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Surface Electrodes For A New Type Of Lead-Acid Accumulators Starter Destination

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Abstract

The condition of modern technology of lead-acid accumulators of starter appointment is considered, shortcomings are noted it. It is offered to use the superficial electrodes of new type received from the pure lead alloyed by tellurium, the mechanical and corrosion properties of electrodes and to increase their resource allowing to improve considerably in a design of batteries.
The article is intended for engineers and technical specialists of the accumulator industry.

Keywords: Lead-acid accumulator, current tap, positive electrode, negative electrode, superficial electrode, specific capacity, active mass, corrosion.

Introduction

The main requirements for lead-acid accumulators can be attributed primarily operational safety, service life and specific energy characteristics.The considerable attention is paid to a question of labor costs at operation of batteries and environmental friendliness of their production. And, at last, the significant characteristic of batteries is their initial cost.

The powder manufacturing techniques of electrodes of lead-acid accumulators applied now differ in high labor input and the content of ecologically harmful processes: hot molding of lead, receiving lead powder, preparation of paste, a spread made pastain plates, drying of plates, etc. An alternative to this technology may become a new technology for manufacturing electrode electrochemical method, which does not contain the above harmful processes [1].

One of the main technological processes by production of lead-acid batteries is technological process of production of electrodes. The main efforts of developers of

accumulators on increase in specific power characteristics of the starteraccumulators are directed on reduction of thickness of plates, search of the alloying additives in an alloy, etc. receptions, - practically reached a technological limit and don't solve a problem of further increase of specific power characteristics of lead-acid accumulators.

The majority of attempts of improvement of technology of current tapsare reduced to rational selection lead-tin-calciumand other alloys for the positive electrodes increasing their mechanical and corrosion properties, thus technological process remains powder.

Experiments

Authors of article conducted a number of the researches directed on search of the technological decisions providing the increased mechanical and corrosion properties of terminal. For this purpose, current tapthe samples were made from pure lead. The part of samples is processed by pressure, part of samples from pure lead were alloyed by tellurium.

It is expected that the samples processed by pressure will increase durability of plates of current tap, and the lead alloying tellurium will allow to improve corrosion properties of a current tapand to increase its mechanical durability [2].

The data presented in Figures 1-3 photographs metallographic samples were obtained using a SEM microscope and fluorescence confocal Raman spectrometer Omega Scope, showing a structure of Pb and Pb-Te alloys.

Figure 1 shows the morphology of pure lead in Figure 2 - alloyed of tellurium in a proportion of 0.05% by mass of the current tapand Figure 3 - alloyed of tellurium in a proportion of 0.10% by mass of the current tap.

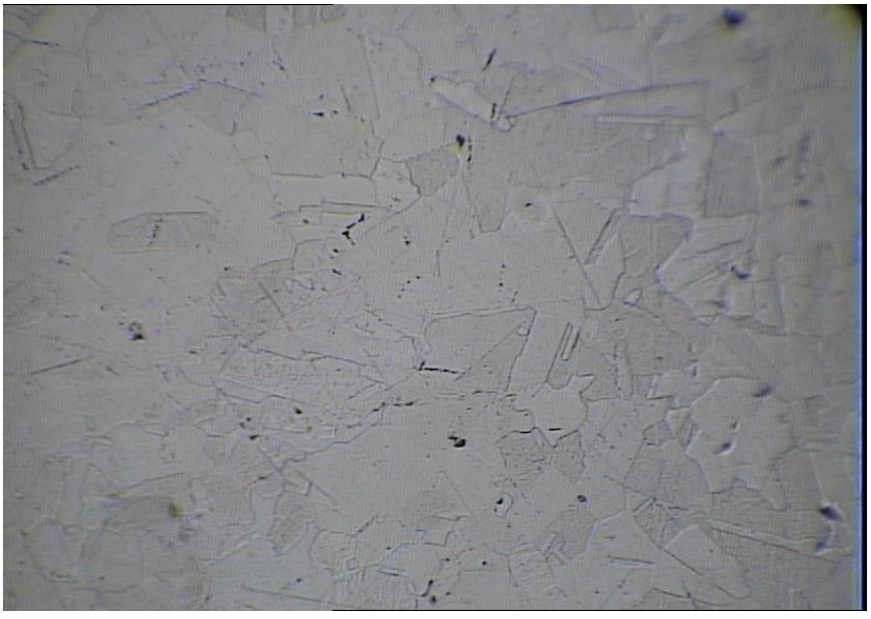


Figure 1 - Structure of pure lead Pb (20x42x8)

