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Generalization And Assessment Of Results Of Researches On Creation Of The Starter Batteries With Superficial Electrodes

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Abstract
The article presents the results of researches on creationof a new type of starter battery. The conducted researches and results of tests, on definition of characteristics of experimental samples of electrodes and accumulators give the grounds to recommend to the industrial enterprises introduction of new technology in a mass production. The expected terms of development can make from 6 to 12 months.

Keywords: accumulator, electrode, superficial electrode, capacity, specific energy, self-discharge.

INTRODUCTION

Technical characteristics and cost of lead-acid accumulators in many respects depend on quality of electrodes and manufacturing techniques of current tapsfor them[1]. The basis of the modern mass production of electrodes of lead-acid starter batteries appointment is smearing technology.The tendency of further development of this technology, in relation to the starter batteries, is reduced to reduction of thickness of lattices for the purpose of increase of specific electric characteristics of accumulators. This way has the technological limit on lattice thickness.To reach significant results on further reduction of thickness of lattices carry out a lead alloying the metals giving to a lattice additional durability (antimony, calcium, tin, etc.).Lead-antimony alloys give the chance to accumulators to maintain deep categories that doesn't manage to be reached so far, applying lead-calcium alloys [2]. Along with optimization of design data, other direction of improvement provides introduction of additives to the active masses and electrolyte allowing to increase efficiency of absorption of oxygen and to create prerequisites for creation of the pressurized accumulator. For this purpose use low-antimonial and without antimonial alloys.Works on search of structure of the separator providing existence of a large gas pores in the direction from a positive electrode to a negative electrode [3] are conducted.The main material for a lattice of nonperforming lead acid accumulators is a lead-calcium-tin (Pb-Ca-Sn) alloy [3].It is noted that this alloy is subject to strong corrosion at high temperatures. The researches conducted in work [4] show that addition of tellurium can lead to improvement of mechanical durability and anticorrosive firmness of a current tap.Slices of pure lead and the lead alloys containing 0,1%, 0,06%, 0,1% of tellurium subjected to cold rolling and annealing within one hour at a temperature of 250 °C. Research of structures showed that alloys with the content of tellurium of 0,1% and 1% differ in grain size a little. Growth of grains in lead stops at the content of tellurium in number of 0,1%.

The development of new technologies to improve the mechanical properties of lead alloys discussed in work [5].The received results allow to formulate the following conclusions and offers:

- noticeable increase of mechanical properties of lead accumulator alloys can achieve by cleaning them from nonmetallic inclusions;
- effective cleaning of lead accumulator alloys can be carried out by short-term ultrasonic cavitational processing of liquid fusions;
- the experimental way of ultrasonic cavitational processing can be the basis for industrial technology of receiving a high-quality lead alloy.

Research of corrosion resistance of lattices of lead-acid accumulators is reflected in work [6] where it is shown that decrease in the maintenance of an antimonial component in an alloy leads to decrease in currents of oxidation of ions of iron, therefore, to deterioration of ionic conductivity of a corrosion layer.It is noted that with the low content of antimony it is necessary to enter the alloying additives (tin, cadmium) increasing corrosion resistance and increasing conductivity of a contact corrosion layer into lead alloys. It is shown that simple decrease in the content of antimony leads to decrease not only conductivity of a corrosion layer, but also to deterioration of mechanical, foundry and corrosion characteristics.The high content of an antimonial component promotes significant increase in speed of gas emission as antimony has a low overstrain of release of hydrogen that limits service life of accumulators.

The technology of receiving electrodes of superficial type of the necessary thickness in relation to traction and stationary accumulators is considered in work [7]. The decision is reached by compensation of forces of internal tension at electrochemical formation of active weight by means of an elastic-stretchable armor.

Researches of corrosion resistance of lattices of lead-acid accumulators with composite covering [8] are known. In this work the assumption was made that the increased corrosion resistance of a lattice with a composite covering will be provided not only creation of an external corrosion-resistant

layer, but also more uniform structure of a surface of lead material.

The theory of the lead accumulator can't be considered completeas evidenced by the publication of foreign and domestic authors.Despite more than century history of creation of lead-acid accumulators also a number of the questions connected as their production, and with operation isn't solved.Unresolved are environmental problems caused with preparation of paste from lead powder on the basis of the sulfuric acid which is the main source of pollution of floor spaces and adjacent territories.

