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SIGNIFICANT CHARACTERISTICS OF LEAD AND ALLOYS WITH ANTIMONY IN THE PRODUCTION OF SMALL ARMS AMMUNITION

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Summary: *The use of lead and its alloys is significant for military purposes (the production of revolver, handgun, rifle and other bullets). Bullets for small arms ammunition are mostly made of a two component alloy of lead and antimony. Bullets can be made only of lead/antimony alloy (lead bullets) or with a jacket (usually made of CuZn alloy) in which lead and antimony core is placed. Due to the specific purpose, the quality of lead and alloys with antimony must be high in order to provide the required ammunition characteristics: bullet velocity, accuracy (chemical composition and homogeneity of alloys), effects on the target (mass, shape, hardness), bullet weight (chemical components, type of alloys, density), pressure of powder gases (bullet hardness), the reduction of barrel lead process (chemical composition, hardness) ... This paper will present the results of the chemical composition (Optical emission spectrometry), hardness according to Vickers HV1 method and densities for two deliveries of refined lead and seven lead/antimony alloys. The obtained results present the characteristics of refined lead and lead/antimony alloys used for production of bullets for small arms ammunition, and are a good basis for designers of bullets for designing products and obtaining defined requirements.*

Key words: *lead, lead/antimony alloy, bullets for small arms ammunition, chemical composition, hardness according to Vickers HV1, density*

1. INTRODUCTION

The use of lead and its alloys with antimony is significant for the production of sheets, tapes, pipes, wires, batteries, plates for protection against radioactive radiation, chemical apparatus, lead paints, military purposes (production of rifle and other bullets)…

A two component alloy of lead and antimony is used for the production of small arms ammunition. Bullets can be made only from the lead/antimony alloy (lead bullets), or bullets with jacket (mostly of CuZn alloy), in which lead and antimony core is placed.

Lead is quite soft, ductile metal and can be cut with a knife.[1] Hardness according to Brinell is only 4 kp/mm^2, according to Vickers 5 N/mm^2 [3] and according to Mohs scale 1,5, yield strength is from 0,5 to 0,8 kp/mm^2, tensile strength from 1,1 to 1,9 kp/mm^2, contraction 100% and elongation up to 50%. It belongs to heavy metals, its density is 11,34 g/cm^3. The structure, as with other metals with a cubic face-centered crystal lattice, consists of polygonal grains with twins. The melting point is low, 327°C, so recrystallization after the deformation occurs already at room temperature. Therefore, hardening of lead by cold deformation is not possible. In the case of electrolityc lead, the grains growth occurs already at 100°C.

Antimony occurs in four allotropic modifications: a stable metallic form and three metastable forms (explosive, gray amorphous and yellow) [2]. Metallic antimony is a brittle, silvery, shiny-gray metal, of Brinell hardness 30-58 kp/mm^2, Vickers 30-60 N/mm^2 [3], according to Mohs scale its hardness is 3, tensile strength 11,4 MPa , density 6,68 g/cm^3 and a melting point of 630,5°C (at the same time, its volume decreases and when it solidifies, it increases). Elemental antimony has got a layered structure whose layers are consisted of joined, wrinkled, six-membered rings. Nearest and next-nearest neighbors form an irregular octahedral complex, where the three atoms in the same double layer are slightly closer than the three atoms in the next. This relatively dense packing is the cause of the high density (6,68 g/cm^3), but the por connection between layers leads to the low hardness and brittleness of antimony. [4]

Significant characteristics of alloys from which lead bullets and cores for small arms ammunition are made are chemical composition, hardness and density.

According to the recommendations, lead bullets and lead cores are made of refined lead and antimony.

The chemical composition of refined lead by grades is given in the Table 1. [5]

The chemical composition of refined antimony by grades is given in the Table 2. [6]

Lead and antimony alloys are denoted PbSbX , where the X refers to percentage content of antimony in the alloy in mass fractions, while the content of permitted impurities is conditioned by the basic standards for refined lead and antimony.

