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METABK 55(1) 29-32 (2016)
UDC – UDK 669.4:620.18:620.17:621.35=111

MICROSTRUCTURE AND PROPERTIES OF PbCa GRADE ALLOYS FOR STARTING BATTERY GRIDS

Received – Primljeno: 2014-01-30
Accepted – Prihvaćeno: 2015-06-26
Original Scientific Paper – Izvorni znanstveni rad

The paper presents results of the studies into microstructure and mechanical properties of PbCa grade alloys for starting battery grids. Three lead-calcium alloys with alloy additions of aluminium, tin, silver and magnesium were studied. Lead alloys were produced in laboratory tests from industrial master alloys and pure elements. The examined alloys have monophase microstructure of tin solid solution in the lead. The range between liquidus and solidus temperatures is c.a. 10 °C. The mechanical properties alloys depend on the amount of tin. PbCa alloys exposed to the process of natural ageing increase their strength, proof strength and hardness, simultaneously the plasticity decreases.

Key words: lead alloys, microstructure, mechanical properties, starting battery

INTRODUCTION

Together with aluminium, copper, zinc and tin also lead belongs to the group of metals commonly used in industry. The scope of its application is still limited, mainly due to its hazardous influence on people and animals (lead accumulates in living organisms). Lead compounds are strongly hazardous. It leads to strict limitations when it comes to production of primary lead, therefore its recycling is continuously being developed. At present the total amount of secondary lead exceeds 60 % of the total amount of lead produced. World production of lead is currently 10,6 Mt [1, 2].

The structure of lead usage as well as the production of lead products and semi-products, depends on the development of a few lead-depen-dent branches. It is mainly the starting battery industry, consuming ca. 80 % of lead production and the amount is still rising. This is the reason why lead is described as single-use metal. The increasing application of lead in the starting battery industry is caused by development of automotive industry and by lack of competitive solutions in terms of chemical energy sources, and decreasing application level of lead in other industrial branches, due to health-safety reasons [1].

The composition of lead alloys for construction of starting batteries, precisely battery grids (used for production of plates and alternating sets of cathodes and anodes), is permanently being optimized. Among such lead alloys are ones with calcium, aluminium, tin and silver (eg. PbCa0,1AlSn1) but also antimony (over 1 %), arsenium, selenium and tin, eg. PbSb1,7Sn0,2Se. Lead alloys applied for the purposes of starting battery grids are not regulated by European standards. European numeric system of lead and lead alloys includes, however, a material group of alloys marked as A including four subgroups selected according to their composition (EN 12659:1999 standard). Therefore the presented in the paper materials can be included into EU standard [1, 3-5].

Lead is prone to plastic deformation or wear due to its low yield limit and hardness. Mechanical properties of lead can be increased by application of alloy additions. The most popular of them is antimony in the amount of 10 %, and the alloys including this addition are generally called hard lead alloys. Lead alloys include also small amounts of: Sn, As, Ca, Cu, Bi, Se and Te [6-8].

The percentage of tin (0,2 - 1,5 %) depends on standards of a specific starting battery producer. The anode and cathode grids may be produced out of calcium alloy but it is common that only anode grids are made of the mentioned alloy. Cathode grids in such case are made of the alloys representing the second group, the one including antimony, arsenium, selenium or occasionally tin (hybrid batteries). Both anode and cathode grids can be produced out of lead and antimony only [1, 3, 4].

MATERIALS AND METHODS

The PbCa alloys were optimised by additions of silver and tin or pure magnesium. Tests included three alloys: PbCa0,1AlSn0,5Ag (A), PbCa0,1AlSn0,2 (B), and PbCa0,1AlSn0,2Mg0,1 (C). Lead alloys were made in laboratory from industrial master alloys (CaAl15 and PbAg1) and pure ingredients. The process of melting was conducted in a crucible furnace in 500 °C. The process resulted in production of flat billets, which were later rolled at ambient temperature to a thickness of 2 mm.

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A microstructure examination was carried out with as cast samples using metallographic microscope OLYMPUS GX71. The thermal analyses (TA) of PbCa alloys were performed using automatic thermal-derivative analyser with Crystaldimat software by Z-Tech. The analyses were conducted in a range of temperature from 400 - 150 °C. Phase composition was determined by X-ray diffraction method using the XRD 7 Seifert-FPM device with a cobalt lamp. The measurements were performed in angle range of 2Θ: 10 - 100 º.

