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REGULAR ARTICLE

Mechanical Properties of Pb–Sn–Ba Grid Alloys for Lead-Acid Batteries Produced by Melt Spinning Technology

V.A. Dzenzerskiy*, S.V. Tarasov†, D.O. Redchyts‡, V.A. Ivanov§, O.V. Sukhova**

Institute of Transport Systems and Technologies of National Academy of Sciences of Ukraine, 49005 Dnipro, Ukraine

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This work concerns innovative approach to prepare Pb–Sn–Ba grids for lead-acid batteries which provides their enhanced structural stability and mechanical properties allowing functionality and prolongation of service life at high temperatures. To have these properties in the Pb–Sn–Ba grids, two roll melt spinning technology is applied that provides a greater to extreme environments resistance to fatigue, higher mechanical properties, thermal (for high temperature exposure) stability. As a result, far less disposal and environmental hazard will be posed by longer-lived lead-acid batteries with the Pb–Sn–Ba grids prepared using melt spinning technology compared to those fabricated by conventional methods.

Keywords: Lead-acid batteries, Environmental hazard, High-temperature grids, Melt spinning technology, Rapid cooling, Structural stability, Mechanical properties.

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1. INTRODUCTION

Lead-acid batteries have been used for decades in many different applications that include motorized vehicles, power supplies, telecommunication systems, and various household duties [1-3]. Unfortunately, the toxic, hazardous, flammable, explosive materials contained in lead-acid batteries may bring about lots of pollution accidents, contaminating environment and damaging ecosystem [4-6]. The biggest environmental issue with lead-acid batteries involves the lead component that has potentially dangerous health impacts. In the stages of manufacturing, lead exhaust may be released as air pollution or waste mixtures that may be discharged into soil and waterways.

Despite of the environmental risks they pose, lead-acid batteries have remained widely used because of their reliability, low cost, and high starting current. The industry still must deal with millions of lead-acid cells, already existing and those that will be produced in the future with development of economy [1]. This implies that the amount of battery waste will increase. Therefore, the new production technologies that prolong service life of lead-acid batteries are required in view of the diversity, emergency, and the serious consequences of the environmental accidents that may be caused by these batteries.

In some automobile and industrial applications, lead-acid batteries work at temperatures that reach up to 60 °C. But in the more enclosed space of equipment, battery can be heated up to higher temperatures. Like backup power systems, in the field, batteries for military equipment can be also heated up due to exposure to direct sunlight or lack of ventilation in server systems and communication devices. The higher operating temperatures lead to much more rapid corrosion of the positive grids resulted in the problems causing premature failure of the batteries that do not exhibit proper performance properties [7]. The elongation and the ultimate tensile strength must be high to give the grids adequate stiffness. Furthermore, these mechanical properties must remain rather steady, which means that ageing kinetics at room temperature should be slow [8].

Alloys with desired properties can be developed by tailoring the microstructure, either by controlling the composition or by processing [9, 10]. Therefore, researchers search for alloying elements that can improve properties of pure lead [11-13]. Among such elements are barium and tin, which additions to lead increase tensile strength and creep resistance [14-20]. Besides, barium introduction into lead-tin alloys increases hardness, reduces electrochemical activity and, consequently, increases corrosion stability [21]. Barium also keeps these properties steady because overageing is prevented. The presence of high content of tin inhibits the overageing processes of the lead-based alloys as well [22]. In addition, tin aids in the electrochemical properties of the grids by preventing passivation and permitting recharge of batteries from the deeply discharged condition.

But nowadays, there is no improvement without de-

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* Correspondence e-mail: itst@westa-inter.com
† tsv.transmag@gmail.com
‡ redchits_da@ua.fm
§ iva.dp.ua@gmail.com
** olenasukhova0@gmail.com

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veloping new production technologies that ensure prolonged service life of lead-acid batteries. Ways of controlling the microstructure by processing include deforming the grids by a rolling operation and casting the grids at varying rates of cooling. Grid materials are prepared by various manufacturing technologies, such as conventional book mould casting, rolling of strip followed by expanding, continuous casting of strip followed by expansion, continuous grid casting, and continuous grid casting followed by rolling [23]. However, these technologies involve relatively slow cooling rate of the manufactured grid materials. But the slower the rate of solidification of the alloys, the higher is the amount of segregation of alloying elements across the section of the manufactured products, which deteriorates their structural stability [24, 25].