Lead-antimony alloys form a simple eutectic system (Figure 1.). The eutectic point is at 88,9% Pb + 11,1% Sb and 252°C. An α –solid solution rich in lead dissolves

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3,5% Sb at the eutectic temperature, and only 0,44% Sb at 100°C. The β-solid solution, rich in antimony, dissolves about 5% Pb at the eutectic temperature. The melting point of lead is lowered by the addition of antimony, and the melting point of antimony by the addition of lead. Since α- and β-solid solutions are separated primarily from the melt during cooling, and not pure metals, from Raoult's low does not apply.

Table 1. Composition of lead grades SRPS EN 12659 : in % (percentage mass concentration)

Designation	Lead content min.	ELEMENTS									
		Ag max.	As max.	Bi max.	Cd max.	Cu max.	Ni max.	Sb max.	Sn max.	Zn max.	Totally
PB990R	99,990	0,0015	0,0005	0,0100	0,0002	0,0005	0,0002	0,0005	0,0005	0,0002	0,010
PB985R	99,985	0,0025	0,0005	0,0150	0,0002	0,0010	0,0005	0,0005	0,0005	0,0002	0,015
PB970R	99,970	0,0050	0,0010	0,030	0,0010	0,0030	0,0010	0,0010	0,0010	0,0005	0,030
PB940R	99,940	0,0080	0,0010	0,060	0,0020	0,0050	0,0020	0,0010	0,0010	0,0005	0,060

Table 2. SRPS C.E1.200 :1988 Refined antimony in block – Technical conditions

Type	Designation	Sb min.	As max.	Pb max.	Fe max.	S max.	Totally remaining
1	Sb 99,60	99,60	0,08	0,20	0,05	0,04	0,03
2	Sb 99,50	99,50	0,10	0,27	0,05	0,04	0,04
3	Sb 99,5	99,5	0,16	0,30	0,06	0,04	0,04

