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Features Of Technology Of Superficial Electrodes For The Appointment Starterny Lead-Acid Accumulators

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Abstract
Researches on creation of the new production technology of lead-acid accumulators of starting appointment are conducted. For this purpose, current tapsmade from lead, tellurium doped, produced samples electrode surface type.The structure of current tapsis investigated, their hardness, durability is determined. Power characteristics and corrosion properties of electrodes are investigated. The metallographic structure of active weight is given, its phase structure is defined.The technology of accumulation of active weight on the current tapsalloyed by tellurium is fulfilled. During research it is established that the new technology allows to raise specific power characteristics of accumulators when using electrodes of superficial type, to solve environmental problems by production of lead-acid accumulators, allows to gain considerable economic effect at introduction of technology of superficial electrodes.

Keywords: lead-acid accumulator, superficial electrodes, active weight, current tap, corrosion.

Introduction

The proceeding demand for the lead-acid accumulators of starterny appointment (LAASA) and increase of requirements to their power characteristics dictate need of their further improvement.The classical smearingproduction technology of electrodes used at production of lead-acid accumulators practically reached a threshold of the technological limit at a thickness of conductor cables of 0,8-1,0 mm. Therefore search of new constructive decisions and technologies for their further improvement is actual.

One of the directions of improvement is creation of the new technology considering features of a design the starter of accumulators: big starting currents, high specific volume capacity of the accumulator, resource, etc. For providing big starting currents it is necessary to have rather big area of plates.To receive the big area of plates of electrodes perhaps due to their quantity, therefore, at the set tank volume they have to be thinner, have the sufficient constructive durability and high corrosion resistance.

One of options of increase of durability and corrosion resistance of electrodes is the alloying of plates of a current tap tellurium.

For definition of possibility of use of thin lead plates when receiving the superficial electrodes of new type alloyed by tellurium pilot studies on corrosion resistance, conductivity, durability and hardness were conducted.

Description of research

In work [1] electrochemical experiments on research of characteristics of lattices of the current tapsalloyed by tellurium in proportions from 0,01-1,0% of weight were made. Experiments were directed on increase in hardness and firmness against corrosion of lattices from Pb-Te of alloys in solution of sulfuric acid.These researches are conducted on the electrodes made on classical smearing technology. Results of researches show that introduction of tellurium to lead lattices of current tapsleads to crushing of grain of current taps, increase of their corrosion resistance and acceleration of reaction of release of oxygen for binary alloys of Pb-Te, thus the technology of obtaining active weight remains smearing [1].It is shown that introduction of Te to lead plates allows to reduce permeable corrosion of positive lattices and, as a result, to increase battery service life.

The purpose of the researches conducted by us is creation of corrosion-resistant superficial electrodes from the plates of lead alloyed by tellurium, definition of structure of active weight and the main power characteristics of electrodes for creation of the accumulator of new type. Experiments were for this purpose made on:

- to determination of percentage of the tellurium in an alloy providing its mechanical durability and sufficient corrosion resistance;
- determination of conductivity of the electrodes alloyed by tellurium depending on percentage of tellurium;
- to working off of technological process of accumulation of active mass of superficial electrodes of new type;
- to definition of power characteristics of superficial electrodes.

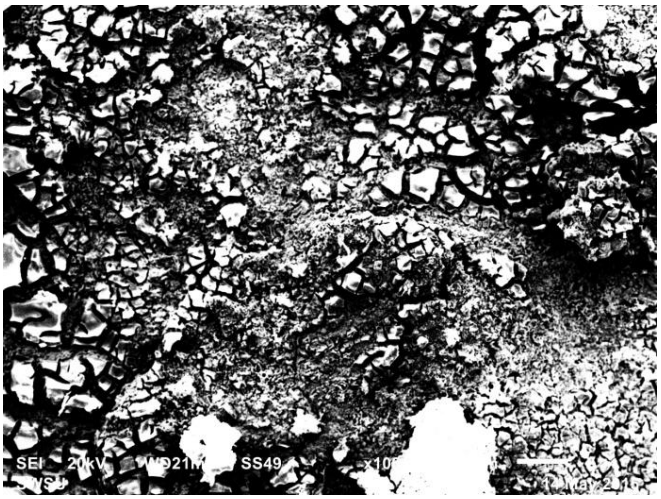
Great practical interest represents application of Pb-Te of binary alloys for positive superficial electrodes of new type. Distinctive feature of obtaining active mass of superficial electrodes of new type is the technology of accumulation of active weight in the galvanic way by oxidation of a lead basis of a current tap in solution of sulfuric acid. [2].