All samples collected for mechanical properties examinations were cut perpen-dicularly to the rolling direction (RD) and examined by single-axial tension test using universal testing machine INSTRON 4505 at ambient temperature and rate of 10 mm / min (initial deformation rate $8{,}3 \cdot 10^{-3}$ s^{-1}, sample dimensions *w* **x** *h* **x** *l*: 2 x 4 x 20 mm). A proof stress $R_{p0.2}$, tensile strength R_m and total relative elongation A_{20} were measured. The Brinell hardness of alloys was tested according to ISO 6506-1:2014 (a steel ball diameter of 1 mm, load 10 N and measuring time 120 s). The reverse bend tests according to ISO 7799:1985 were also performed. Samples for these tests were cut perpendicularly to the rolling direction (sample dimensions *l* x *w* x *t*: 100 x 20 x 2 mm). The mechanical properties were examined immediately after rolling and during natural aging for 3 months.

RESULTS AND DISCUSSION

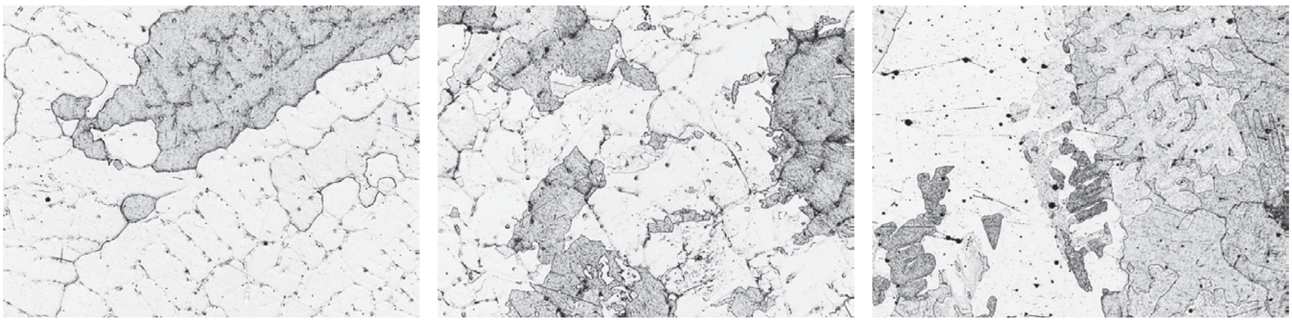
The examined PbCa alloys have approxi-mately monophase microstructure consisting mainly of tin solid solution in the lead (Figure 1). Small amount of calcium containing phase [Pb_3Ca or $(PbSn)_3Ca$] resulting from concentration of this element in alloy (0,05 %), is arranged along the grain boundaries with aluminium and silver rich phases [4, 9].

Results of thermal analysis of PbCa alloys are presented in Figure 2. One visible temperature decrease arrest was noted on the cooling curves. The first derivative curves were shown more information about crystallization of three lead-calcium alloys.

Based on the cooling curve analysis, the non-equilibrium liquidus temperature of PbCa0,1AlSn0,5Ag (A) alloy was found at approximately 325,5 °C. At this temperature first lead dendrites become nucleated from the melt. This point is clearly visible as a sudden change in the first derivative curve. During further cooling the lead solid solution phase continued to grow up to temperature of 315,6 °C, where the non-equilibrium solidus temperature was observed. Similarly, non-equilibrium temperature of liquidus and solidus of PbCa0,1AlSn0,2 (B - at 329,9 °C and 318,0 °C respectively) and PbCa0,1AlSn0,2Mg0,1 (C - at 325,5 °C and 315,1 °C respectively) alloys were determined. Taking into consideration battery grid production process, liquidus and solidus temperatures are the most important parameters.

In Figure 3 the X-ray diffraction patterns of the PbCa alloys are shown, confirming of presence of solid solution of lead. Peaks of the other phases (mainly Pb_3Ca) are not observed since the concentration of these phases in the structure is very low.

The mechanical properties of PbCa alloys directly after rolling were shown in Table 1. The most resistant is A alloy, whose tensile strength is 50 MPa and proof strength is 46 MPa. The alloys with 0,2 % Sn are less strong. Tensile strength of B and C alloys is 38 and 37 MPa, respec-



a) b) c)

Figure 1 Microstructure of alloys: a) PbCa0,1AlSn0,5Ag, b) PbCa0,1AlSn0,2, c) PbCa0,1AlSn0,2Mg0,1

