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# EVALUATION OF IMPURITIES INFLUENCE ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ZINC ALLOYS

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## ABSTRACT

This paper presents especially the results of microstructure and mechanical properties investigation results of selected zinc (Zn) and zinc alloys (ZnAl15). In the frame work of this paper were performed investigations of the microstructure using light and scanning electron microscopy as well as analysis of the chemical composition of the tested materials, there are also carried out. The investigations were performed on samples of pure Zn as well as of zinc-aluminium alloy ZnAl115 with the chemical composition conforming with the commercial standard concerning especially the yield strength obtained after chemical composition modification and the measurement of the impurities amount as well as the hardness and microhardness of the tested commercially available and modified Zn alloys. The presented tests results carried out using light microscopy allowed the determination of the microstructures obtained after the production process of materials from pure zinc and selected zinc alloys.

**Keywords:** Zinc alloys, microstructure, microhardness, recycling, alloying additives.

## 1. INTRODUCTION

Zinc is one of the heavy metals that types (from Z1 to Z5) are covered by the standard BS EN 1179: 1998. Depending on the manufacturing method of (eg. rectified, electrolytic, refined steel or secondary) these alloys can be contaminated with varying amount of impurities include Pb, Cd, Fe, Cu, As, Sb and Sn mainly that promotes hot cracking during the forming and intergranular corrosion.



Zinc and its alloys belong to the group of non-ferrous metals, in which iron is not a major component and may be most alloying element. They can be divided into three main groups: light metals (Al, Mg, Ti) and their alloys, heavy metals (Zu, Zn, Ni, Sn, Pb, Cd) and their alloys and metals and alloys with lower use of (Co, Zr, Mo, W, Cr, Mn, Pd, Ag, Au, Pt one). The classification of non-ferrous metals and their alloys is presented in Figure 1.

The main components of commercial available zinc alloys are: aluminium, copper, and in less amounts manganese. The basic groups of the zinc alloys include zinc-aluminium, zinc, aluminium and copper, zinc, manganese and copper, zinc, copper and titanium, and other alloys. The last two groups are used seldom in the industry and are almost not widespread. Most alloys can be used for casting or moulding processes. Alloys containing more than 5.4% are recognised as casting cast aluminium alloys only [1-10].

Zinc-aluminium alloys are the most common used of all zinc alloys, and are also most thoroughly investigated. Zinc-aluminium alloys with a concentration of 3 to 30% Al, are called "znal", they contain further up to 5% Cu and 0.006% Mg. These alloys exhibit the structure of eutectoid  $\beta$  solid solution (Al with Zn) and  $\alpha$  (Zn with Al), which should be interpreted on the basis of the Zn-Al equilibrium diagram (Figure 2). Eutectoid transformation causes contraction of the alloy and the dimensional changes also causes aging the alloy at room temperature, even extending over several years. To prevent this negative there is used up to approx. 0.1% Mg addition, which affect the increase in resistance of Al Zn alloys to intergranular corrosion [18-20].

## 2. INVESTIGATION METHOD

The investigations were performed on samples of tree pure Zn castings as a reference value, as well as of four zinc-aluminium ZnAl15 alloy with the chemical composition conforming with the commercial standard, presented in Table 1 and 2. The added elements were iron, copper, magnesium and cadmium in amount up to ca. 0.03 wt. % as presented in table 1. The material for the investigation was provided in the form of a wire having a diameter of 3 mm and a length of 80 mm, 130 mm and 180 mm respectively, subjected to cold working consisting in pulling. The ZnAl cast signed as 609007<sup>1)</sup> was additionally heat treated, composed of homogenising in a chamber furnace during 6h at a temperature of 250 °C [11,14-17].