A few advantages to produce grid materials may offer melt-spinning method that utilizes a rapid cooling to transform melted base materials into grids. The cooling rates achievable by melt spinning are within the range from 10^4 to 10^6 K/s [26]. Due to rapid cooling, liquid-quenched alloys have nonequilibrium uniform structure that gives them unique performance properties and assures good stability [27, 28]. Among several variations of melt spinning process, twin roll method is most applicable because it ensures a high degree of control over the thickness of the battery grids [29, 30].

Since no information has been found in the literature about application of twin roll spin melting method to prepare high-temperature Pb–Sn–Ba grid materials for lead-acid batteries with significantly longer lives, an investigation has been made of the grids obtained by this process to improve their mechanical properties and, in such way, to decrease demand for manufacturing new batteries.

2. EXPERIMENTAL

To carry out an investigation on the structural and mechanical properties of the Pb–Sn–Ba alloys, four different battery grid compositions were studied. These grids were prepared in the following compositional ranges (purity better than 99.9 %): Ba (0.030-0.052 wt. %), Sn (1.08-1.33 wt. %), Pb – the balance. The battery grids were manufactured by two roll melt spinning method [31]. The melt heated up to 425 °C was jetted between the steel rollers rotated at a speed of 120 min^{-1}. The consistent thickness of the grids was achieved by applying the distance between the rollers equaling to 0.6 mm. A cooling rate of the grids was estimated at a level of $3.8 \cdot 10^5$ K/s [14, 26].

To simulate high-temperature battery operating conditions, the samples of Pb–Sn–Ba grid alloys were annealed at 80 °C for ageing times which cover a period between 5 hours after manufacturing and 3200 hours. Microstructure was characterized by scanning electron microscopy using REM-106I device. The X-ray diffraction examination was performed using DRON-2.0 diffractometer with the monochromatic Cu-K_α radiation.

Microhardness (H_μ) was measured by PMT-3 Vickers indenter. Measurements were done on chemically polished surface of the specimens by using 0.196 N load at room temperature. Tensile stretching machine P-0.5 was used to determine the tensile strength (σ) and elongation to failure (δ) of the grid materials. The uncertainty of the measured mechanical characteristics did not exceed 3 %.

3. RESULTS AND DISCUSSION

In the as-quenched state (immediately after spinning), the specimens of grids exhibit relatively low tensile strength which values range from 19 to 25 MPa (Fig. 1). Meanwhile, tensile strength tends to slightly decrease (by 10 %) with increasing a tin content of the strips as grid materials. During first eight hours of age-annealing process at 80 °C, the tensile strength of the grids increases by 13-14 MPa, which exceeds the initial value by 55-65 %. Such sharp increase in the tensile strength may relate to nonequilibrium grid structure obtained during melt spinning process. It involves oversaturation of a lead-based solid solution and formation of a more uniform fine structure. The grain boundaries have nearly the same composition as that within the grains due to rapid cooling.

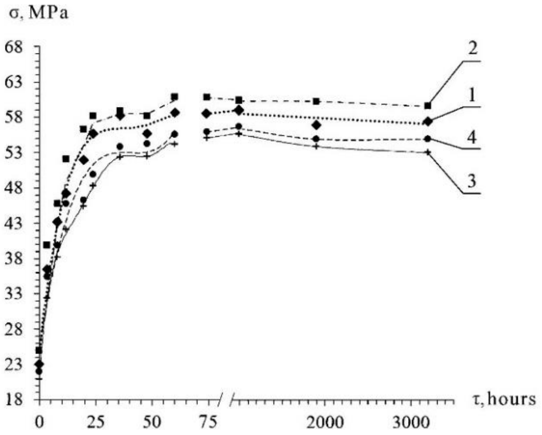


Fig. 1 – Tensile strength vs. annealing time at 80 °C of $PbBa_{0.03}Sn_{1.0}$ (1), $PbBa_{0.05}Sn_{1.0}$ (2), $PbBa_{0.03}Sn_{1.3}$ (3) and $PbBa_{0.05}Sn_{1.3}$ (4) grid alloys

The improvement in uniformity of the grain structure has also occurred under the influence of Ba that inhibits grain growth. As a result, the processes of precipitation hardening accelerate, which significantly increases tensile strength of the battery grids during first hours of age-annealing [32, 33]. Besides, additions of barium to lead are known to increase ageing ability of the alloys that involves the formation of strengthening Pb_3Ba precipitates from a supersaturated lead-based solid solution [21, 29].