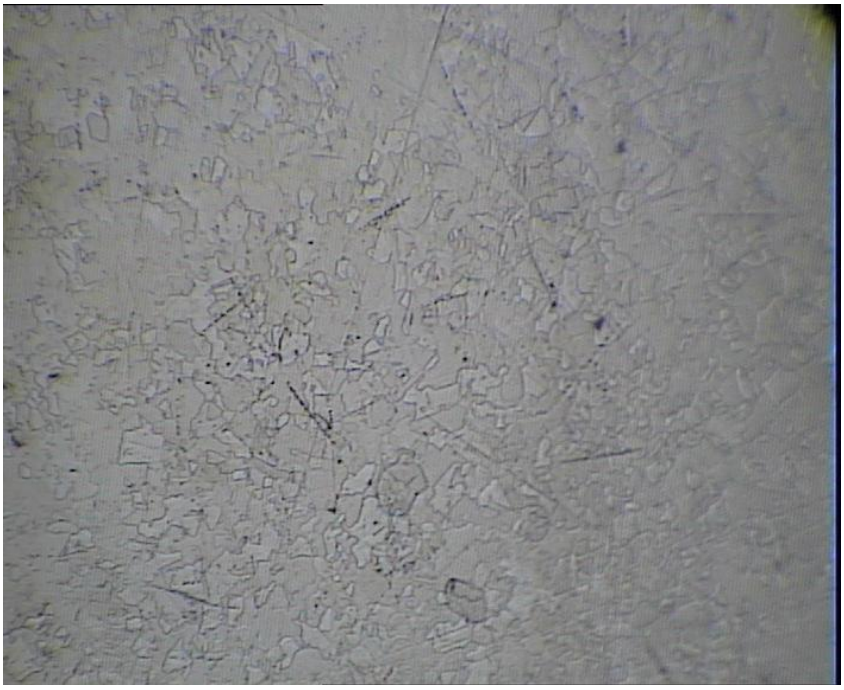


Figure 2 - Structure of the lead alloyed by Pb-Te-0.05% of tellurium (20x42x8)