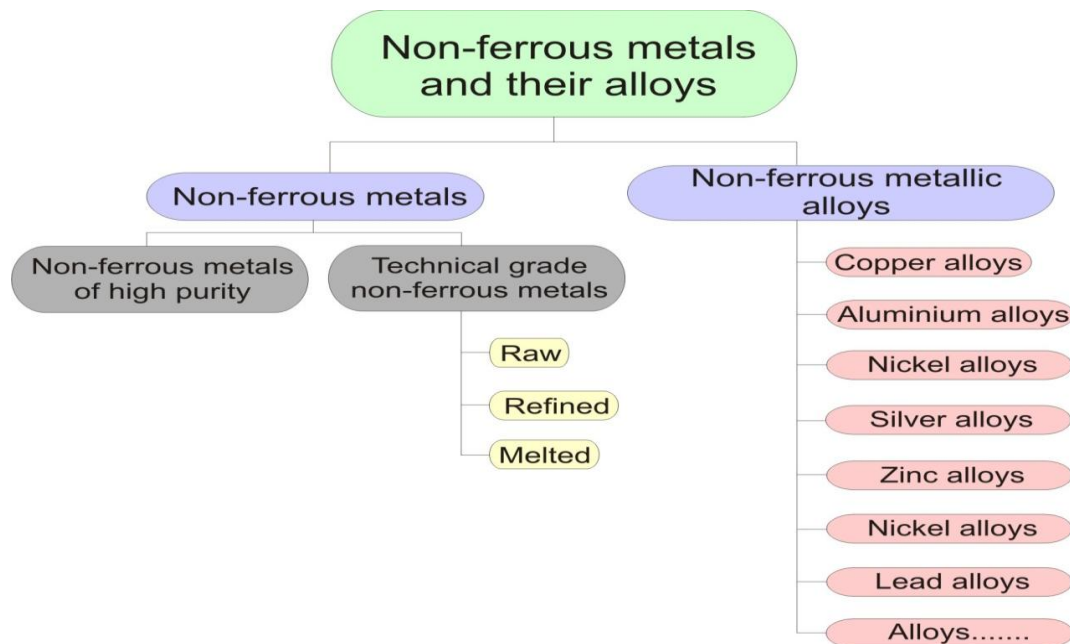
Observation of the microstructures of the tested materials were performed using light microscopy F-My supplied by Olympus at magnifications in the range of 50-1000 times, as well as a scanning electron microscope Zeiss Supra 35 at an accelerating voltage of 20kV. Analysis of the chemical composition was performed using a ARL3460 spectrometer. Static tensile strength test were performed on an universal testing machine Test Gmbh according to the polish standard [12]. Microhardness measurements were performed by Vickers hardness tester according to the standard [13] on the device Galileo Isoscan. The measurements were performed with a load of 1,961 N with 10 indentations for one measurement result.

## 3. INVESTIGATIONS RESULTS

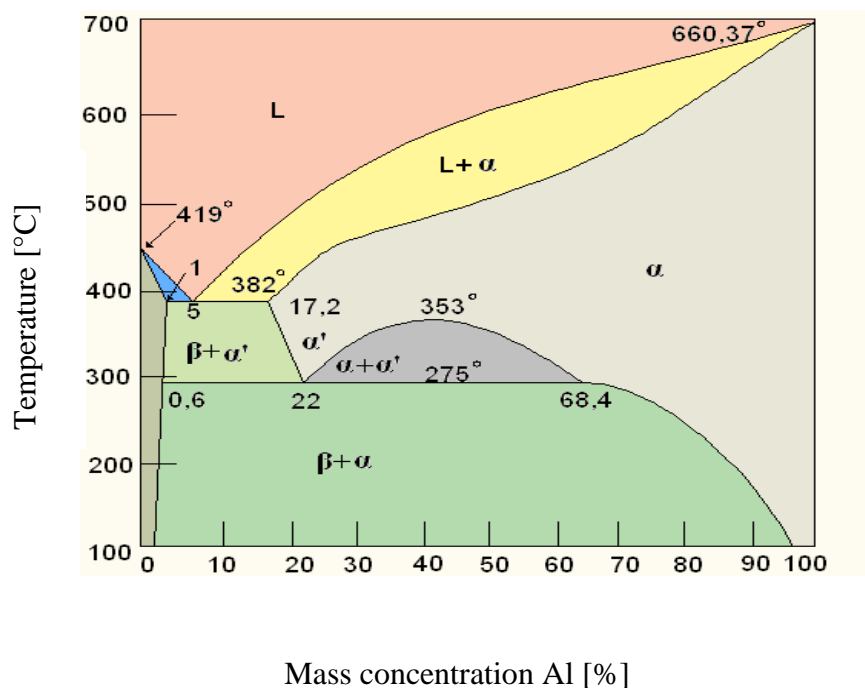
By mind of the carried out analysis based on the light microscope structure investigations, it was found, that the microstructure of Zn is characterized by relative large irregular grains (Fig. 3), with the size in the range up to 50  $\mu$ m while the ZnAl15 alloys have a microstructure consisting of smaller grains (Fig. 4). The most dangerous – in terms of properties deteriorations - contaminants present in the zinc are Pb and Sn, because they form a triple low-melting-temperature eutectic (Zn+Pb+Sn), which precipitates at the grain boundaries (Fig. 3). While the ZnAl15 alloys are composed of two compounds: the  $\eta$  solid solution, and eutectic ( $\eta + \alpha$ ). The  $\eta$  solid solution is a terminal solid solution of aluminium in zinc. The  $\alpha$  eutectic is distributed in areas of the  $\eta$  solid solution. In the dendrites there are present at the room temperature some minor secondary separation of the  $\varepsilon$  phase and alternating  $\alpha$  phase which have precipitated as a result of changes in the solid state (Fig. 4). The  $\alpha$  phase is converted during the eutectoid transformation and therefore they observed as not uniform precipitations and are coloured dark during etching. Small additions of Mg to the ZnAl15 alloys cause a delay of the eutectoid decomposition of the  $\alpha$  phase, but these additions does not stop this decomposition. Whereas the addition of Cu accelerates the eutectoid decomposition. Tables 1 - 2 show the chemical composition of the