As annealing time increases up to 24 hours, tensile strength of the battery grids reaches the maximum values. Further prolongation of annealing time up to 3200 hours at 80 °C does not lead to essential strengthening of the grids. Changes in the values of tensile strength do not exceed 3 MPa after ageing during 120–3200 hours. As Fig. 1 shows, tensile strength changes proportionally to the increase in barium content and inversely proportional to the increase in tin content of the battery grids at each stage of ageing.

The changes in elongation values, as expected, are consistent with the changes in tensile strength (Fig. 2). Elongation to failure of the battery grids tends to drop sharply during first 8 hours of ageing, but, with annealing prolonging from 72 to 3200 hours, elongation does not noticeably change. Unequivocal dependency of this characteristic on Ba concentration of the grids has not been established. Meanwhile, this feature is governed by tin content since some increase in the ductility of the grid materials is observed with increasing amount of Sn.

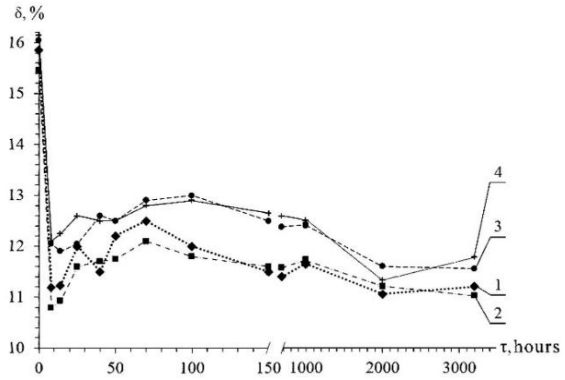


Fig. 2 – Elongation vs. annealing time at 80 °C of $\mathrm{PbBa_{0.03}Sn_{1.0}}$ (1), $\mathrm{PbBa_{0.05}Sn_{1.0}}$ (2), $\mathrm{PbBa_{0.03}Sn_{1.3}}$ (3) and $\mathrm{PbBa_{0.05}Sn_{1.3}}$ (4) grid alloys

The results of microhardness measurements have proved to show trends similar to those observed for tensile strength (Fig. 3). Peaks are seen on the microhardness curves over the same period, the magnitude of which depends on the barium content of the battery grids. Peaks appearance may relate to precipitation processes accompanied by formation of barium-containing phases. Further prolongation of ageing up to 700-750 hours is succeeded by monotonic decrease in microhardness. Nevertheless, microhardness values produce sufficient mechanical properties for handling of the investigated battery grids in operating conditions. In the annealing time range of 750-2800 hours, microhardness remains practically unchanged, so no loss of strength occurs. This conclusion can be confirmed by metallographic investigations of the battery grids obtained by melt spinning method (Fig. 4).

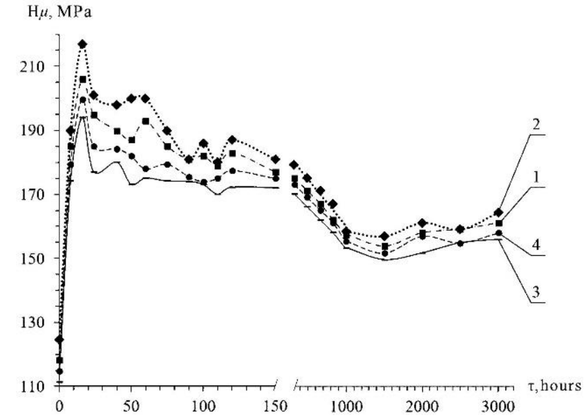


Fig. 3 – Microhardness vs. annealing time at 80 °C of $\mathrm{PbBa_{0.03}Sn_{1.0}}$ (1), $\mathrm{PbBa_{0.05}Sn_{1.0}}$ (2), $\mathrm{PbBa_{0.03}Sn_{1.3}}$ (3) and $\mathrm{PbBa_{0.05}Sn_{1.3}}$ (4) grid alloys