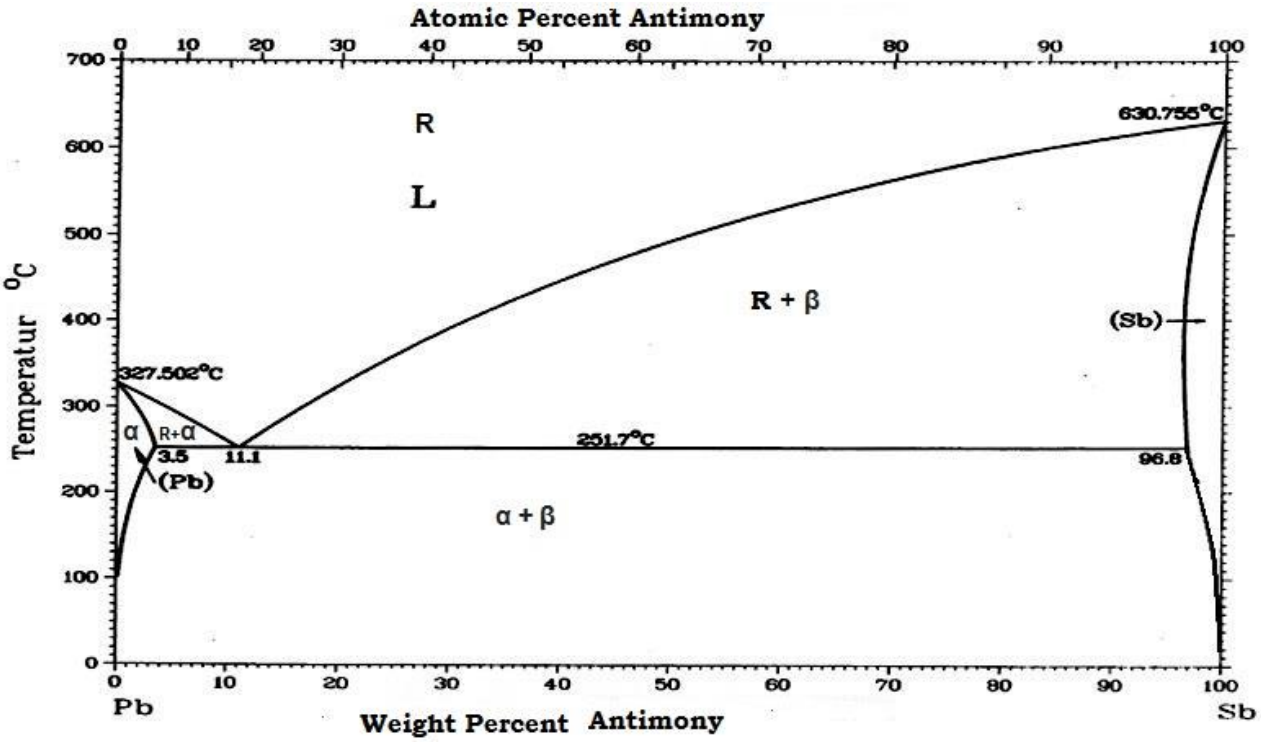

Figure 1. State diagram Lead - Antimony

On the state diagram of the lead-antimony, it should be understood that the left from 3,5% Sb is the α –solid solution with a separated β- precipitate, from 3,5 to 11,1% Sb primary α –solid solution and eutecticum (α + β), at 11,1 % Sb only eutecticum (α + β) , from 11,1 to 95% Sb β-solid solution and eutecticum (α + β) and from 95 to 100% Sb β –solid solution with a separate α- precipitate. In the phase field, the designation ''α + β'' refers only to type of crystals actually present. Nothing is said about their distribution and size i.e. whether it is a primary crystal, eutecticum or and the absolute amount. The alloy structure must be derived based on the course of crystallization.

The structural rectangle in Figure 2. provides data on the type and the amount of the structural components in an eutectic system. It shows that, in the case of equilibrium, the alloy with 50% Pb + 50% Sb contains 54% of eutecticum, 44% of primary β –solid solution and 2% of α- precipitate.

On the colling curves, separation of primary crystals gives an inflection point, and solidification of the eutectic melt, i.e. the rest of the melt, occurs at constant temperature gives wich is presented as a plate on cooling curve. Figure 3. shows a selection of various colling curves of the lead-antimony system. While pure lead (curve 1) and pure antimony (curve 5) show stoppage at a melting temperature of 327°C and 630°C, respectively, all hypoeutectic alloys have an inflection point, which shows the primary separation of α- solid solution (curve 2), and all hypereutectic alloys have an inflection point that shows the primary separation of β –solid solution (curve 4). All Pb-Sb alloys which contain Sb between 3,5 and 95% show stoppage at eutectic temperature of 252°C, caused by the solidification of the eutecticum (curves 2,3,4). The cooling curve for eutectic alloy shows change in cooling rate only during eutectic reaction which is illustrated as a plate. (curve 3). The length of the eutectic stoppage, assuming the same weight of the melt, is proportional to the amount of solidified eutecticum, so it is the largest in the eutectic alloy. [1]