tested alloys. ZnAl15 zinc alloys containing up to 15% of Al in the group of middle range Al-containing alloys (8 to 18% of Al). Figures 3 - 7 show the microstructure of the investigated materials: zinc and its ZnAl15 alloys.



**Fig 1:** Classification of non-ferrous metals and its alloys [16,17]



**Fig. 2:** Equilibrium diagram Zn - Al [1]

**Table 1.** Classification of zinc and its alloys – according the material group and chemical composition [15]

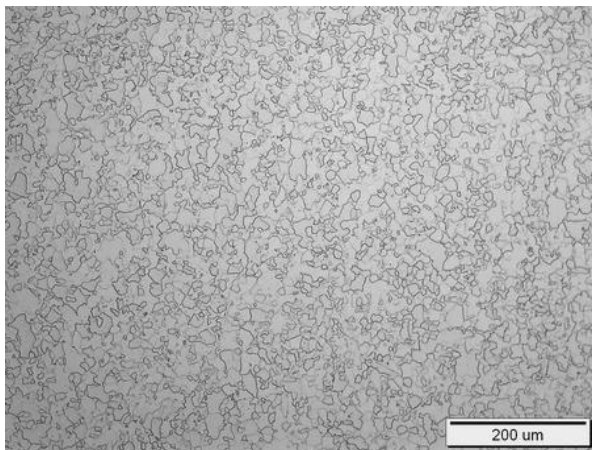
Alloy type	Amount of the alloying additives, mass %		Acceptable additives, mass %			
Zn99,99	Zn	min 99.99	total Pb Cd Pb+Cd	≤ 0.001 ≤ 0.005 ≤ 0.005 ≤ 0.006	Sn Fe Cu balance	≤ 0.001 ≤ 0.003 ≤ 0.002 ≤ 0.12
ZnAl15	Zn	84 - 86	total Pb Cd Pb+Cd	≤ 0.17 ≤ 0.005 ≤ 0.005 ≤ 0.006	Sn Fe Cu balance	≤ 0.001 ≤ 0.05 ≤ 0.01 ≤ 0.12
	Al	14 - 16				