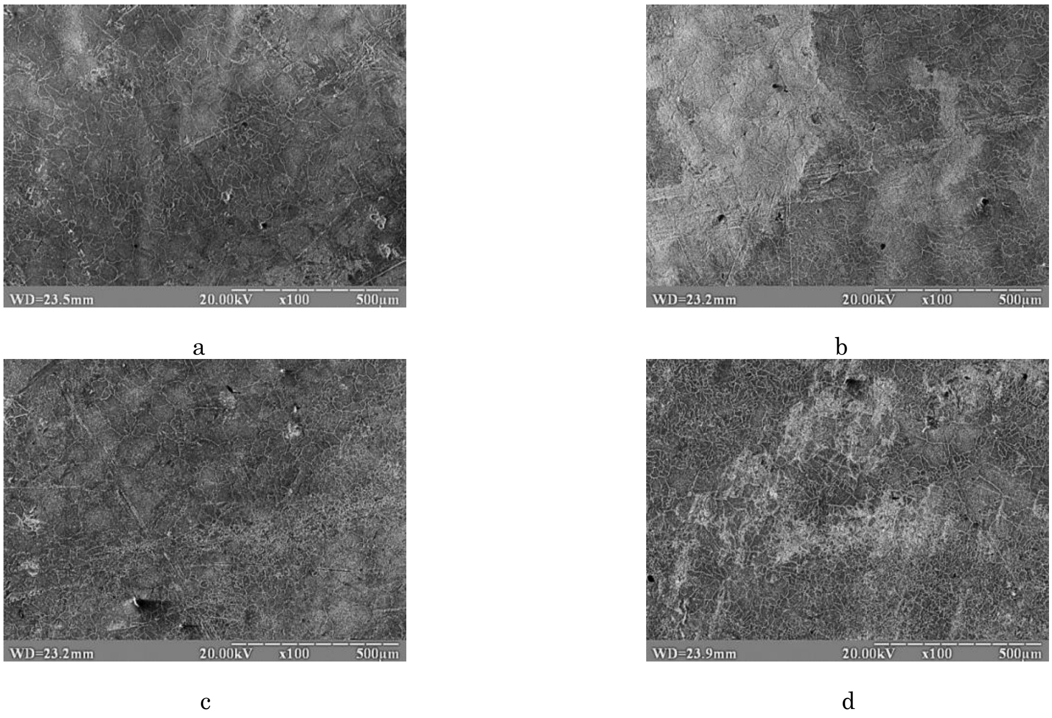
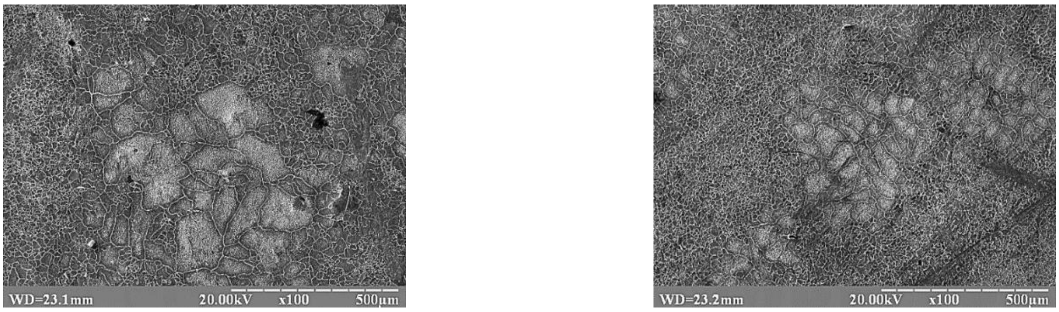


Fig. 4 – Microstructure of the grid alloys after age-annealing at 80 °C for 72 (a, c) and 3200 (b, d) hours: a, b – $\mathrm{PbBa_{0.03}Sn_{1.0}}$; c, d – $\mathrm{PbBa_{0.05}Sn_{1.0}}$

As shown in Fig. 4, the grids produce fine dispersed grains, which shape is close to globular. The age-annealing of the grids of the same composition does not lead to noticeable changes in the grain size. Meanwhile, the grain size of the rapidly quenched battery grids of different compositions tends to decrease with barium content increasing. So, the addition of barium refines the grain structure of the battery grids, which may protect the grains from recrystallization. Barium addition also stabilizes the grain structure so that the over-ageing phenomenon is blocked and thereby gives the material a better stability and reliability [21].