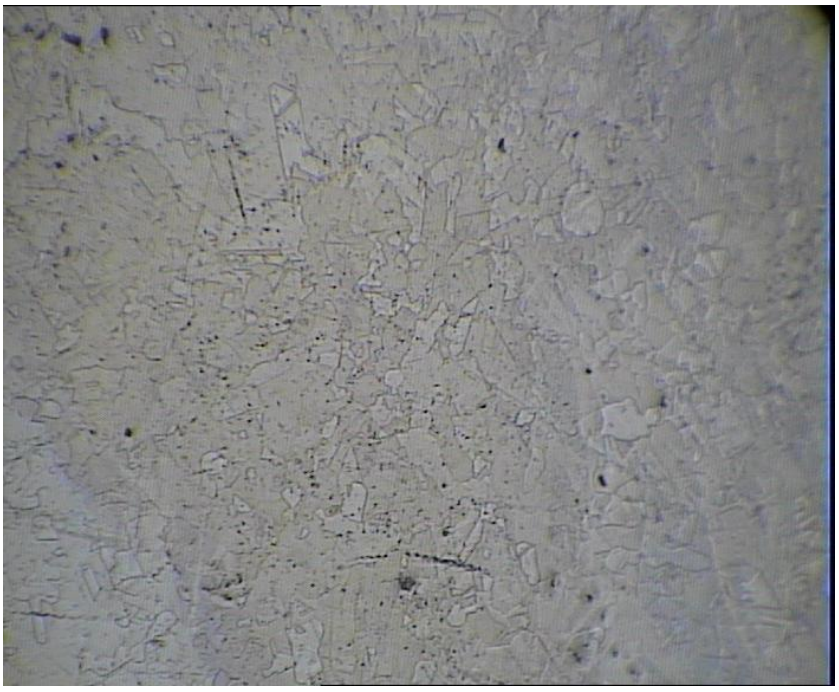
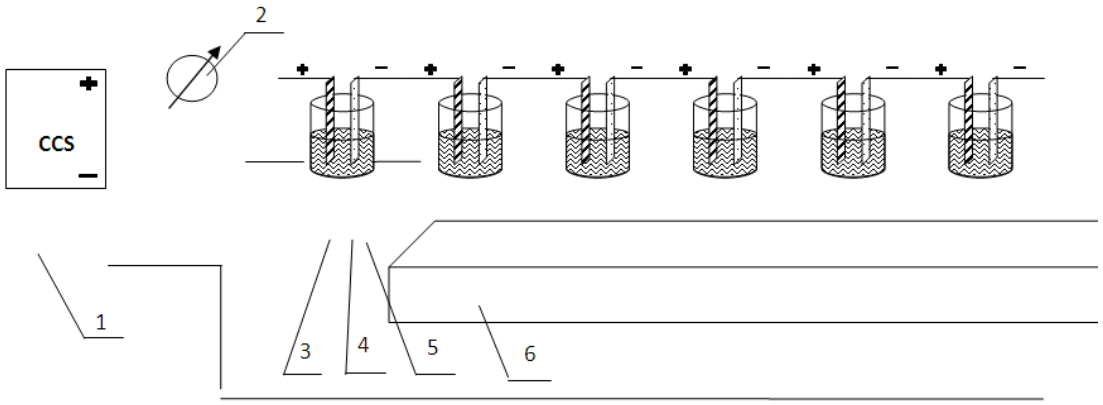


Figure 3 - Structure of the lead alloyed by Pb-Te-0.10% of tellurium (20x42x8)

The structure of not alloyed lead contains grains of the large sizes, not regular areas (fig. 1), alloys with Rb-0,05 and 0,10 mass% are observed. Those have a fine grain and regular borders (fig. 2, fig. 3). The small structure of grains of plates of Pb-Te is more preferable from positions of corrosion resistance.

The most subject to impact of corrosion is the positive electrode. Researches of corrosion properties of the current tapreceived by an alloying tellurium in the ratio of 0,05% and 0,10% of the mass of a current tapwere for this purpose conducted.

Researches of corrosion properties it was carried out on six samples of current tapsby the accelerated technique which essence is reduced to that examinees current taps are located in the electrolyte having the increased temperature then made process of electrochemical oxidation. For receiving an assessment of influence of an alloying tellurium two samples were made of pure lead and intended for comparison purposes, four samples were made of the lead alloyed by tellurium. Initial preparations of current taps were weighed previously on analytical scales, results of weighing were fixed. Preparations were located in solution of sulfuric acid with a density of 1,27 g/sm^3 and were connected consistently to a current source according to the scheme shown in figure 4:



1- Adjustableconstantcurrentsource.
2- voltamperemeter.
3- Examineeelectrode.
4- -Antielectrode (minus).
5- Electrolyte.
6- Thermostat.

Figure 4 - Scheme of tests for corrosion resistance.

The modes of corrosion tests by the accelerated technique:

- Current - 0, 35 And/sq.m.
- Electrolyte temperature – plus 65 0C.
- Etching time – the 40th hour.

Upon completion of tests electrodes were washed out and dried within 30 minutes in a drying cabinet. After drying with initial and examinees of electrodes friable weight was removed. Electrodes were weighed on analytical scales again. Thus losses of mass of lead due to corrosion were defined. Results of weighing are given in table 1.