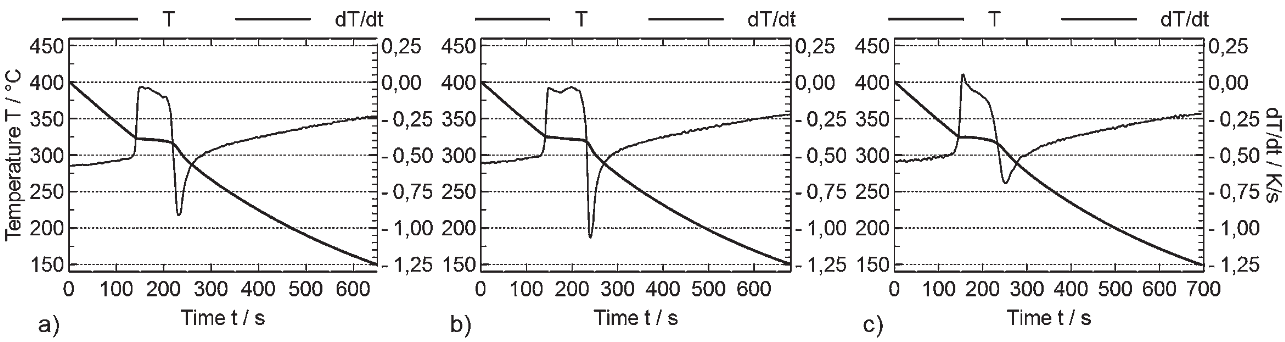


Figure 2 Cooling and first derivative curves vs. time of: a) PbCa0,1AlSn0,5Ag, b) PbCa0,1AlSn0,2, c) PbCa0,1AlSn0,2Mg0,1 alloy

tively. Proof strength of both alloys is 30 MPa. The alloy with the highest tin concentration and silver addition has the lowest plasticity (A_{20} = 10 %). Elongation after fraction of the others alloys is in the range from 18 to 20 %. The results of bilateral bending tests correspond with plasticity. Maximal number of reverse bends is 9, 11 and 10 for A, B and C alloys, respectively. Hardness of tested alloys after rolling is on similar level – values from 9 to 11 HB.

The results show that PbCa alloys undergo natural ageing (Figures 4, 5, 6). Tensile strength and proof strength of these alloys increase with the time (Figure 4). Alloy A is characterized by the highest increase as well as the highest values of these parameters (R_m from 50 MPa directly after rolling to 62 MPa after three months natural ageing and $R_{p0.2}$ from 46 to 56 MPa, respectively). Alloys with lower Sn concentra-tion are characterized by lower increase of these parameters. At the same time, plasticity of these alloys decreases. The highest decrease of elongation after fracture A_{20} was noticed for C alloy, from 18 % directly after rolling to 9 % after one month; and for B alloy from 20 % after rolling to 13 % after 2 month natural ageing. For the alloy with 0,5 % Sn the decrease of A_{20} is not such significant (Figure 4c). The hardness of PbCa alloys undergoes minor fluctuation and increases about 1 HB after one month of natural ageing (Figure 4d). During next month of ageing, only hardness of alloy with magnesium addition still increases up to 12 HB. Hardness of the other alloys decreases. After second month, hardness of alloys remains invariable or increases (A alloy). The number of reverse bends decreases with time of natural ageing (Figure 4e). The highest decrease was noticed for A alloy, whose N_b changes from 9, directly after rolling, to 3 after two months. The B alloy is characterized by the lowest decrease of N_b values, from 11, directly after rolling, to 9 after three months. These results show that the mechanical properties are dependent on tin concentration in alloy, which has the most important influence in alloy properties designing.

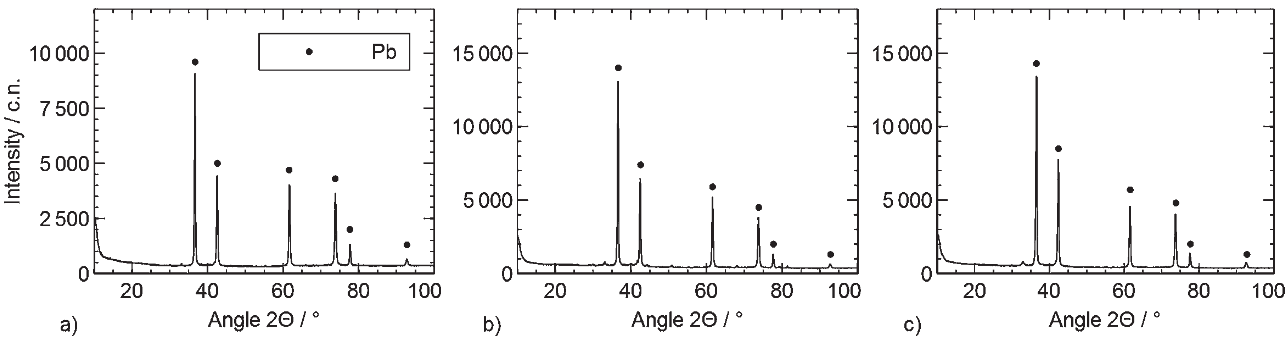


Figure 3 X-Ray patterns of analysed alloys: a) PbCa0,1AlSn0,5Ag, b) PbCa0,1AlSn0,2, c) PbCa0,1AlSn0,2Mg0,1