**Table 2.** Chemical composition of the analysed pure zinc and zinc-aluminium alloy

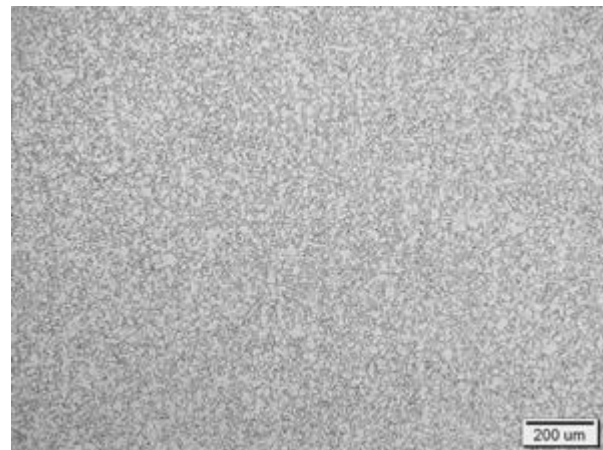
Chemical composition of the investigated alloys, wt. %										
Casting sign 033										
Cast 1	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	99.995	0.0007	0.0014	0.0012	0.0009	0.0005	0.00019	0.0001	0.0001	0.0001
Casting sign 036										
Cast 2	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	99.996	0.0008	0.0004	0.0013	0.0008	0.0005	0.00019	0.0001	0.0001	0.0001
Casting sign 037										
Cast 3	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	99.997	0.0003	0.0004	0.0003	0.0003	0.0009	0.00011	0.0001	0.0001	0.0001
Casting sign 108										
Cast4	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	99.997	0.0007	0.0005	0.0003	0.0003	0.0006	0.00016	0.0001	0.0001	0.0001
Casting sign 609005										
Cast5	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	85.86516	14.10214	0.02777	0.00242	0.00188	0.00035	0.0001	0.00019	-	-
Casting sign 609006										
Cast 6	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	85.9281	14.04744	0.01976	0.00179	0.00224	0.00038	0.00012	0.00016	-	-
Casting sign 609007										
Cast 7	Zn	Al	Fe	Pb	Cu	Cd	Mg	Sn	As	Ti
	85.5884	14.37212	0.02821	0.00178	0.00839	0.00045	0.0001	0.0001	-	-



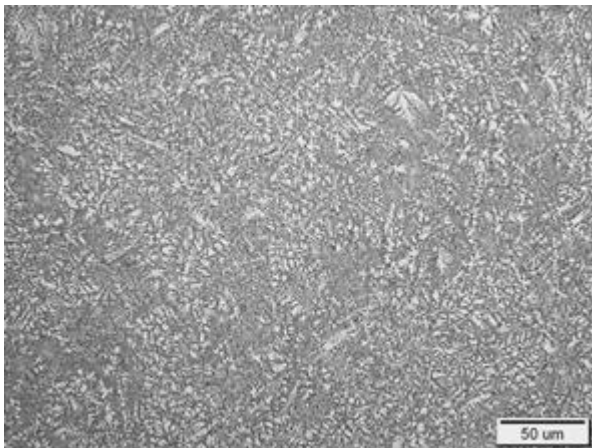
Based on the observations of fracture in a scanning electron microscope it was determined the fracture type of the samples after the static tensile test at room temperature and the effect of the alloying elements on the fracture type. It was found that after the decohesion in a tensile test, all Zn samples and ZnAl15 alloy samples are characterised with a regular (circular) cross-section (Figs. 8 and 9a). Zn samples are characterized by a mixed fracture with a predominance of brittle fracture share (Figs. 8 and 9b). At the fracture of the Zn samples were observed craters and fracture planes with sharp surfaces of the brittle fracture type with visible edges. The ZnAl15 zinc alloy Fig. 10b) is characterised by a ductile fracture.



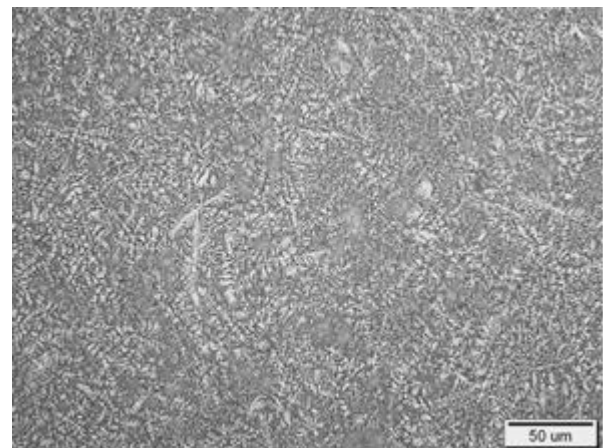
**Fig.3:** Grained microstructure of the Zn alloy, casting 037



