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PHYSIC-CHEMICAL PROPERTIES Pb-Ca-Sn BASED ALLOYS

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In recent years to improve the structure and useful characteristics of alloys it is widely used advanced methods for their receiving related to non-equilibrium crystallization under conditions of the accelerated cooling of the alloys, in particular, methods of quenching from the liquid state. The different processes of the production (gravity casting, continuous casting, rolling expansion and casting expansion) are capable of imparting the large plastic strain and high dislocation density in the material [1]. The total amount of these lattice defects is the crucial factor which determines the evolution of the morphology and the kinetics of the phase transformations that can occur during the service life.

The studies samples of alloy composition: Pb - 0,05% Ca - 1,1% Sn were prepared according to the modern industrial technology, including continuous cast billets and rolling it into a tape with thickness of 0.85 mm with a deformation degree of 93% (commercial tape) and also by quenching from the liquid state (QLS) jet melt from a temperature of 700 K between rotating steel shafts with a speed of 120 rev / min which have a gap of 0.5 mm in between.

The research of mechanical properties of alloy foils $PbCa_{0.05}Sn_{1.1,}$ which was held on the day of their production, showed a higher limit microhardness and lower ductility industrial belts as compared with QLS –tape.

The images of microstructures are shown in fig. 1

The results of microscopic research showed dispersed, close to the globular shape of the grains in QLS -tape. The photomicrographs are shown in fig.1 indicate that artificial aging QLS sample does not lead to significant changes in grain size for samples with the one chemical composition. The estimation of grains size of different alloys showed a slight tendency for their crushing with an increase of the barium part.

The microstructure of the rolled samples is characterized by large elongated grains in the rolling direction with more defects on the surface (fig.1a).The exposure of an industrial sample at 80^0 C during ~ 3200 hours is upgraded to microcrystalline structure with no apparent orientation in the presence of relatively small grains in the structure of the tape, indicating that the processes of recrystallization in the alloy and confirmed by mechanical testing that showed softening exposed to a current of 3200 hours pumped films compared with the test results for even newly received samples.