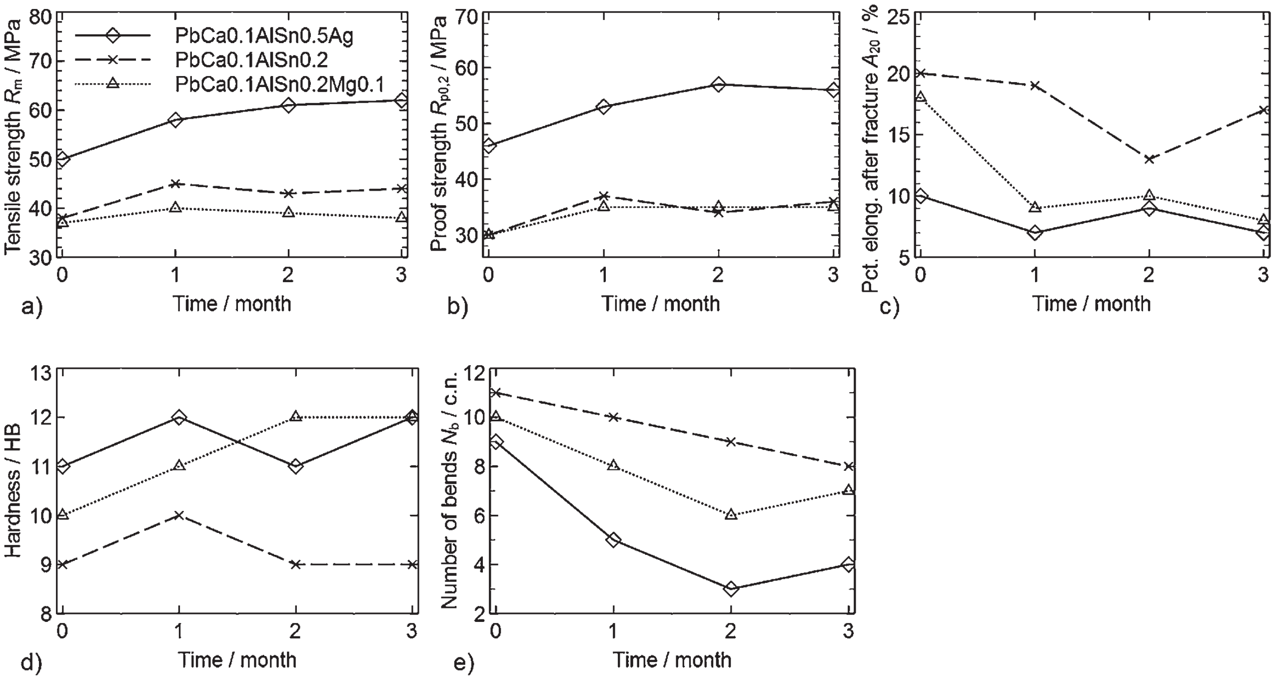


Figure 4 Influence of natural ageing on mechanical properties of PbCa alloys: a) tensile strength, b) proof strength, c) percentage elongation after fracture, d) Brinell hardness, e) number of reverse bends

Table 1 **Mechanical properties of PbCa grade alloys**

Alloy	Tensile strength R_m / MPa	Proof strength $R_{p0.2}$ / MPa	Percentage elongation after fracture A_{20} / %	Hardness / HB	Number of reverse bends N_b
PbCa0,1AlSn0,5Ag	50	46	10	11	9
PbCa0,1AlSn0,2	38	30	20	9	11
PbCa0,1AlSn0,2Mg0,1	37	30	18	10	10

CONCLUSIONS

The presented examinations covered lead-calcium alloys, similar to currently applied for starting battery grids and battery cores, with chemical composition modifications. The modifications included concentration of tin and silver and magnesium additions.

The examined PbCa alloys have approxima-tely monophase microstructure consisting mainly of tin solid solution in the lead. The range between liquidus and solidus temperatures is limited, from 10 to 12 °C, and it is much-desired in grids manufacturing technology. The mechanical properties of mentioned alloys depend mainly on the amount of tin. Alloy additions, such as silver and magnesium, are not very significant, certainly, because of amount of these additions in alloy composition (below 0,1 %). PbCa alloys, which are exposed to the process of natural ageing (3 months) increase their strength, proof strength and hardness. Simultaneously, the plasticity (A_{20} and N_b) decreases.

Developed PbCa0,1AlSn0,5Ag alloy was tested in production of starter batteries. Currently, test batteries are examined in electrical and endurance tests.

Acknowledgments

The study was conducted as part of Innovative Economy Operational Programme's Research and Development Project 01.03.01-00-086/09-00 entitled "Advanced technologies for production of functional materials for conducting, conversion and storing of energy". The Project is co-financed from European Regional Development Fund resources as part of Innovative Economy Operational Programme, 2007-2013.

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Note: The responsible translator for English language is A. Matuga, Katowice, Poland