**Fig. 5:** Grained microstructure of the Zn alloy, casting 037



**Fig.4:** Microstructure of the ZnAl15 alloy casting 609005 - dendrites of the  $\eta$  solid solutions, eutectics ( $\eta+\alpha$ )

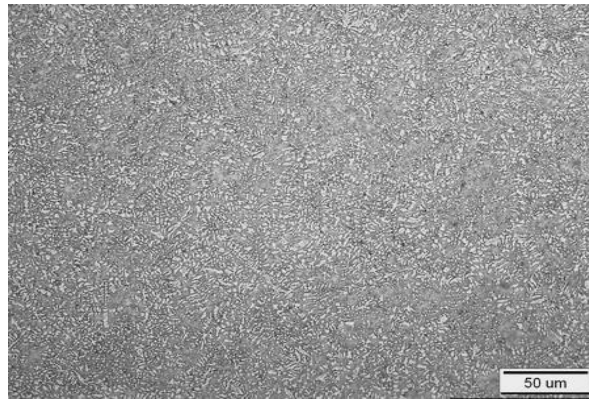


**Fig.6:** Microstructure of the ZnAl15 alloy casting 609007 - dendrites of the  $\eta$  solid solutions, eutectics ( $\eta+\alpha$ )

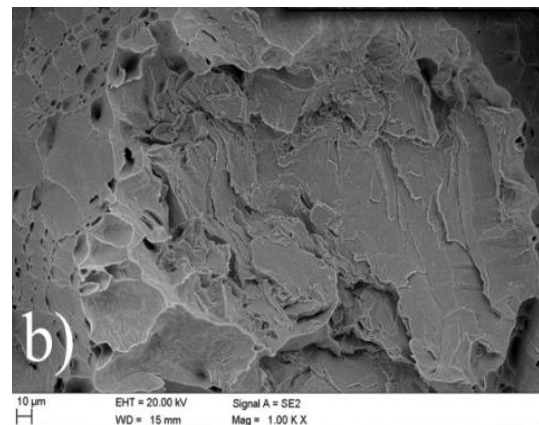
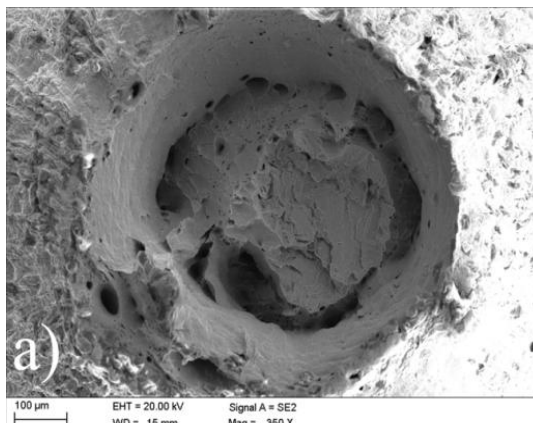




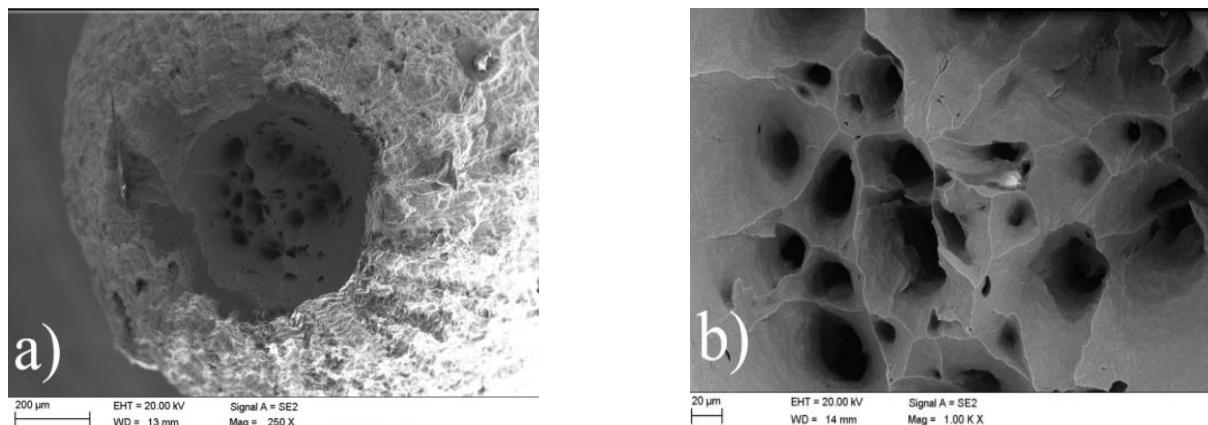
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**Fig.7:** Microstructure of the ZnAl15 alloy casting 609007 - dendrites of the  $\eta$  solid solutions, eutectics ( $\eta+\alpha$ )

