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INFLUENCE OF THE COOLING METHOD ON STRUCTURE FORMATION OF PB-0.1%CA-0.3%SN BATTERY ALLOY

Having some number of advantages, nowadays lead-acid batteries are occupying a significant partition of secondary power systems market, and their improvement mainly occurs as a result of polishing of batteries' specific characteristics and materials consumption reducing. At the same time some special attention is given to operating characteristics and properties of current collectors, as to an important component whose quality largely determines the durability of batteries. In present work the investigations of physicochemical properties and structure of Pb-0.1%Ca-0.3%Sn alloy specimens been conducted. The samples were obtained in three different ways – by using of two industrial methods (casting and rolling) as well as an experimental method which is based on quenching from a liquid state. The investigations results showed some significant differences in structure and properties of quenched strips and its give a possibility to urge the necessity of further researches of tempered strips during exploitation.

Keywords: lead-acid battery, current collector, lead alloy, quenching from liquid state, structure, mechanical properties, corrosion properties.

Володіючи низкою переваг свинцево-кислотні акумуляторні батареї на сьогоднішній день займають суттєву частину ринку вторинних джерел струму, а їх вдосконалення переважно йде шляхом підвищення питомих характеристик батарей та зменшення матеріалоємності виробництва. Особлива увага при цьому приділяється експлуатаційним характеристикам та властивостям струмовідводів, як важливого компоненту, якість котрого в значній мірі визначає довговічність акумуляторних батарей. В представленій роботі проведено дослідження фізико-хімічних властивостей та структури заготовок сплаву Pb-0.1%Ca-0.3%Sn для виробництва струмовідводів. Зразки було отримано трьома різними способами – двома промисловими (лиття та прокатки), а також експериментальним методом, що ґрунтується на гартуванні з рідкого стану. Результати дослідження показали суттєві відмінності у структурі та властивостях загартованих з рідини стрічок і дають підставу говорити про необхідність проведення подальших досліджень їх властивостей у процесі експлуатації.

Ключові слова: свинцево-кислотний акумулятор, струмовідвод, свинцевий сплав, гарт з рідкого стану, механічні властивості, корозійні властивості.

Обладая рядом преимуществ, свинцово-кислотные аккумуляторные батареи на сегодняшний день занимают значительную часть рынка вторичных источников тока, а их усовершенствование в основном идет по пути повышения удельных характеристик батарей и снижения материалоемкости производства. Особое внимание при этом уделяется эксплуатационным характеристикам и свойствам токоотводов, как важного компонента, качество которого во многом определяет долговечность аккумуляторных батарей. В представленной работе проведены исследования физико-химических свойств и структуры заготовок сплава Pb-0.1%Ca-0.3%Sn для производства токоотводов. Образцы были получены с использованием трех различных способов – двух промышленных (литья и прокатки), а также экспериментального метода, основанного на закалке из жидкого состояния. Результаты исследований показали существенные отличия в структуре и свойствах жидкозакаленных лент и позволяют говорить о необходимости проведения дальнейших исследований их свойств в процессе эксплуатации.

Ключевые слова: свинцево-кислотний акумулятор, струмовідвод, свинцевий сплав, гарт з рідкого стану, механічні властивості, корозійні властивості.

1. Introduction

Nowadays lead-acid batteries (LB) are occupying the leading positions among known chemical current sources for automotive and railway transport, systems and devices of autonomous power supply systems. At present stage the further development of LB production technology is related with the improvement of batteries' specific energy capacity (ratio of capacity to the weight of the battery), their technical characteristics and durability. Thereby the main focus is related to the production materials capacity, to the usage of new manufacturing methods of batteries' components and to the improvement of production technologies of the whole battery.

One of the main components of LB is a battery current collector (grid), which serves as the current collector in reactions of charge / discharge, as well as the active mass carrier. During battery's serve the grid experiences some alternating loads, which occurs as a result of active mass specific volume change [1], as well as mechanical impacts – vibrations and hits during automotive duty. In this regard, one of the main requirements to the grid is high mechanical durability.

A well-known and effective way to increase the durability of lead alloys is the use of the quenching from the liquid state (QLS) method during the thin strips production for grids manufacturing [2]. Providing of the QLS allows to improve tensile strength and to boost the physicochemical properties of strips made of the positive grid alloy, containing (wt. %): Pb-0.05% Ca-1.1% Sn in comparison with industrial rolled strip of the same chemical composition. In turn, determination of the impact of the QLS on physicochemical and strength properties of the negative grid alloy Pb-0.1%Ca-0.3%Sn has research and practical interest.

