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ANALYSIS OF PROCESSES DETERMINING PB-CA-SN ALLOY STRIPS PROPERTIES, PRODUCED BY CASTING-ROLLING TECHNOLOGY FOR ELECTRIC-CHEMICAL ACCUMULATORS

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Досліджено вплив технологічних операцій на формування мікроструктури і властивостей стрічок сплава Pb-Ca-Sn для електрохімічних акумуляторів під час різних етапів виробництва за технологією безперервної розливки-прокатки.

Ключові слова: *розливка-прокатка, Pb-Ca-Sn сплав, структура, властивості, електрохімічний акумулятор, стартова батарея.*

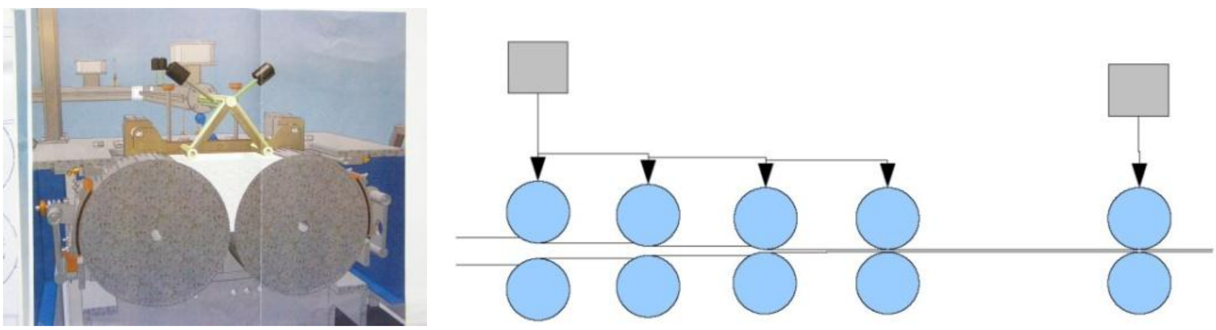
Pb-Ca-Sn alloy strips micro structure and properties forming processes on various technological stages of casting-rolling technology production studied.

Key words: *casting, rolling, Pb-Ca-Sn alloy, structure, properties, electric-chemical accumulator, battery.*

Introduction. Pb-alloys used as main battery-grid material still for many transportation applications. A worldwide Pb-metal production/usage is 10Mt/year [1]. Global lead-acid battery demand amounted to 494.82 million KVAh in 2015, up 3.5% from a year ago [2]. A safety work of lead-acid chemical accumulators (battery), used in railway and automotive transportation, determined in most on materials properties of grids, that works as framework for electric active mass and current conductor of battery in the same time. The battery grid, works in hard conditions, reverse mechanical loading, vibrations, electric-chemical corrosion. Grid properties requirements is wide: (electric) conductivity, low electric resistance, mechanical strength, in high-active electrolyte electric-corrosion resistance, uniformity (stability) in chemical system (grid-active mass- electrolyte), eth. Electric active metals only: Pb, Li, Zn, Cd this requirements serve. Not much electric-chemical systems known, accumulating electrical energy in reversible reactions [3]. The Pb-Ca-Sn alloy strips microstructure/properties forming processes in casting-rolling-punching technology analysis on various technological stages is the aim of this article.

In [4] three various Pb-alloys (PbCa0,1AlSn0,5Ag, PbCa0,1AlSn0,2, and PbCa0,1AlSn0,2Mg0,1) properties, structures researched. Micro photography of microstructure is presented. No deformation influence on microstructure acquired.