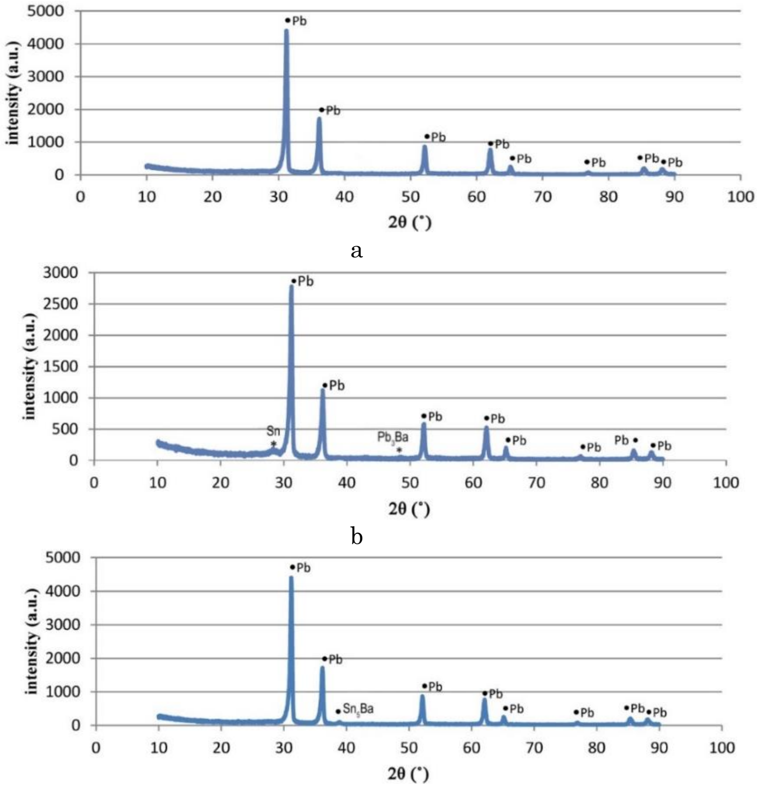
As a tin content of the battery grids increases, the grains show a distinct variation in size due to recrystallization processes: larger grains misoriented with respect to surrounding smaller grains are observed after annealing at 80 °C for 3200 hours (Fig. 5). The observed structural changes indicate that barium has the better effect on grain refinement and recrystallization blockade. However, mechanical tests do not reveal the strength loss; therefore, it may be concluded that the battery grids produce small amount of the recrystallization zones that can significantly affect the mechanical properties [34].



a

b

Fig. 5 – Microstructure of $PbBa_{0.03}Sn_{1.3}$ (a) and $PbBa_{0.05}Sn_{1.3}$ (b) grid alloys after age-annealing at 80 °C for 3200 hours



a

b

c

Fig. 6 – Diffraction patterns of $PbBa_{0.05}Sn_{1.3}$ grid alloy in as-quenched state (a), after annealing at 80 °C for 10 hours (b) and after annealing at 80 °C for 24 hours (c)

X-ray analysis indicates that the grids in the as-quenched state do not contain tin- or lead-based phases alloyed with barium (Fig. 6a). So, barium does not contribute to modification effects. But extremely high cooling rates during two roll melt spinning process reduce the crystal grain size of the oversaturated lead-based solid solution due to significant overcooling and increase in the amount of crystallization nuclei. Therefore, rapid cooling serves to produce a very fine grain size and reduced tin and barium segregations.

At earlier stages of age-annealing (during first 10 hours), diffraction patterns of the melt-quenched battery grids reveal the formation of strengthening Pb_3Ba precipitates that create relatively high internal microstresses in the materials (Fig. 6b). Being unstable and easily soluble, these precipitates disappear during further annealing (within the time range from 11 to 24 hours), with dispersed intermetallic Sn_5Ba particles of higher microhardness precipitating (Fig. 6c). At that, on annealing, the internal microstresses in the battery grids caused by precipitation of Pb_3Ba particles may aid the formation of more stable Sn_5Ba precipitates that contribute to ductility of the alloys.