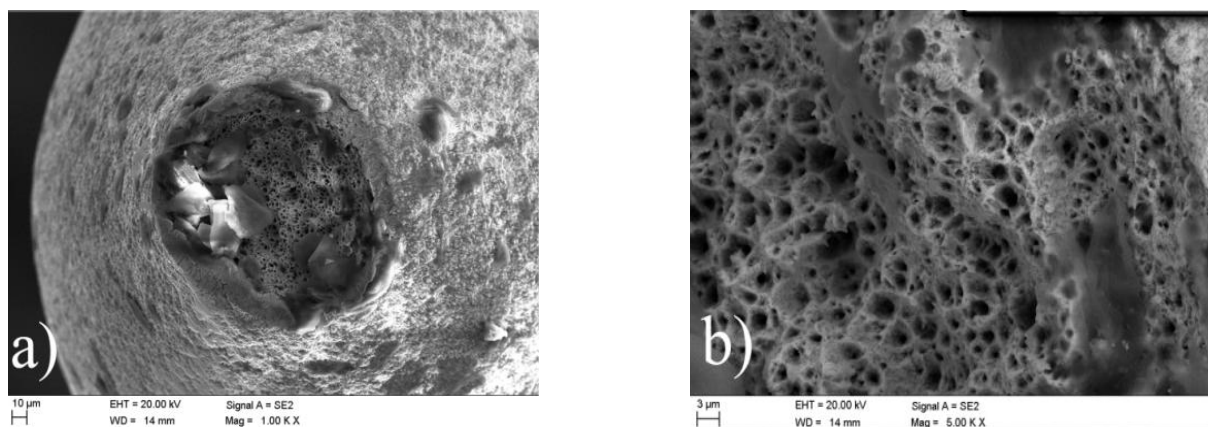


**Fig. 8:** Fracture of the Zn sample after strength test, casting 033, a) break in the areas of large elongation, b) mixed fracture with higher brittle fracture share



**Fig.9:** Fracture of the Zn sample after strength test, casting 108, a) break in the areas of large elongation, b) mixed fracture with higher brittle fracture share

Microhardness test results made it possible to determine the effect of alloying elements on the tested zinc and zinc alloys. The highest microhardness (HV ) was measured for the zinc casting 033, which has the highest addition of Mg, Cu and Fe, and the lowest value was determined for zinc casting 037.



**Fig. 10:** Fracture of the Zn sample after strength test, 609006, a) break in the areas of large elongation, b) ductile fracture, craters on the break surface

Together with the increase of the cadmium content the microhardness of the Zn alloys decreases. The higher content of Cd addition and lower Cu content reduces the microhardness of the Zn alloys 108. The values of microhardness are showed in Tables 3 and 4.

The statistic tensile strength test was performed on a universal testing machine TEST GMBH in accordance with DIN EN 10002-1, Metals - Tensile testing - Part 1: The method of the test was carried out at room temperature. For the test were used a wire-shaped material having a diameter of 3 mm and a length of 180 mm. The test parameters are presented in Table 5.

The results of the static tensile tests allow a determination the effect of alloying elements on the mechanical (Rm) and plastic (A) properties of the zinc and its alloys, and in the case of melt 6,090,071) the effect of temperature in the heat



treatment process involving annealing. The test results of mechanical properties of zinc and its alloys are shown in Tables 6 and 7 and Figs. 11-14.