Now the leading foreign and domestic-owned firms conduct the researches directed on search of the progressive, constructive and alternative technological decisions allowing to improve considerably power characteristics of lead-acid accumulators in general and the starter, in particular, by addition of barium, tellurium and other metals.

The analysis of references shows that the majority of attempts of improvement of current tapsare reduced to rational selection of lead-tin-calcium alloys for positive and negative current taps, thus technological process remains powder.

The purpose of this work is the analysis of results of the conducted researches on creation of the superficial electrodes of new type alloyed by tellurium, definition of their electric characteristics and characteristics of the accumulators manufactured on their basis.

1. **Task formulation**

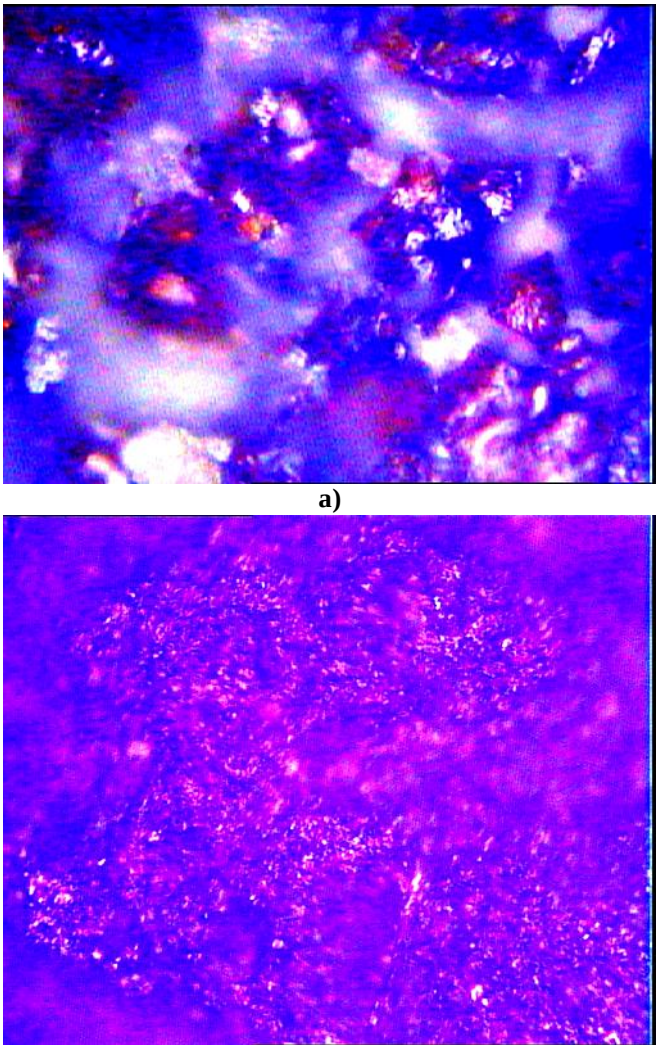
To improve the electrical characteristics of the specific starter batteries need alternative technologies, allowing to increase the specific energy characteristics.The task consists in finding new technological solutions for production of starter batteries which can replace classical smearing technology.

2. Solution

Authors of this work offered the alternative technology capable to replace the existing smearing technology. It is technology of superficial electrodes. Its main similarity to technology of superficial electrodes Plante, is obtaining active weight by galvanic building in the electrolyzer. Difference and advantage of new technology before technology Plante consists in opportunity to receive the necessary thickness of the increased active weight by regulation of the modes of formation.

The new technology allows to make both positive, and negative superficial electrodes. The advantage of this technology consists also that it considerably reduces the production and capital expenditure connected with development and a mass production of accumulators, considerably reduces cost of production of starter batteries. The new technology easy to implement,as borrows many technological operations of smearing technology, in it isn't harmful to human health processes.