As a result, both the tensile strength and the microhardness of the battery grids are found to improve with increasing barium content. The improvement in the elongation is due to the change in precipitation mode from Pb_3Ba to Sn_5Ba with increasing tin content. These precipitated dispersed particles hinder structural changes caused by grain boundary movement. The alloys exhibit peak mechanical properties after 24 hours of age-annealing. The limitation to increasing the annealing time is related to the hardening kinetics and the mechanical properties of the alloys.

So, to produce a stable structure, the alloys must contain chosen barium and tin content to convert strengthening Pb_3Ba precipitates to more stable, stronger, and more effective Sn_5Ba intermetallic particles. It allows achieving microstructural stability, particularly at elevated temperatures where grain boundaries are more mobile.

4. CONCLUSIONS

New approach to conventional manufacture technologies for the Pb–Sn–Ba grids of lead-acid batteries that involves two roll melt spinning process has been proposed in this work. The technology provides rapid cooling at a rate of $3.8 \cdot 10^5$ K/s from 425 °C to room temperature to ensure structural stability and to develop suitable microstructure of the battery grids with enhanced mechanical properties at high service temperatures of up to 80 °C.

In the as-quenched state, microstructure of the lower and higher barium content Pb–Sn–Ba grids, prepared at various tin contents, consists of uniform grains of a supersaturated lead-based solid solution. Segregation of alloying elements within the grains does not virtually distinguish from that in the grain boundaries. If the content of barium is increased, but the content of tin is kept the same, the grain size decreases. At that, by increasing the area of grain boundaries, the tensile strength increases. The addition of barium enhances tensile strength and hardness of the battery grids, while the addition of tin increases their elongation to failure. Besides, the tensile strength and hardness of the battery grids significantly increase during first 24 hours of age-annealing at 80 °C. With annealing time prolonging up to 3200 hours, the mechanical characteristics remain almost unchanged.

The properties of the Pb–Sn–Ba grids are attained by precipitation hardening that involves the formation of Pb_3Ba precipitates at earlier stages of annealing and Sn_5Ba precipitates during further annealing. By producing more stable Sn_5Ba precipitates instead of Pb_3Ba and reducing or eliminating grain boundary movement, the microstructural stability of the battery grids can be achieved at elevated temperatures. The grids exhibit steady properties, i. e. no deterioration with ageing.

In summary, two roll melt spinning grid-production technique provides a better means of controlling the microstructure and achieving superior mechanical properties of the Pb–Sn–Ba battery grids even after manufacturing. All these improvements are focused on developing successful engineering product demonstrating promising application potential: such advanced batteries can provide durability and performance of military equipment in harsh operating conditions.

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Механічні властивості сплавів Pb–Sn–Ba для струмовідводів свинцево-кислотних акумуляторів, отриманих методом гартування з розплаву

В.А. Дзензерський, С.В. Тарасов, Д.О. Редчиць, В.А. Іванов, О.В. Сухова

Інститут транспортних систем і технологій, Національна академія наук України, 49005 Дніпро, Україна

В роботі запропонований інноваційний метод виготовлення сплавів системи Pb–Sn–Ba для струмовідводів свинцево-кислотних акумуляторів, що забезпечує підвищення їх структурної стабільності та механічних властивостей з метою покращення функціональності та подовження терміну служби за високих температур. Для досягнення вказаних властивостей, струмовідводи зі сплавів системи Pb–Sn–Ba виготовляли за технологією двохвалкового гартування з розплаву, яка дозволяє підвищити їх опір руйнуванню, збільшити механічні характеристики, покращити термічну стабільність за високих температур експлуатації. Завдяки застосуванню струмовідводів Pb–Sn–Ba свинцево-кислотних акумуляторів з подовженим терміном служби, виготовлених за технологією двохвалкового гартування з розплаву, зменшується потреба в утилізації та знижується небезпека для навколишнього середовища порівняно з акумуляторами, виготовленими із залученням традиційних методів.

Ключові слова: Свинцево-кислотні акумулятори, Екологічна небезпека, Високотемпературні струмовідводи, Технологія двохвалкового гартування з розплаву, Швидке охолодження, Структурна стабільність, Механічні властивості.