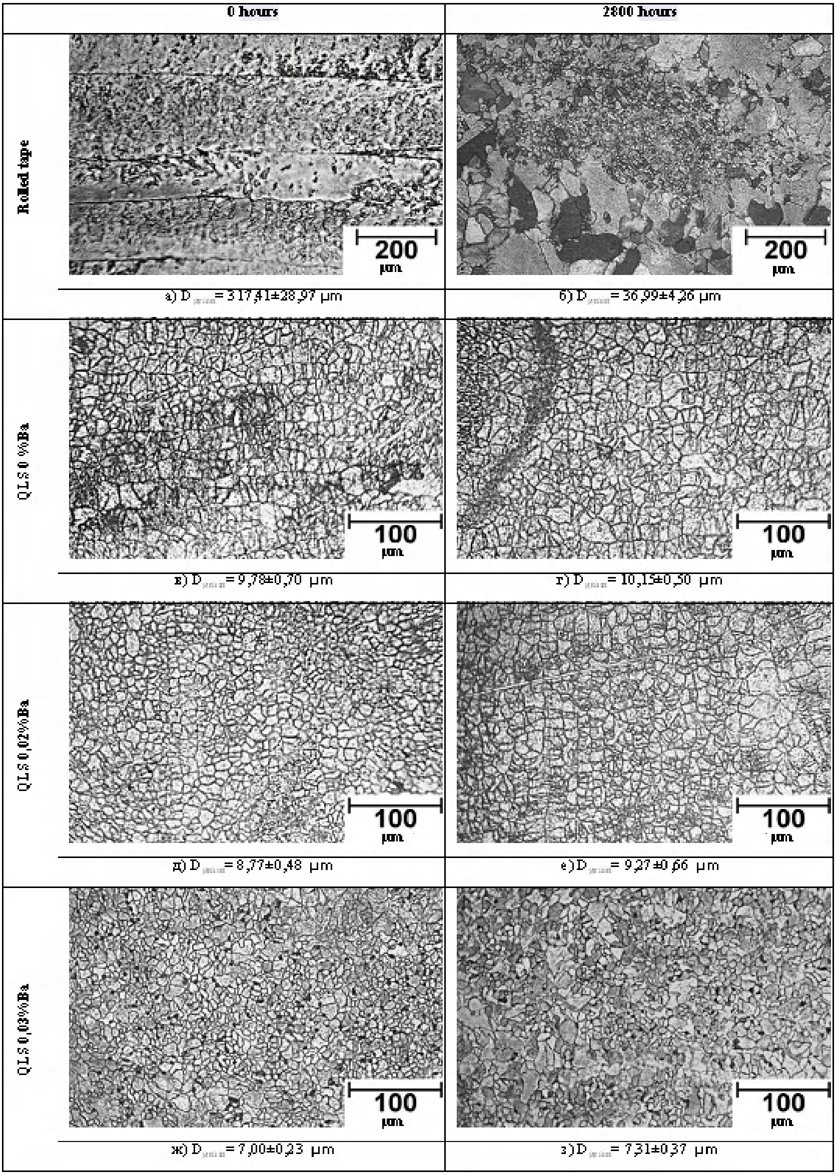


Fig. 1. The structures of the samples D – an average size of the grain

Crystallization under conditions of the non-equilibrium alloy cooling using the spinning method also allows to achieve more strength samples than alloy samples (hardness increased more than in 3.5 times).

Researching results of the samples with the fine structure features indicate a much larger (about 3 times) level microtension in the industrial belt compared to QLS- feed the same chemical composition, in a certain measure may affect the temperature threshold early recrystallization processes.

In support of the above assumption suggests no marked changes in the structure QLS- samples and noticeable degradation of mechanical properties. It should be noted that the observed gradual decrease in microhardness at the stage of ~ 200-700 hours of exposure at 80o C can be explained by the occurrence relaxation may surface, processes, accompanied by some reduction of internal pressure (dot defects vacancies) in the primary structure of dispersed alloys, in turn, do not lead to significant changes in tensile strength.

The corrosion resistance of the investigated alloys was determined by reducing the weight of the samples after their alloys oxidation in potentiostatic conditions and the removal of the surface oxide tape. The studied samples in plates with geometric surface 1x1 dm2 kept at the potential of 2.15 V. triple electrode slot in 4.8 M sulfuric acid solution at 400C.

The corrosion mass loss of the sample in g/cm2 calculated by the formula:

$$\Delta m=(m_0- m_t)/S, \qquad (1.1)$$

where : m_0- initial weight of the sample, g.;
m_t mass of the sample after the removal of corrosion products, g.;
S – surface of the sample to the test,.

The determination of corrosion rate of differentiation of the kinetic curve was carried out according to the formula:

$$\nu =\delta(\Delta m)/ \delta t, \qquad (1.2)$$

where : $\delta(\Delta m)$ – weight change of the sample at a the given time,; δt - the time interval h.

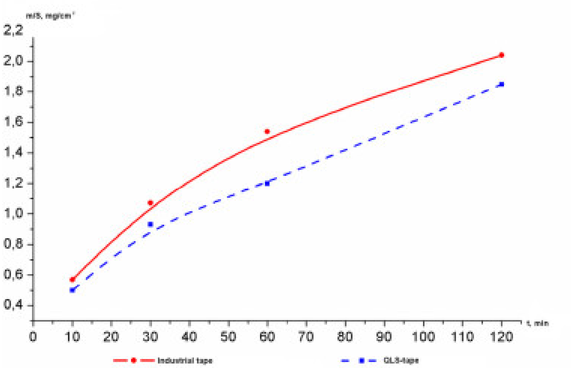
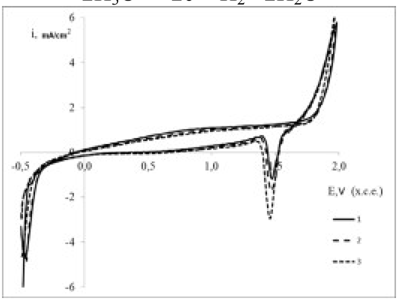


Fig. 2 The dependence of a weight reduction of alloy electrodes from corrosion time

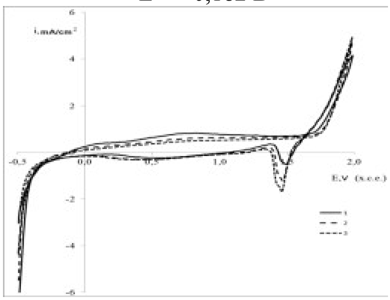
Corrosion testing QLS-samples indicate their greater sensitivity to oxidation compared with rolled strips. But given the fact that the battery pack to provide adequate adhesion and formation of dense conductive transition layer between the active mass and shunts its surface should undergo some degree of corrosion [1], as well as increased stability of the structure and mechanical properties of QLS-tape. Further research is promising.