Researches of structure of current taps and active weight depending on percentage of tellurium in Pb-Te alloy.

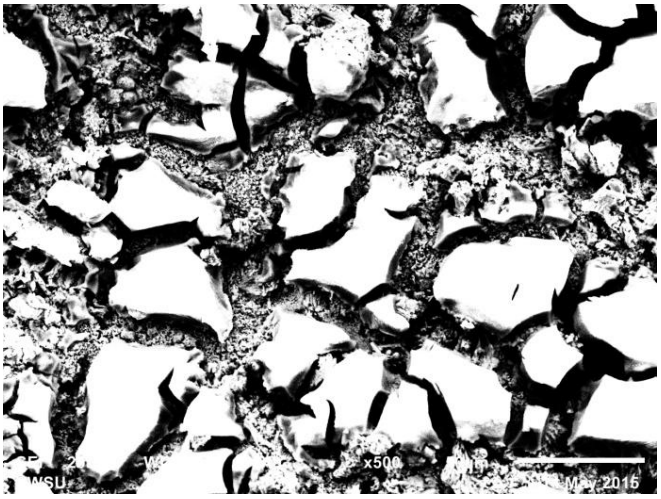
The technology of superficial electrodes of new type created by us earlier for stationary and traction accumulators [3] is applicable and for the starter batteries regarding formation of active weight. Differences in a design consist that for

receiving big starting currents starter electrodes have to have the sufficient area. It can be provided due to bigger quantity of plates, so for the fixed tank volume they have to be thinner.From here requirements to thickness of plates and their mechanical durability follow. Thus thickness of a plate (section) has to provide formation of necessary thickness of the active weight which is required for receiving current of sufficient size, and its basis current tap, has to pass sufficient currents.

Initial material of researches were Pb-Te binary alloys from mix of pure lead (99,99mas. %) and tellurium (99,99mas. %) two proportions: 0,05 and 0,1mas. %. Alloy Te of which current taps were made. For research samples of the following sizes and a form were made: rectangular thickness of 2,0 mm, the sizes of 8,0x170 mm in number of 10 pieces. On the made samples active weight was increased. The structure of metallographic samples of active weight is given in figures 1, 2.

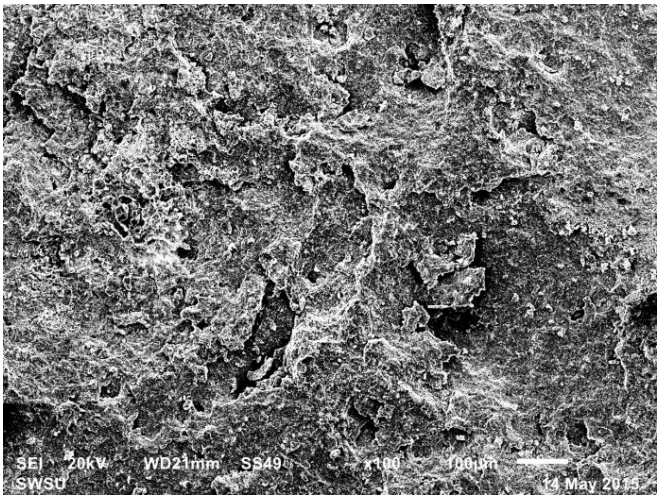


a)



b)

Fig. 1 - Structure of active weight without tellurium with increase: a) 100x; b) 500x



a)

b)

Fig. 2 - Structure of active weight with the content of tellurium Pb-Te-0.05мас. % with increase: a) 100x; b) 500x

It is possible to note that the structure of active weight received on an electrode from pure lead has obviously not uniform structure. The active weight received on an electrode from Rb-Te's alloys 0,05 and 0,1mas. the % has high-porous and with a big area a working surface.