Materials and methods. Study of PbCa0,1Sn0,3 alloy strips microstructure, produced by casting-rolling technology process (Fig. 1). The 450°C melt casts in twin-roll casting machine. The 360 mm diameter roll of casting machine has internal cooling channels with fluid (water) T=25°C, following deformation (rolling) in semi-continuous 5-stand rolling mill "Punching Line" (Sovema) to decrease thickness from slab S_{slab} = 70 mm to strip S_{strip}=0,9..1,0 mm with ε = 5%..50% strain rate in each rolling stand.



a *b*

Fig. 1. Twin roll casting machine (a), formation (rolling) scheme (b)

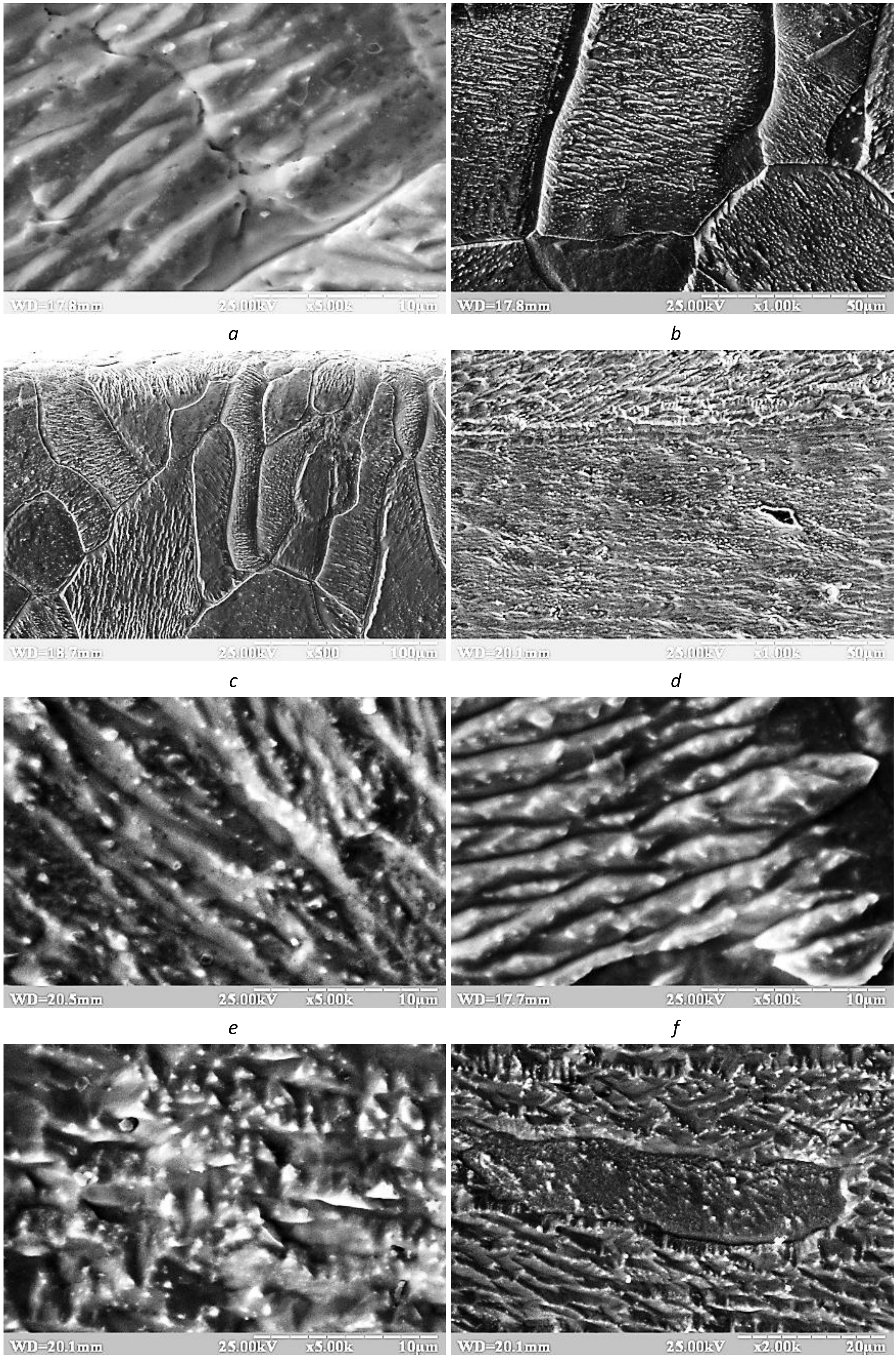


Fig. 2. PbCa0,1Sn0,3 alloy micro structures of continuous casting-rolled strips

Results. Indeed, the study of thin strips (grids) quality of electric-active metals for battery should be more extensive. Grids, thin strips (battery current) is irreplaceable base of almost all electric-chemical battery construction. In present time well known technologies of battery grids production is: casting, rolling, combined process. Each technology has advantages and limitations. The significant differences in microstructure, properties of strips of each technology production is present. That differences does determinate a final operational properties in final product (battery).