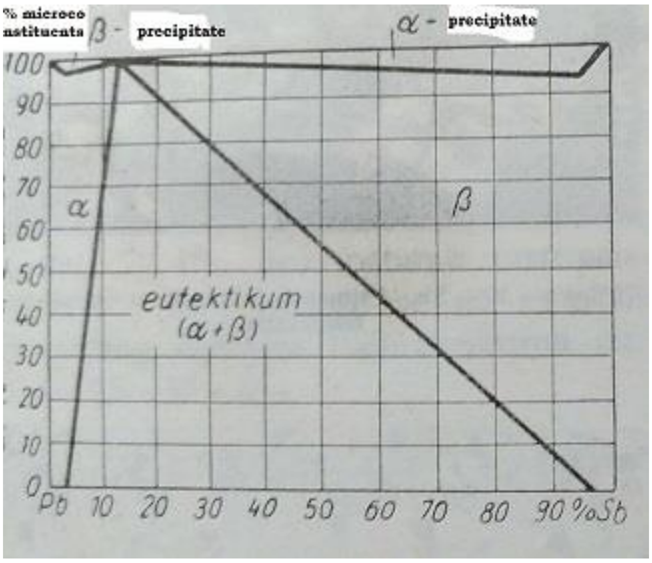

Figure 2. Structural rectangle of lead - antimony alloy

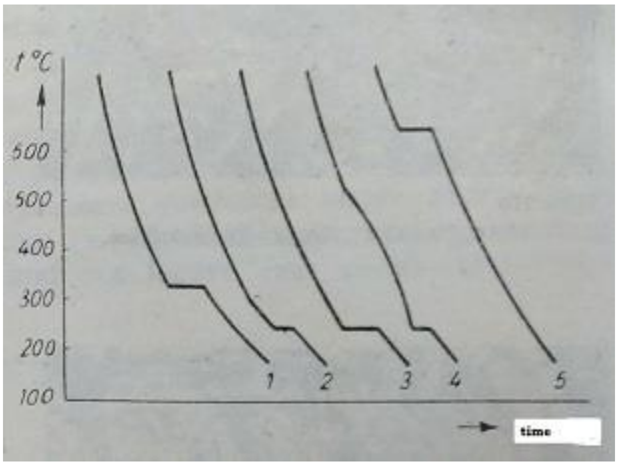

Figure 3. Cooling curves of lead-antimony alloys:
1 : 100% Pb, 2: PbSb5, 3: PbSb11, 4: PbSb60, 5: 100%Sb

2. EXPERIMENTAL PART

Determination of characteristics is performed on delivered samples (1,2,7,8,9), as well as on samples produced in our production (3,4,6) from refined lead and antimony (composition stated in Table 3.).

Table 3. Refined antimony for sample alloying 3,4,6
In % (percentage mass concentration)

Grades des.	Sb	As	Pb	Fe	S
Sb 99,60	99,67	0,002	0,109	-	-

Chemical composition of refined lead and PbSb*X* alloys is determine by the Optical emission spectrometry (OES) by spark excitation according to Standard SRPS ENV 12908 Lead and lead alloys – Analysis with optical emission spectrometry (OES) by spark excitation [7] on device *Spectro Maxx F LMX 06* .
For each sample, five to ten analyses have been performed, based on the quantity delivered, and on different samples.

Determination of hardness of refined lead and antimony, as well as their alloys, was performed in accordance with Standard SRPS EN ISO 6507-1:2018 – Metal materials – Vickers hardness test method - Part 1: The testing method [8] with HV1 load on device *Falcon 500 Inova Test.* The hardness is tested on five separate samples, two places for each sample, meaning that there were ten measurements for each sample with a known chemical composition. Determination of density of the samples was performed according to the Standard ISO 2781 : 2018 – Rubber, vulcanized or thermoplastic [9], by the method A: sample weight and the mass of water equal to the volume of the sample is determined using a balance with a spring (the accuracy 0,0001 g). The apparent mass of tested sample once immersed in water is less than the sample weight in air by the mass of water displaced, where the volume of displaced mass of water is equal to sample volume for testing. The test sample was free of cracks and dust, and weighed at least 2,5 grams. For all samples of refined lead, antimony and alloys, the measurement was performed on three different pieces.

3. RESULTS AND DISCUSSION

The results of chemical composition of refined lead and PbSb*X* alloys are given in the Table 4. The table shows the results of the mean content values with the corresponding standard deviation. From the obtained results, it can be concluded that the quality of refined lead is in accordance with requirements of the Standard, and that it corresponds to grade PB970R. PbSb*X* alloys in its chemical composition contain impurities in accordance with allowed content of impurities, which is determined by the impurities content of refined lead and antimony. In further analysis, it can be claimed that it's a binary PbSb*X* alloy, and that the influence of impurities can be disregarded. A very small standard deviation for all elements shows that all samples are homogeneous, i.e. the chemical composition is uniform.

The hardness results according to the Vickers method with HV1 load of refined lead and PbSb*X* alloys are given in the Table 5. The table shows results of mean hardness values with the corresponding standard deviation. The hardness of refined lead conform to theory according (to Vickers method – 5 N/mm^2 [3]). The obtained hardnesses

Table 4. Chemical composition of samples of refined lead and PbSbX alloys: Composition in % (percent mass concentration) / Standard deviation