2. Purpose

Determine the effect of quenching from the liquid state on the structure and physicochemical properties of the Pb-0.1%Ca-0.3%Sn alloy for negative current collectors of the lead-acid batteries.

3. Experiment

The samples of negative current collector alloy (wt. %): Pb-0.1%Ca-0.3%Sn, obtained according to three methods: industrial casting, rolling and experimental method of QLS have been investigated.

Cast samples were prepared using the split cast mold. The temperature was controlled in the range of 150 ± 5°C (mold) and 450 ± 2°C (melt) that corresponds to the industrial casting temperature conditions of crystallization in billet plants (casting machines). Samples of the rolled strips of 0.7 mm thick were prepared on industrial machine with a standard deformation ratio of 94%.

The QLS strips were produced by jet melt crystallization with initial temperature of 425°C between oppositely rotating at 120 rpm steel rolls with a gap of 0.6 mm. The cooling rate was evaluated in amount of $\sim 3.8 \cdot 10^5$ K/s according to [3].

Tensile tests of cast and rolled samples were conducted in accordance with GOST 1497-84 and GOST 11701-84 on tensile machine P-0.5. Mechanical tests of QLS strips were made on laboratory's tensile testing machine according to the requirements of GOST 11701-84.

The microhardness measurements (H_v) were carried out in accordance with the requirements of GOST 9450-76 on microhardness tester PMT-3 with a load of 20 g. Before measuring the samples surface being chemically polished to remove oxides and to obtain sharp prints. The sample preparation for structure studies was carried out by chemical polishing and etching in solutions of acetic acid with different proportions of hydrogen peroxide. Photographs of the microstructure were obtained by using an optical microscope with NEOPHOT-21 with mounted digital camera. Determination of grain size in the alloy structure was carried out by cross-sections method according to the GOST 5639-82. X-ray diffraction (XRD) was carried out on a diffractometer DRON-2.0 in monochromatic copper radiation.

The corrosion resistance of the alloys was determined by the mass loss of alloy samples after their oxidation in potentiostatic conditions and removing of surface oxide layer [4]. Tests were performed using a potentiostat P-5848. Test samples in the form of plates 2x1,5 cm were kept at a potential of 2.15 V in three-electrode cell in a 4.8M solution of sulfuric acid at 40°C. The auxiliary electrode was platinum, reference electrode was hydrogen, connected to the cell through the Luggin capillary. All potentials are given relatively to this electrode. Times of anodic polarization of electrodes were 10, 30, 60, 180 min. Such parameters of the corrosion tests are even more hard compared to the operating conditions at real battery electrodes while the method provides some relative rapidity of the corrosion test.

4. Results and discussions

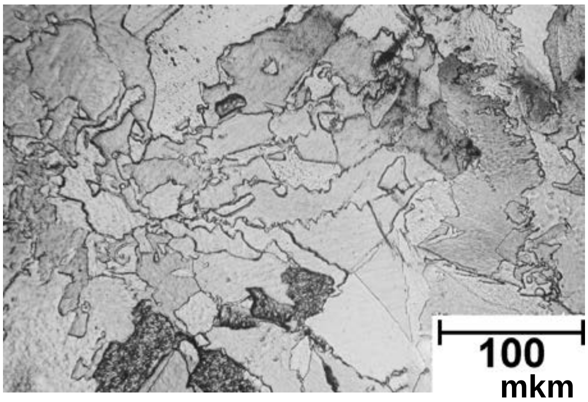
Results of mechanical tests of Pb-0.1%Ca-0.3%Sn alloy samples are presented in Table 1. They show that using the different methods of species production from the negative grid alloy allows the tensile strength increase up to 45 MPa and elongation about 24% on the day of receipt.