Table 1 - Results of corrosion tests of electrodes

Sample	Electrodeweight, g		Difference in weight,g
	Theinitial electrode	After tests	
Lead plates from pure lead (2 pieces)	10,295 10,345	10,075 10,013	0,220 0,332
The lead plates alloyed tellurium of 0,05% of weight (2 pieces)	10,19 10,15	10,167 10,126	0,0225 0,0232
The lead plates alloyed tellurium of 0,1% of weight (2 pieces)	9,605 9,700	9,580 9,677	0,0246 0,0228

The analysis of data of table 1 shows that losses of mass of plates of the lead alloyed by tellurium proceed much more slowly, than at plates from pure lead. It gives the chance to make plates of current taps thinner and allows to increase their total in the semi-block, so and specific power characteristics of the accumulator.

Research of process of oxidation of lead with receiving dioxide of lead depending on properties of a lead current tap.

In the classical production technology of electrodes of lead-acid accumulators, current tapsare made of lead with addition of antimony and other materials increasing its durability, molding properties and corrosion resistance.

These researches allow to choose rational option of a design of an electrode and to fulfill technology of formation of active mass.

The mechanism of oxidation of a surface of lead with receiving dioxide of lead is studied in the electrochemical way insufficiently and the unambiguous theory of this process is absent.

Formally electrochemical process of obtaining the active mass (PbO2) can be presented by the following equation (1):

$$Pb + 2H_2O \leftarrow \rightarrow PbO_2 + 4H^+ + 2e \qquad (1)$$

Actually it is multistage reaction, and in the course of formation of active mass of superficial electrodes taking partoxidizers (ions of ClO_4^- and NO_3^-) and sulfuric acid. The low density of sulfuric acid (1,08-1,09 g/sm3) can indirectly testify to an important role of molecules of H2O at a certain stage of reaction.

In this work influence of properties of a lead current tap on corrosion process was investigated.For this purpose, samples were produced from the current tap lead grades: C1, C2, C3, which were tested for corrosion resistance.

In figure 5 dependence of corrosion resistance of lead current tapsdepending on quality of the used lead is shown (i.e. from purity of metal).

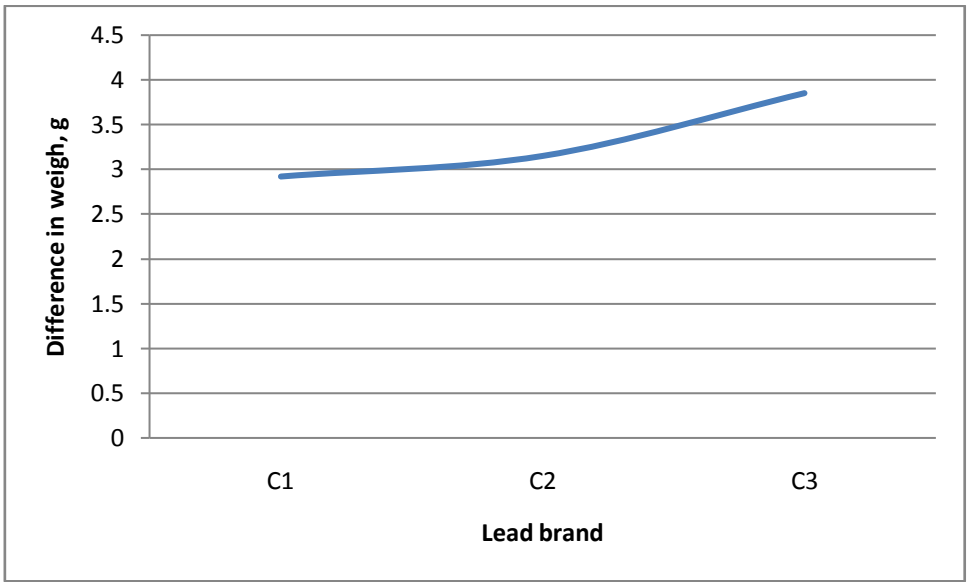


Figure 5 - Corrosion resistance of lead of different purity.

Data of figure 5 confirm need of use for production of current tapsof pure lead of brand (C0,C1).