Designation of sample	**Designation of material**	**Lead composition**	**Elements**									
			Ag	As	Bi	Cd	Cu	Ni	Sb	Sn	Zn	S
Sample 1	PB970R	99,979 0,0026	0,0017 0,00001	0,001 0,00012	0,0111 0,00006	<0,00005 0,000	0,00054 0,00014	0,00013 0,00001	0,001 0,00008	0,00028 0,0001	0,00013 0,00003	<0,0010 0,000
Sample 2	PB970R	99,977 0,0019	0,00058 0,00001	0,001 0,0014	0,0153 0,00006	<0,00005 0,000	0,00077 0,00041	0,00013 0,00002	0,001 0,00007	0,00033 0,0001	0,00047 0,00017	<0,0010 0,000
Sample 3	PbSb1,26	98,717 0,0172	0,0016 0,00005	0,0029 0,00021	0,0105 0,00013	<0,00010 0,000	0,0021 0,0026	0,00021 0,0001	1,26 0,0172	<0,00030 0,00001	0,00051 0,0008	0,002 0,00038
Sample 4	PbSb2,43	97,55 0,0412	0,0016 0,00007	0,0048 0,00017	0,0104 0,0001	<0,00010 0,000	0,0010 0,00015	0,00027 0,00005	2,43 0,041	<0,00030 0,000	0,00021 0,00005	0,0024 0,00046
Sample 5	PbSb4,48	95,50 0,028	0,0019 0,00003	0,0011 0,00028	0,0115 0,00008	<0,00010 0,000	0,00041 0,00004	0,00042 0,00007	4,48 0,0028	<0,00030 0,000	0,00019 0,00001	0,0019 0,00016
Sample 6	PbSb6,57	93,39 0,10	0,0018 0,00003	0,0137 0,00018	0,0102 0,00012	<0,00010 0,000	0,00077 0,00002	0,0002 0,00009	6,57 0,10	<0,00030 0,000	0,00024 0,00001	0,0028 0,00022
Sample 7	PbSb9,1	90,84 0,0385	0,0014 0,00001	0,0012 0,00015	0,0054 0,00004	0,00048 0,00003	0,0391 0,00021	0,0032 0,00009	9,1 0,0381	<0,00030 0,000	0,00029 0,000	0,0019 0,0004
Sample 8	PbSb11,06	88,92 0,182	0,0022 0,00052	0,0014 0,00023	0,0131 0,0019	<0,00010 0,000	0,00076 0,00046	0,00043 0,00009	11,06 0,185	<0,00030 0,000	0,00029 0,00002	<0,0010 0,00007
Sample 9	PbSb12,45	87,52 0,795	0,0026 0,00019	0,0079 0,0014	0,0052 0,00025	0,00019 0,000	0,0046 0,0001	0,0016 0,0001	12,45 0,794	<0,00030 0,000	0,00029 0,00002	<0,0010 0,000

Table 5. Hardness HV1 and density (g/cm3) of samples

Designation of sample / Designation of material	HV1 / δ	ρ(g/cm^3) /δ
Sample 1 PB970R	4,67 / 0,07	11,354 / 0,014
Sample 2 PB970R	3,32 / 0,18	11,3337 / 0,022
Sample 3 PbSb1,26	8,60 / 0,48	11,1978 / 0,065
Sample 4 PbSb2,43	10,38 / 0,42	11,145 / 0,030
Sample 5 PbSb4,48	14,08 / 0,53	10,983 / 0,029
Sample 6 PbSb6,57	14,41 / 0,66	10,9515 / 0,179
Sample 7 PbSb9,1	15,10 / 0,43	10,7714 / 0,156
Sample 8 PbSb11,06	13,1 / 0,57	10,503 / 0,0377
Sample 9 PbSb12,45	16,77 / 1,0	9,954 / 0,122
Refined antimony Sb 99,60	68,8/4,71	6,65/0,038

for tested samples of 3,32 and 4,67 N/mm^2 confirm this. Although by chemical composition they belong to the same 970R group, differences in hardness values were obtained for different deliveries.. These differences may be the result of the chemical composition (different content of impurities affect the course of crystallization in microvolumes), the origin of the refined lead (whether it's obtained from ores or recycling process), technological production process (cooling speed and other conditions of lead crystallization)...

In order to answer the question about differences in hardness of two tested samples of refined lead, it would be nessesary to know all information about lead production. Since no complete information is available it is only possible to speculate .

Therefore, this information must be kept in mind in the process of designing and manufacturing of bullets for small arms ammunition. In the production process of bullets for small arms ammunition, the chemical composition of refined lead and antimony is controlled, and based on it, the criteria for the raw materials acceptance for alloy production is carried out, in order to obtain alloys with the required characteristics.