Table 1

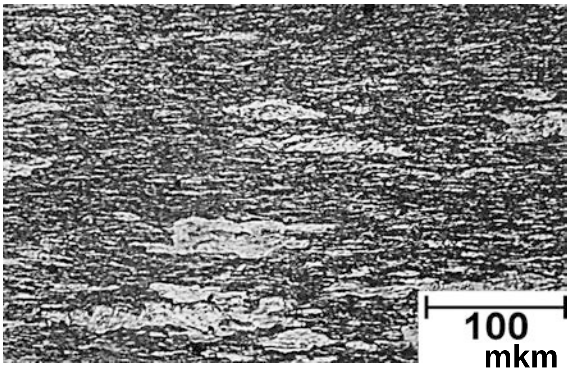
The results of tensile test of alloy Pb-0.1%Ca-0.3%Sn samples

Sample	Ultimate tensile strength (*UTS*), MPA	Elongation (*E*),%
Cast Alloy	35,3 ± 0,3	24,4 ± 0,5
Rolled strip	45,4 ± 0,3	17,4 ± 0,5
QLS strip	44,2 ± 0,5	20,8 ± 0,5

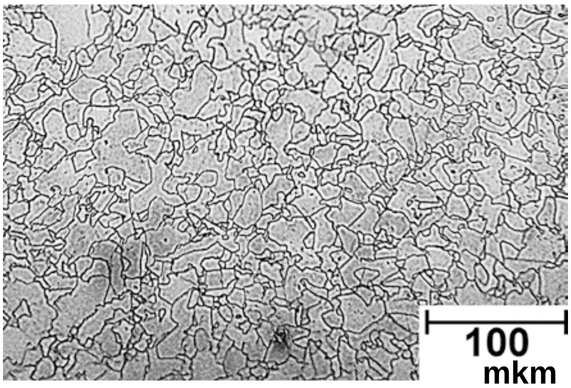
It was noted earlier [5] that the Pb-0.1%Ca-0.3%Sn alloy is characterized by significant sensitivity to changes in temperature conditions of crystallization. In the mold temperature range 60 ÷ 170°C the tensile strength may vary from 45 to 33 MPa, which is associated with the formation of the structure, namely with the precipitation of primary phase of Pb_3Ca during the crystallization, which probably acts as a structure modifier providing nucleation centers for the rest of the liquid [6]. It should be noted that as a result rugged “tooth” structure [7] with different grain size scale in cast alloys (Fig. 1 *a)* is formed. Rolling leads to the structure orientation with a possible grains crushing that is evidenced by a significant difference in average grain size (d_g) in cast and rolled samples (Fig. 1 *a*, *b)*. Noteworthy is the fact that due to changes in temperature conditions of crystallization of cast samples according to [5] it is possible to obtain values of the tensile strength of up to 44 MPa, comparable with test results of the rolled strip, i.e. attained level of internal stresses in the alloy when casting may be so high that the subsequent rolling does not lead to significant improvement in strength properties. As a result of grains crushing and the accumulation of a critical level of structure tension it can assume some strip softening, as shown in an example of influence of the degree of deformation on the strip’s tensile strength [8].



a) Cast alloy, d_g = 77.9±10.9 mkm



b) Rolled strip, d_g =10.6±1.2 mkm



c) QLS strip**,** d_g = 12.4±2.2 mkm

Fig. 1 - The microstructure of the Pb-0.1%Ca-0.3%Sn alloy samples.

Structure of the QLS strips (Fig.1*c)* is different on comparative uniformity: lack of rugged “tooth” structure and texture of rolling. Noteworthy is that for the casted Pb-0.1%Ca-0.3%Sn alloy the decrease in temperature of the mold and a corresponding increase in the cooling rate leads to a significant strengthening and refinement of the grain size as a result of precipitation of modifying phase of Pb_3Ca [9]. Thus the QLS strips with a smaller grain size in the structure differ on the same level of tensile strength. It allows us make an assumption about the differences of phase and structure formations of quenched from the liquid strips during crystallization. Probably as a result of crystallization with high cooling rate during quenching (~$3.8 \cdot 10^5$ K/s) the stage of precipitation of modification phase Pb_3Ca from liquid significantly decelerates and results a greater initial substitutional supersaturation of lead-based solid solution with calcium whose atomic radius (0.197 nm) is larger than lead's (0.175 nm). This may be also indicated with XRD-data: the period of the crystal lattice of a solid solution of lead-based alloy tempered from the liquid state is a = 0.4954 nm (in the rolled sample this period does not exceed 0.4950 nm). At the same time, the level of microstresses Δa/a and the dislocation density of the rolled strip on average is 6% and 25%, respectively, higher than in the QLS strip. It should be noted that melt crystallization has features in the formation of crystallization texture compared with rolling texture: unlike rolling texture direction [100] with the QLS primary crystallization texture is [111] direction. About the differences between structure formations mechanism also suggests the existence of the QLS strip equiaxed structure unlike the "toothed" structure of cast alloy Pb-0.1%Ca-0.3%Sn (Fig.1).

