be obtained by solution treatment subsequent to casting, for 15-60 minutes at 200-245°C followed by spraying or quenching the grids with water, and aging at room temperature.

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3. An antimony lead alloy according to Claim 1 or Claim 2 in which the selenium content is 0.01-0.1%.

4. An antimony lead alloy as claimed in Claim 1 or Claim 2 or Claim 3 which includes 0.025-0.1% Ag.

5. An antimony lead alloy as claimed in Claim 1 which comprises 2.2-2.8% Sb, 0.03-0.06% As, 0.01-0.04% Se, and 0.015-0.03% Sn, the remainder being lead and impurities.

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