The hardness of PbSbX alloys increases by increasing antimony content (Figure 4. curve 1), until at the eutectic point (11,1 % Sb) occurs decrease in hardness, and after that, the hardness continues to increase. The hardness of the alloy depends on the type and quantity of structural components of the alloy, their distribution and size, i.e. whether it is a primary crystal, eutectic or precipitate. The structure of the alloy must be derived based on the course of crystallization. The structural rectangle in Figure 2. provides data on the type and quantity of structural components in a eutectic system.

The increase in hardness with an antimony content of up to 3,5% (α-solid solution with separated β-precipitate) is significant and the hardness increases from about 5 N/mm^2 to about 12 N/mm^2. The increase in hardness with antimony content from 3,5 to 11,1 % (primary α - solid solution and eutectic (α + β)) is insignificant and increases from 14,08 HV1 (Sb content 4,48 %) to 15,10 HV1 for an antimony content of 9.1%.
Hence, when added twice the amount of antimony, the hardness increases by only one HV1 hardness unit.

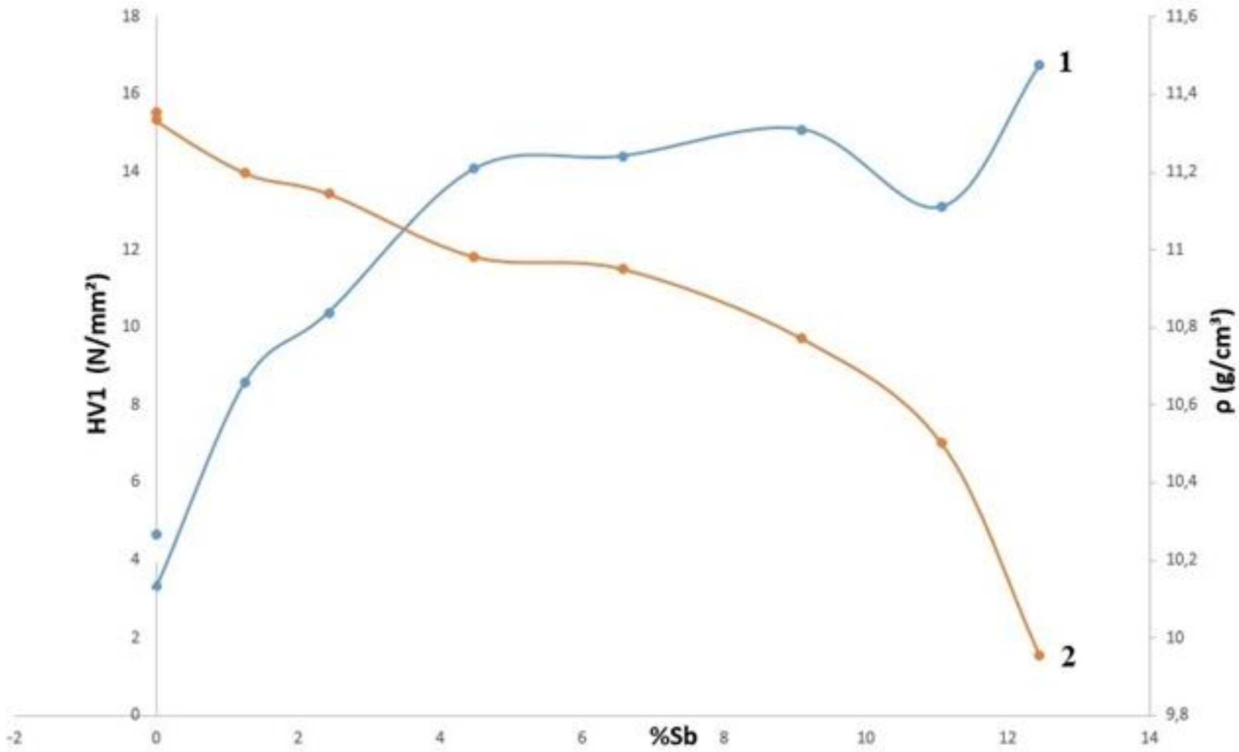

Figure 4. Dependence of Vickers hardness HV1 (curve 1) and density (curve 2) on antimony content obtained in this research

If the hardness of the alloy is an important characteristic for the product, it is recommended that no more than 5% antimony be added to the alloy, as this will result in twice as much antimony being consumed and very little influence on hardness.