A study of properties of strips, produced of combined technology casting-rolling process ("Punching Line", Sovema), needs a detail analysis of phase and structure changes, on every stage of production process.

The final structure of battery strips (grids) is a result of some in series actions of technology process. It should be separate two stages of PbCa0,1Sn0,3 alloy strips structure formation: casting-rolling in twin-roll machine, and rolling in 5-stand semi-continuous rolling mill Punching Line. Considering melting temperature of this alloy T_{melt} = 327°C [5], start temperature of recrystallization range is (-87…+27°C), that significantly for analysis conditions of structure forming PbCa0,1Sn0,3 alloy on every stage of production process.

On casting-rolling stage the melt solidification occur in touch contact on rolls surfaces of casting-rolling twin roll machine. Then, this solid areas has deform and inner liquid layers of slab solidification go on, that, in same time, new formed crystals keep deformation on. That processes keep going in continuous slab temperature descending. First stage of production is hot forming of strip in liquid-solid state. Second stage is hot/semi-hot forming in solid state strip with recrystallization processes in line. After that, following stage is warm (soft) deformation stage with recrystallization processes keep going. Accordingly, first is hot deformation, with dynamically structure forming, then warm deformation, with obstructed dynamically structure forming.

A signs (markers) of specified processes is shown on microphoto Fig. 2, a-c: localized deformation zones (Fig. 2, a), shift sliding along grain boundaries signs (Fig. 2, b), grinding grain (Fig. 2, c).

The "Punching Line" 5-stand semi-continuous rolling stage should be viewed like stair-step deformation with single-stand deformations does in time periods pause. The deformation distribution between stand, time period of pauses is highly important. A grain structures and thin structures (dislocations) rebuilding of PbCa0,1Sn0,3 alloy is going, in fact, in repeated multiple deformation conditions, with previous, relict, deformations action loss stability, and following rebuilding of structures on following deformation, due to the accumulation and the change of internal energy due to the redistribution of dislocations. This may vary dislocation density substructure, cell dimensions, angles, their disorientation. Since the deformation temperature of the alloy is in the temperature range of recrystallization, it is warm deformation.

Well known, for warm deformation is inherent allocation of excess phases, formation of impurity atmospheres at dislocations, dynamic strain aging and other processes [6]. The time period of pauses between rolling stands is significant, that determinate static rebuilding conditions of deformed structures and phase transformation probability in alloy. Analysis of the microstructure of 1,5 mm and 0,9 mm-thickness strips revealed elongated grains (Fig. 2, d), substructure with elongated cells (Fig. 2. e), particulate separation, obviously Pb3Ca phases, Sn3Ca (Fig. 2, f), evidence of the dynamic strain aging, signs of dynamic recrystallization (Fig. 2, g) and areas of localized deformation, indicating "staggered" stress distribution near grain boundaries (Fig. 2, h).

Mechanical properties is dependent on agening, increases from 40…45 MPa in "after rolling" state to 50...55 MPa (tensile strength) after 3 month natural agening.

CONCLUSIONS

Structure forming of battery's PbCa0,1Sn0,3 alloy thin strips on different stages of casting-rolling-punching process is complex of multiple factors: across crystallization, dynamic recrystallization, heat deformation, agening. Mastering of structure development possibilities on every stage process could be used for achieve given properties of battery's strips. Processes should be studying detailed, analysis to improve quality of electric-chemical accumulators (battery) thin strips (grids), production technology, to improve mechanical properties, corrosion resistance of strips-grids.

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