In figure 6 the average speed of formation of active mass of the current tapsfrom C1, C2, C3 lead processed by pressure is shown. Initial preparations of current taps for positive and negative electrodes were made in the form of lead plates and were exposed to pressure on the press in the range of 20-80 kPas then were located in electrolyte: solution of sulfuric acid with a density of 1,09 g/sm^3 with additives of ions of ClO_4^- in number of 10-12 g/l and NO_3^- in number of 1,2-2,0 g/l, current density on the studied samples made 20 mA/sm^2, formation electrolyte temperature plus 20-25^{0}C. Time of formation varied within 18-36 hours. Upon termination of process electrodes were exposed to a sink and drying. The active mass of samples was cleaned off to a current tapand weighed on analytical scales with an accuracy ±1mg. According to weighing the schedule presented in figure 6 is constructed.

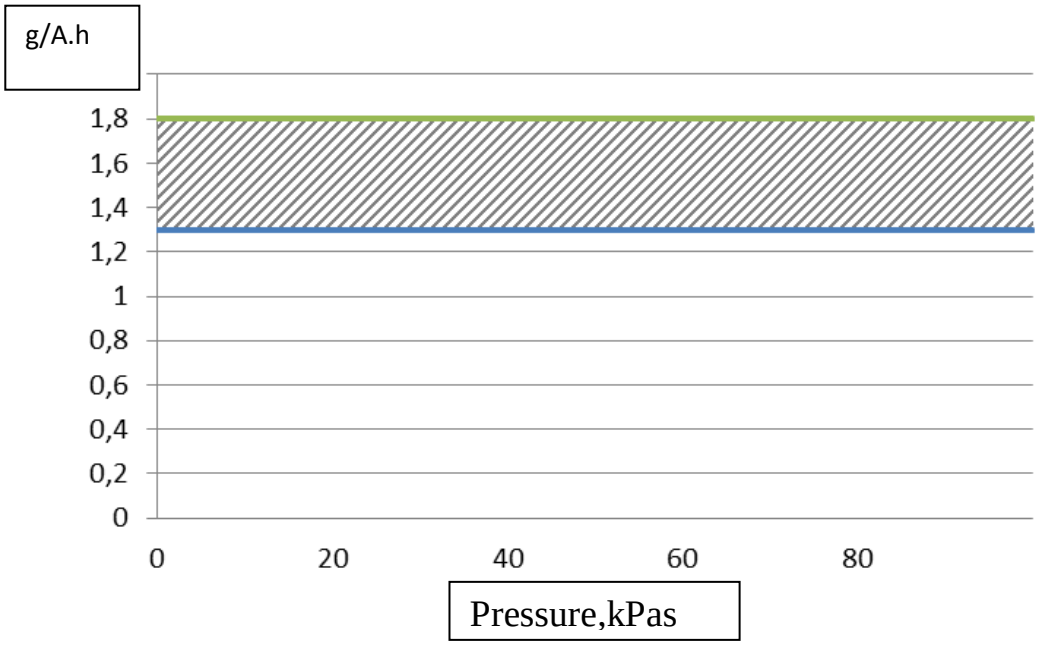


Figure 6 - Dependence of speed of electrochemical receiving activemass from pressure size.

As appears from figure 6 processing by pressure practically doesn't influence the speed of formation of active mass. Key parameters of active mass also practically don't differ from parameters of mass of the initial (not processed) current taps: modification β-PbO_2, porosity of 50-55%.

Thus, the speed of obtaining active mass and its structure depend generally on the formation modes, processing of plates pressure influences process of accumulation of active mass a little.

Technology of formation of active mass in the electrochemical way for positive and negative electrodes

The size of active mass of an electrode determines its capacity, power and resource characteristics. Process of formation of weight is quite long: (12-30) hours therefore represents practical interest to optimize it on duration as it is included in the general production cycle of production of the accumulator and affects its prime cost.For optimization of process of formation of active mass on tests ten current taps having the identical geometrical sizes were put. Before processing samples were located in carapaces, were weighed and then plunged into forming solution everyone in separate capacity. For creation of identical conditions of accumulation of active mass samples connected consistently and were connected to one power supply. Control of accumulation of weight was exercised visually and by means of a micrometer. Current of the mode of accumulation of weight in the course of experience was supported at the level of 20 мА/см^{2}the areas of a current tap. Measurement of

thickness of mass was performed each two hours. Results of measurements are given in table 2.