The given fact that the alloys of Pb-Ca-Sn are aging [10], and for the Pb-0.1%Ca-0.3%Sn alloy hardening is associated with the release of Pb_3Ca phase, aging of supersaturated QLS strips likely must be accompanied with a more intense increase in strength properties. Hopping tendency of QLS strips hardening was previously observed in the samples of the Pb-0.05%Ca-1.1%Sn alloy for the positive current collector [11]. It is noteworthy that QLS strips for the negative collector Pb-0.1%Ca-0.3%Sn (QLS strip (-)) have higher initial strength properties than QLS strips of the positive grid alloy (QLS strip (+)) (Table 2). At the same time the QLS strip (+) is characterized by higher plastic properties and elongation parameters.

Table 2

Mechanical properties of QLS strips in the day of receipt

Sample	Ultimate tensile strength (*UTS*), MPa	Elongation (*E*), %	Microhardness (H_w), MPa
QLS strip (-) Pb-0.1%Ca-0.3%Sn	42.1 ± 0.4	20.8 ± 0.5	106.8 ± 1.5
QLS strip (+) Pb-0.05%Ca-1.1%Sn	18.6 ± 0.3	25.8 ± 0.6	78.6 ± 1.2

One of the most important performances of battery alloys is corrosion resistance. In-service the negative electrodes of the battery are exposed to a relatively minor corrosive action, and the active mass on the grid surface oxidizes to PbO at discharge and regenerates to metallic lead (Pb) at charge [12]. However, in the literature [1, 10] the corrosion resistances of alloys for positive and negative electrodes are often compared. In favor of the QLS strips (-) corrosion characteristics research necessity indicates the possibility of significant changes in physical and chemical properties of materials as a result of non-equilibrium crystallization conditions, and the lack of such data in the known literature. The results of corrosion tests initially showed slightly lower corrosion resistance of QLS strips for the negative current collector compared to the same characteristic of strip for positive current collector (Figure 2). The most intensive corrosion occurs at an early stage in the time interval of 10-30 minutes, which is probably indicative of the belt layer formation of the corrosion products on the surface, preventing further interaction of electrolyte and strip. In what follows in the course of natural aging corrosion resistance of the negative collector increases substantially, as evidenced by a sharp change in the slope of loss of mass by time (from 0.021 to 0.006 mg / cm^2) after holding for 180 min. Over time, this trend should only increase. Probably a positive role in this is played by different grain size of the QLS sample dispersed structure and the uniformity of the corrosion rate of interruption into sample.

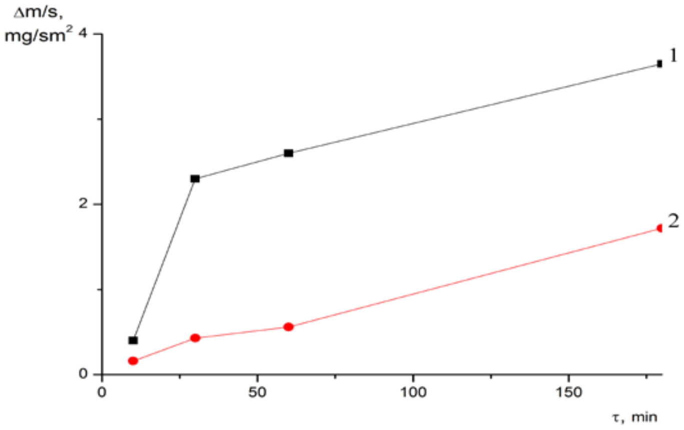


Fig. 2. The dependence of mass loss of the samples at the date of samples receipt (1- QLS strips Pb-0.1%Ca-0.3%Sn, 2- QLS strips Pb-0.1%Ca-1.1%Sn)

5. Conclusions

The results showed that the use in the manufacture of QLS strips Pb-0.1%Ca-0.3%Sn alloy for negative grid production impact on the material's structure and the parameters of the fine structure tempered from the liquid state samples, which means that the performance and corrosion characteristics of the time, given the tendency said alloy to aging and possible structural recrystallization. Therefore, the practical interest is to compare an evaluation of the microstructure and properties of the QLS strips and the industrial strips rolled said alloy during aging.

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