Authors of this work conducted researches and practical approbation of new manufacturing techniques of electrodes from the lead alloyed by tellurium. The main requirement to the alloying materials consists that they shouldn't worsen conductivity of a lead basis of a current tapboth its corrosion and mechanical properties. In the conducted researches as the alloying material tellurium in proportions of 0,05 and 0,1% of weight was used. The structure of alloys was observed with application of a microscope of SEM with a confocal Raman and fluorescent spectrometer of Omega Scope, (figure 1).



a)

b)

Figure 1 The structure of the lead: a- pure lead, b - alloyed by tellurium of 0,05% of weight.

It can be seen that the structure of the alloyed lead (fig. 1b) is finely dispersed compared with the structure of pure lead (1a).Such structure possesses higher hardness, durability and the increased anticorrosive ability [2] as the fine-grained structure and thin intergrain layers, close penetration of corrosion into inside layers of metal.

3. Tests of electrodes

For receiving comparative results of test were carried out on ten cells from usual lead and ten cells of the current tapsalloyed by tellurium in a proportion of 0,05% of weight.

3.1 Technique of experiment and results

For determination of corrosion resistance current tapswere exposed to anode polarization in a standard cell where as negative counter electrodes the sheet of pure lead was used.Density of solution of sulfuric acid made 1,27 g/cm^3. The tested cells were located in the thermostat temperature in which was established +60 °C. Current of polarization was established at the rate of 20 mA/cm^2 the areas of an electrode from 2 parties.

Duration of time of polarization made 20 hours. After that current tapswere dried up andfrom themmechanically removed loose layer- the product of the anode corrosion PbO2.By weighing on analytical scales comparison of sizes of the remained mass of the alloyed and pure current tapsfrom lead was carried out. Results of tests are given in table 1.

Table 1-Results of corrosion tests

Initial weight of electrodes, g	P_1- weight before carrying outtests, g	P2-weight after carrying out tests, g	Loss of weight from corrosion (P_1 - P_2)
The average weight of 10 samples from pure lead	507	489	18
The average weight of 10 samples of 0,05% of weight alloyed by tellurium	510	508,5	1,5

As seen fromthe table corrosion properties of the lead basis alloyed by tellurium are 12 times higher, than is exemplary from pure lead.

The carried-out mechanical and electric tests showed that durability (hardness) of the alloyed conducting basis is 25-30% higher, than bases from pure lead. The received results allow to predict substantial increase of a resource of a positive electrode of the accumulator.

Conductivity of the current tapbasis alloyed by tellurium in a proportion of 0,05% of weight, practically didn't change.

Experiment on increase of active weight and determination of size of specific capacity of electrodes was separately made. For these purposes were grouped from the alloyed cell current tapsin number of 5 pieces and on them by a galvanic way active weight on new technology was increased.Electrolysis modes: density of electrolyte is 1,05 g/cm^3, current 20 mA/cm^2 from both parties, time of 20 hours, temperature of electrolyte is 25 °C. After carrying out electrolysis electrodes were dried at a temperature of +80 °C within 30 minutes. Then from them active weight mechanically was removed and separate weighing of a current tapand active weight was made.

Specific capacity of an electrode was determined by a formula:

C_{sp}= m·[KiM]·1000/4,46 (m_{am} + m_{ct}) [Vt·h/kg],

where: m_{am} - the weight of active weight;

KiM- utilization ratio active mass,%;

m_{ct} – the remained current tapweight.

Estimated specific capacity of the electrode draw up

C_{sp}=0, 140·0,5·1000/4,46·(0,140+0,360) = 31,4 A·h/kg

E_{sp} =31,4·2/ 0,5 = 125,6 Vt· h/kg

The electrodes made of the alloyed lead passed tests by determination of energyparameters.Cells from electrodes which were located in electrolyte with a density of 127 g/cm^3 were for this purpose created, were loaded with current 2,5A at a voltage of 2,3 volts then were exposed to 20 hour category. 10 such cycles were carried out. The following power characteristics of electrodes are received:

- capacity of an electrode 25 A·h;
- specific capacity on weight 50 A·h/kg;
- specific capacity on volume 125A·h/l;
- specific energy on the mass of 32,8 Vt·h/kg;
- self-discharge of electrodes, % per day 0,14

Tests were carried out at a temperature of 26-28 °C.