To achieve the highest optimum hardness, it is recommended to provide an alloy with 4 to 5% antimony. At the eutectic point (only eutectic ($\alpha + \beta$)), there is a drop in hardness, due to the structure of the alloy that is being produced, that is the reason why is not recommended to make alloys that are in the zone around the eutectic point (10,5 to 11,5 % Sb). After the eutectic point, with the antimony content increase, the hardness of the alloy increases (12,45% Sb – hardness 16,77 HV1). Due to the high price of refined antimony (five to seven times more expensive than lead), there is a stand that it is not economically viable to produce alloys with antimony contents higher than 11,5% since it produces small increase in hardness.

The results of the densities of refined lead and PbSbX alloys are shown in Table 5., and the average density values with related standard deviation are provided. The obtained results for the density of refined lead match the literature value 11,34 g/cm^3 [1] (11,3337 and 11,354 g/cm^3). Small differences (in the second decimal place) probably come from the presence of impurities that are within the limits prescribed for refined lead. The obtained results for the density of refined antimony coincide with the literature value of 6,68 g/cm^3 [2] (6,65 g/cm^3).

With an increase in the antimony content in the alloy, the density of the alloy decreases due to the addition of alloying antimony with a lower density than the base metal, which is shown in Figure 4. - curve 2. As the bullet mass or core of small arms ammunition are directly dependent on the density of the alloy, also taking into account other requested requirements for the product, alloys can be selected during the product design phase and later during manufacturing in accordance with the previously determined alloy characteristics.

CONCLUSIONS

In this research are determined chemical composition, hardness according to the Vickers HV1 method and density for two shipments of refined lead and seven lead/antimony alloys. Based on the obtained results, the conclusions are as follows:

1. The quality of refined lead is in accordance with the requirements of Standard SRPS EN 12659 and corresponds to type PB970R. The quality of the refined lead corresponds to the recommendations for the bullet production and bullet core for small arms ammunition.

2. PbSbX alloys in their chemical composition have an impurity content in accordance with the permitted impurity content, which is determined by the impurity content of refined lead and antimony. The influence of

impurities can be ignored, and all other analysis were performed with assertion that it is a binary alloy PbSbX.
3. The hardness of refined lead is in accordance with the theory (according to Vickers 5 N/mm^2).

The obtained results for hardness of tested samples of 3,32 and 4,67 N/mm^2 confirm this, but also indicate that there are differences for different deliveries even though they belong to the same PB970R group according to their chemical composition. In the process of bullet production of small arms ammunition, the chemical composition of refined lead and antimony is controlled and based on it the acceptance of raw materials for alloy production is carried out. The hardness of the initial raw materials also affects the characteristics of the alloys and should be defined and determined in the raw material verification process, in order to obtain alloys with the required characteristics..
4. The hardness of PbSbX alloys increases with the increase in antimony content (Figure 4.), until in the eutectic point (11,1% Sb) occurs decrease, and after that, the hardness continues to increase. The increase in hardness with an antimony content of up to 3,5% (α-solid solution with a separated β-precipitate) is significant and the hardness increases from about 5 N/mm^2 to about 12 N/mm^2.
The increase in hardness with antimony content from 3,5 to 11,1 % (primary α -solid solution and eutectic (α + β)) is insignificant and increases from 14,08 HV1 (Sb 4,48 %) to 15,10 HV1 (Sb 9,1%). Meaning, when added twice the amount of antimony, the hardness increases by only one HV1 hardness unit.

At the eutectic point (only eutectic (α + β)), there is a drop in hardness due to the structure of the alloy that is being produced. After the eutectic point (11.1% Sb), by increasing the antimony content in the alloy (β-solid solution and eutectic (α + β)), the hardness of the alloy increases (16,77 HV1 – 12,45% Sb).
5. The obtained results for the density of refined lead match the literature value of 11,34 g/cm^3 (11,3337 and 11,354 g/cm^3).
6. Obtained results for the density of refined antimony match the literature value of 6,68 g/cm^3 (6,65 g/cm^3).
7. By increasing antimony content in the alloy, the density of the alloy decreases (Figure 4.) due to the addition of alloying antimony with a lower density (6,68 g/cm^3) from the base metal. As the bullet mass or core of small arms ammunition is directly dependent on the density of the alloy, alloys can be selected in the product design phase based on the determined density dependence of the antimony content in the alloy.

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