To study the electrochemical behavior of the investigated alloys in sulfuric acid solution were obtained for circular polarization potentsiodynamic curves are recorded, for three cycles in the range of potentials from - 0.5 V to +2.0 V(fig.3)

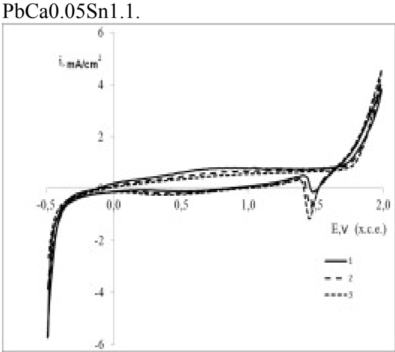
- calculated equilibrium potential of the main backbone processes on a lead electrode in 4.8 M H_2SO_4 solution in terms relative to silver chloride electrode
- $PbSO_4 + H^+ + 2e = Pb + HSO_4^-$ E = - 0,602 B
- $PbO_2 + 3H^+ + HSO_4^- + 2e = PbSO_4 + 2H_2O$ E = 1,522 B
- $O_2 + 4H^+ + 4e = 2H_2O$ E = 1,046 B
- $2H_3O^+ + 2e = H_2 + 2H_2O$ E = - 0,182 B



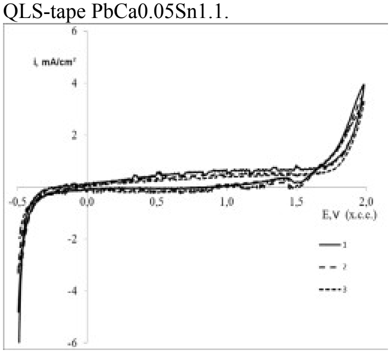
a) Cycle potentsiodynamic curves (three cycles) obtained on the electrode with tape PbCa0.05Sn1.1.



b) Cycle potentsiodynamic curves (three cycles) obtained on the electrode м with QLS-tape PbCa0.05Sn1.1.



c) Cycle potentsiodynamic curves (three cycles) obtained on the electrode with QLS-tape PbCa0.05Sn1.1 ,0.015 % Ba.



d) Cycle potentsiodynamic curves (three cycles) obtained on the electrode with QLS-tape PbCa0.05Sn1.1 ,0.03 % Ba.

Fig. 3. Cycle potentsiodynamic curves (three cycles)

Thus, studies of electrochemical behavior of lead alloys in 4.8 M sulfuric acid solution showed that all the selected lead alloys have similar electrochemical properties, exhibit low electrochemical activity in the high: anodic potentials (about 1.5 V). It should be noted that the alloying of lead components in almost all cases leads to a decrease in the rate of anodic oxidation of the investigated alloys, especially at high anode potentials.

As a result of measurements polarization see that the allocation of PbO2 moved to higher potentials and thereby speed of sulphuring of samples with increasing barium content increases.

Also, it is known [3, 4] that alloys of Pb-Ca-Sn is proned to aging, resulting in an increase robustness and plastic properties of the alloy during aging even at room temperature. Because the QLS-tape was obtained at a degree of disequilibrium crystallization conditions supersaturated solid solution of lead calcium and tin in their structure above, to predict more intense growth robustness properties and is a promising direction for further research material.

Conclusions

1. Hardening of alloys by the spinning method gives a satisfactory quality and geometric dimensions of the strips QLS-tape. The advantage of this method is based on a cost effectiveness because it let to get samples with required thickness directly from the liquid.

2. The method of quenching from the liquid state with addition of an alloying effectively barium element is recommended to the manufacturing process because of following reasons:

a) formation of monophase, microcrystalline, textured structure

b) economic efficiency of the inputting the new technologies of the rapid cooling of the melt to obtain better Pb-Ca-Sn alloys

c) resistance to unwanted sulphuring of samples decreases with increasing amount of barium.

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