Table 2 - Results of accumulation of active mass of current taps

Mode №	Sample№	Current forming, мА/см^2	Time formations, hour.	Thickness the received mass, mm	Conductivity type
1	1-3	20	16	2,4	β-PbO_2
2	4-6	20	18	2,52	β-PbO_2
3	7-9	20	20	2,8	β-PbO_2

After 24 hours process of building was suspended as the demanded thickness of active mass was reached.

Therefore, we can conclude that the necessary thickness scalable active mass depends on the following factors:

- formation current sizes;
- formation time at the set density and temperature
- electrolyte.

The time of formation of the active mass is limited to the size of the cross section of the plate and shell. The process of forming the active composition continues as long as the thickness of the mass reaches the desired value of the electrode.

Optimization of process of formation of active mass of electrodes consists in minimization of time of technological process by selection of size of current of formation, composition of electrolyte, electrolyte temperature at which the necessary thickness of active mass is reached.

The main operation of technology of receiving a positive electrode is electrochemical oxidation of a lead current tap with obtaining porous active mass (generally β-modification - PbO_2).

Current taps place as a positive electrode in an electrolytic cell (the forming bath) as an auxiliary (negative) electrode apply plates from lead.

The electrolyte is sulfuric acid solution (density 1.09 g / sm^2) with additives chloric acid (10-12 g / l) and nitric acid (1.4-1.5 g / l).Process of electrolysis is carried out from a source of a direct current at the current density on a working electrode 100-200 a/m^2, tension on the electrolyzer of 3-5 V, temperature 20-25 ^{0}C. Time of process depends on necessary number of active mass (usual 16 - 24час.).

After the end of electrolysis working electrodes wash out distilled (or cleared) water (10-15 minutes) and dry in a drying cabinet at a temperature of 80-90 of ^{0}C within 30 minutes.

Thus there is a process of formation of a positive electrode of the lead-acid accumulator.

Feature of receiving a negative superficial electrode includes receiving a positive electrode on above to the described technology, and then the specified electrode place in the electrolyzer as a negative electrode where the role of counter electrode is carried out by a lead plate. As electrolyte 10% solution of sulfuric acid serve. Density of current of a polarity reversal of an electrode 100-200 A/m^2, temperature of electrolyte 20-25 ^0C, time of processing of 8-10 hours before achievement of potential of an electrode minus 0,2 V rather cadmic electrodes of comparison.

Then working electrodes are washed out by the distilled water and fall for 15-20 minutes to a bathtub for impregnation in solution of a dilator of Ba $(NO3)_2$, then electrodes dry at a temperature of 80-90 of ^0C within 30 minutes.

All experiments on receiving a negative electrode of superficial type are made within and in volume of experiments of earlier received positive electrodes as the technology of receiving a negative electrode contains all previous operations which are carried out when receiving a positive electrode.

Results and discussion

Researches showed that real option of a design is the electrode of superficial type as it is more technological, the new technology allows to raise specific power characteristics and to solve environmental problems of production of lead acid accumulators.

The lead alloying tellurium allows to receive structures of current taps less subject to corrosion that really can increase a resource of a positive electrode more than much. The structure of active mass received from the current taps alloyed by tellurium corresponds to modification β-PbO_2. Results of researches showed that the lead alloying tellurium allows to receive lead alloys with small structure of grain that does it steadier against corrosion at impact on it of sulfuric acid.

For production of Lead-Acid Accumulators of starter destination with the improved power characteristics it is expedient to use the new manufacturing techniques of electrodes of superficial type allowing to raise specific power characteristics, a resource and to solve the acute environmental problems inherent to classical technology.

Conclusions

1. For the first time in practice of production of the starter batteries it is offered to use superficial positive and negative electrodes of new type.
2. Feature of receiving a negative superficial electrode consists that initial material for its production is the shaped positive electrode.
3. Duration of a production cycle of production of a negative electrode, in comparison with a positive electrode, is increased by time of operation of a polarity reversal and introduction to the active mass of dilators.
4. The offered new production technology of superficial electrodes will allow to increase a resource of operation of the accumulator.

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