4. Tests of experimental samples of accumulators

The tests of 2 samples of experimental accumulators collected according to the scheme 3 of positive and 4 negative electrodes were carried out.Modes tests were planned on the basis of the estimated capacity of 75 A · h. Confirmed following the calculated parameters:

- the accumulator capacity determined by 20 hour mode of the category makes 3,75·20=75 A·h;
- the accumulator capacity determined by 10 hour mode of the category makes 7,5·8=60 A·h.

Other parameters of the accumulator for comparison with foreign and domestic producers are specified in table 2.

Table 2 - Comparison of parameters of experimental samples of accumulators.

Specifications	Serial products									Experimentalsamples
	Producer (country)									SWGU(Russia) SWGU (Russia)
	BOSCH(Germany)	VARTA(German)	TOPLA(Slovenia)	MUTLU (Turkey)	MORATTI (Slovenia)	WESTA(Ukraine)	TORNADO(Russia)	TITAN(Russia)	Tyumen (Russia)	
Capacitance, A·h	74	74	75	75	75	74	77	75	75	75

Specific capacity: - A·h/kg - A·h/l	4,257,95	4,237,95	4,168,2	3,898,06	3,888,06	4,117,95	3,748,27	3,958,06	3,757,35	12,937,5
The specific eneqiya: - Vt·h/kg - Vt·h/l	35,766,84	35,52 66,84	35 67,74	32,64 67,74	34,05 67,74	34,5 66,84	31,39 66,84	33,15 67,74	31,561,76	32,875,0
Service life, cycles	1000	600-1000	noda ta	noda ta	nodat a	noda ta	nodat a	nod ata	800-1000	More 1500
Self-discharge, % day	nodat a	0,1-0,2	noda ta	noda ta	nodat a	noda ta	nodat a	nod ata	0,1-0,7	0,1-0,14
Support ability	Nonp erfor ming	Low-serve d	Low-serve d	Non perf ormi ng	Nonp erfor ming	Low-serve d	Low-serve d	Low-serve d	Low-serve d	Low-serve d
Category current: - the nominal - the maximum	nodat anod ata	0,1-0,2C 3-5C	noda tano data	noda tano data	nodat anoda ta	noda tano data	nodat anoda ta	nod atan odat a	0,1-0,2C noda ta	0,1-0,2C nodat a

5. Results and discussion

The electrodes alloyed by tellurium.

The important characteristic of the alloyed electrodes is their increased corrosion resistance and mechanical durability in comparison with similar characteristics of electrodes from pure lead. The researches of structure of lead conducted by us allow to make the conclusion that the basis of a contact layer has the increased conductivity, and it positively affects characteristics of a self-discharge.

Experiments on accumulation of active mass of electrodes showed the following results. Speed of accumulation of mass of a positive electrode made the size of 1,7-1,9 g/hour at the density of electrolyte of 1,27 g/cm of 3, current 20 ¼Ç/mm2, temperature of electrolyte of 25 °C. The negative electrode contains the same size of active weight as well as a positive electrode as it is made of a positive electrode by its polarity reversal. Its additional formation minus 0,2 B rather cadmic electrodes of comparison is made in the electrolyzer within 10-12 hours to potential. Energy characteristics of superficial electrodes of new type allow to create of the starter batteries of sufficient capacity and wide range of application.

Accumulators with superficial electrodes.

Tests of accumulators of new type and comparison of power indicators with serial samples confirmed real possibility of replacement of classical smearing technology by new technology of superficial electrodes.

The received results of researches in the form of the new production technology of superficial electrodes can be used in production of all types of accumulators of lead-acid system.

Conclusion

1. The new production technology of the starter batteries with superficial positive and negative electrodes is approved.
2. Conditions for the solution of the main environmental problems of production as the new technology doesn't contain any harmful processesare created.As a result treatment facilities become simpler, the production climate in working shops is revitalized, the adjacent territory doesn't become soiled.
3. Introduction of new technology reduces duration of a production cycle of production of accumulators by 30-40% and reduces their prime cost.
4. The design of lead-acid accumulators in the pressurized execution as conductor cables of superficial electrodes don't contain the impurity worsening conductivity becomes simpler.
5. The new technology of superficial electrodes is available to development at any accumulator plant.

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