Tests for durability

The plates of thickness of 1,5 mm alloyed by tellurium 0,05mas were subjected to tests. % - 5 pieces, plates alloyed by tellurium 0,1mas. % - 5 pieces, and plates from pure lead of 5 pieces. One end of a plate was fixed at distance of 20 mm from edge, and by the second end freights of various size were suspended. The size of a deflection was fixed. The scheme of test is submitted in figure 3.

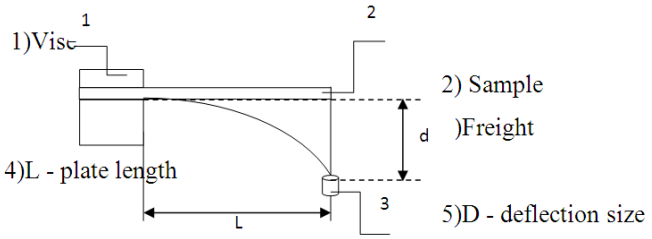


Fig. 3 – Scheme of test for durability Average values of these measurements are given in table 1.

Table 1 - Tests of plates for durability

Sample	Thickness, mm	Cargoweight, g		Incorrectweight, g	
		10	20	50	70
		Deflectionsize(d), mm			
Pb		75	122	168	175
Pb-0,05weight%Te		5	13	130	155
Pb-0,1weight%Te		6	10	123	150

It is noted that the plates alloyed by tellurium have the smaller size of a deflection that testifies to increase in their durability under the influence of a tellurium additive.

Tests for hardness

Tests were carried out on 9 plates of thickness of 1,5 mm. Hardness was defined by Vikkers's method by means of the PMT-3 microhardness gage. Data of tests are provided in table 2.

Table 2 – Results of test of plates for hardness

Plates	Pb	Pb-0,05 weight%Te	Pb-0,1 weight%Te
Thickness, mm	1,5	1,5	1,5
Average value of hardness on five measurements, kgc/mm^2	3.95	5.15	5.20

From data of the table it is visible that the hardness of the plates alloyed by tellurium for 30% exceeds the hardness of plates from pure lead.

Tests for corrosion resistance

Nine plates of positive electrodes thickness 2mm from which cells were collected were subjected to tests. As negative electrodes the plates from lead placed in solution of sulfuric acid in the distilled water were used. Density of solution is 1,27 g/cm3.

For the purpose of reduction of time of tests of a cell were warmed up in the thermostat up to the temperature of +60 °C within 20 days at the density of direct current of 20 мА on cm2. All examinees of a cell were connected consistently and connected to one source of a direct current of 1,3 V. After 20 days the corrosion layer of PbO2 was removed and after drying of plates their weighing on analytical scales was made. Results of weighings are given in table 3.

Table 3 – Results of test of plates for corrosion resistance

Пластины	Pb	Pb-0,05weight%Te	Pb-0,1weight%Te
Thickness, mm	2,0	2,0	2,0
Initialweight, g	10,31	10,22	10,15
Weight after impact of corrosion, g	9,79	10,18	10,12
Losses of weight, %	5	0,39	0,30

Conclusion

Introduction of tellurium to structure of plates allows to increase their corrosion resistance more than by 10 times, and at the expense of it to make electrodes of superficial type of current taps of smaller section that gives the chance to improve specific power characteristics of the lead-acid accumulator.

Research of conductivity of lead plates

Nine plates 2 mm thick everyone were exposed to research. Measurements of conductivity were taken by means of the GW Instek LCR-7821 device. Results of measurements are given in table 4.

Table 4 - Results of measurement of conductivity of plates

Пластины	Pb	Pb-0,05 % weight Te	Pb-0,1 % weightTe
Thickness, mm	2.0	2.0	2.0
Average value of conductivity on three measurements, 1/Om	105,637	105,518	105,621

From the presented results it is visible that conductivity of plates of the % of weight alloyed by tellurium 0,05 and 1,0 are almost comparable with conductivity of plates from pure lead that gives the chance to keep an accumulator self-discharge at the level of 0,1-0,15% per day.

Manufacturing techniques of electrodes of superficial type

In producing of accumulatorsnow for production of current tapstwo alloys are used: lead and antimony and lead-calcium in which antimony and calcium provide, first of all, mechanical properties of an alloy as pure lead is too soft and

fragile [4]. New manufacturing techniques of electrodes are considered in works [5-7]. In these works the emphasis is placed on decrease in prime cost, increase in productivity, search of an optimum ratio of antimony and calcium in alloys by production of lattices of current taps.In a number of parameters minor improvements of indicators of accumulators are noted. In essence this technology remains smearing with all problems inherent to it. In works [8-9] the researches directed on increase of productivity of production and unification of current tapsare conducted.Such technology allows to achieve some reduction of a cycle of formation of positive electrodes, increase in capacity of accumulators, reduction of dispersion of density of electrolyte and dispersion of electric characteristics of accumulators. Thus basic technological processes remain former, the environmental problems of production connected with lead processing aren't solved.

The new technology offered by us allows to receive a number of valuable properties of electrodes by introduction of tellurium to composition of lead: durability, hardness, corrosion resistance that allows to raise considerably specific power and resource characteristics.

The manufacturing techniques of superficial electrodes of new type include the following main technological operations:

- cutting down on a stamp of preparations of current taps from the lead tape alloyed by tellurium;
- clothing of an armor on preparations;
- preparation of forming electrolyte;
- Putting blanks in electrolytic cells;
- connection to a source of a direct current;
- accumulation of active mass of electrodes in the electrochemical way,
- control of thickness of active weight.

Working off of technology of accumulation of active mass of a positive electrode was made in the following sequence: the studied electrodes, and to negative - usual rectangular plates from lead, by the sizes close to the sizes of the studied current taps which carried out a role of counter electrodes were connected to a positive pole of a source.Density of current was established in the fixed values: 10, 20, 30 mA/sm^2 : in the first, second and third electrolytic cell respectively. Concentration of electrolyte made 1,08-1,09 g/sm^3. Potential of a source of a direct current was supported at the level of 3,5 V. Thecurrent of formation was established by size 10, 20 and 30 mA/sm^2. It was controlled: thickness and uniformity of the increased weight on all plane of conductor cables, process time. Results of researches are given in table 5.

Table 5 - Results of formation of active mass of a positive electrode

Current tap№	Formationcurrent, mA/sm^2	Thickness of active weight, mm	Formationtime, hour
1	10	4	32
2	20	4	18
3	30	4	10

Technology of receiving a negative electrode: the first stage of technology completely coincides with the manufacturing techniques of a positive electrode described above. Further the electrode became impregnated in $Ba(NO_3)_2$solution, dried without washing, then became impregnated in H_2SO4 solution with g/sm^3 d=1,085-1,090 density with additives of $HClO_4$ and HNO_3. After easy washing in the distilled water and drying the electrode was connected with a polarity reversal to a source of a direct current and its formation in the electrolytic by current 8A within 10 hours to potential minus 0,2 B rather cadmic electrodes of comparison was made.After easy washing in the distilled water its drying and impregnation in dilator solution like BNF was made. The ready negative electrode after drying can be stored or arrive on assembly of semi-blocks.

Upon termination of process of formation by means of an electronic microscope of JEOL 6610LV the structure of active weight was investigated. The size of a time makes 1-16 microns, porosity of active weight is equal 45-50%. The structure of active weight generally corresponds to PbO2 - β modifications.

Conclusion: Necessary thickness of active weight can be formed by regulation of duration of time of process.

Results and their discussion

Researches showed, the lead alloying tellurium gives the chance:

- to receive structures of current taps of small granularity, with thinner layers between grains that allows at the maintenance of Te of 0,05 - 0,1% of weight in Pb-Te an alloy to give durability to plates, and also to receive structures of current taps less subject to corrosion that really increases a resource of electrodes more than by 10 times;
- to form the active mass of the necessary thickness on a conductor cable the alloyed tellurium by change of current and time of formation, thereby there is a possibility of a variation accumulator capacity size;
- the proposed technological solutions allow to increase considerably specific power characteristics and a resource of the accumulator in general.

Conclusions

For production of lead-acid accumulators of starter appointment with the improved power characteristics it is expedient to use the new manufacturing techniques of electrodes of superficial type allowing to lower considerably production costs of production, to raise specific power characteristics of accumulators and to solve environmental problems the productions peculiar to classical smearing technology.

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