On the basis of carried out investigations it was found that the highest mechanical properties (Rm) have the pure zinc samples 033 and 036, which have a high content of impurities of Mg, Al, Cu and Fe, and the highest mechanical properties (Rm) has the zinc alloy 037 which has a low content of admixtures of these elements (Fig. 11-14).

The elongation is respectively for melting: 108 - 76% 033 - 44% 036 - 87% and 037 - 45%. In the ZnAl15 zinc alloys the highest mechanical properties (Rm) has the sample (6070071), not only because of the high percentage of impurities to amounts of Mg, Al, Cu and Fe, as in the case of pure zinc samples (033 and 036), but also due to the performed heat treatment, consisting of annealing of the rolled material for 6h. The best mechanical properties has the zinc alloy ZnAl15 609006, which has a low percentage of impurities and, in particular 14.04744% Al compared with 609,005 (14.10% Al) and 609 007 (14.37% Al). The results of the elongation test of the ZnAl15 zinc alloys exceeding 100% may indicate the over-plasticity related to the reduction of structural deformation during the strength test. In addition, it can be seen that the heat treatment of the 609007 cast has increased the mechanical properties and decrease of the plasticity compared to other castings.

**Table 3.** Microhardness test results of the pure Zn

Casting	Average microhardness, HV 0.2	Standard deviation	Max value	Min value	Average error
<b>033</b>	41.2	0.3	42.7	40.2	0.62
<b>036</b>	40.9	0.39	42.5	39.0	1.05
<b>037</b>	35.9	0.26	36.9	34.7	0.41
<b>108</b>	39.3	0.15	39.9	38.6	0.14

**Table 4.** Microhardness test results of the alloy ZnAl15

Casting	Average microhardness, HV 0.2	Standard deviation	Max value	Min value	Average error
<b>609005</b>	28.9	0.12	29.4	28.5	0.07
<b>609006</b>	27.2	0.87	29.1	23.5	3.42
<b>609007</b>	28	0.18	28.7	27.4	0.14
<b>609007<sup>1)</sup></b>	40.2	0.08	40.5	39.8	0.04

**Table 5.** Parameters of the static testing strength test

Parameters	Value
Load range, [kN]	0.5 ÷ 1.5
Traverse speed, [mm/min]	8.75

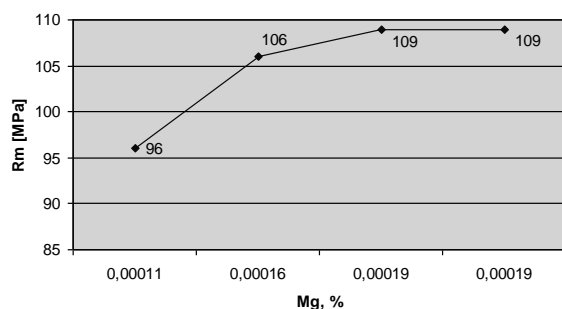
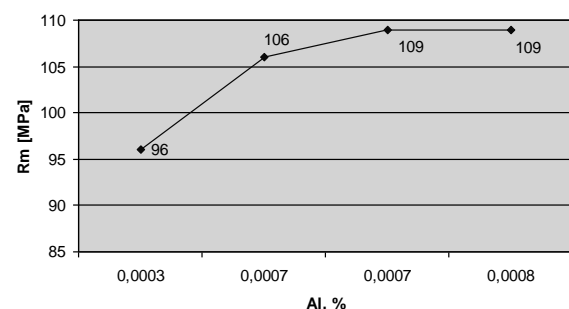


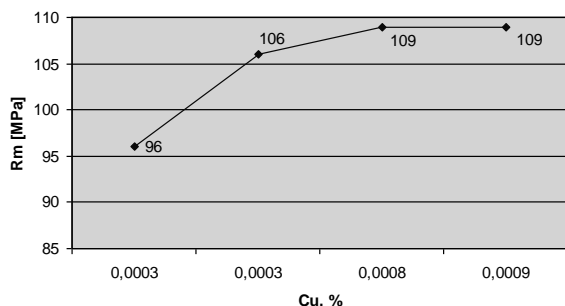
**Table 6.** Investigation results of the mechanical properties of pure Zn

Zinc						
Cast	Sample dimensions				Mechanical properties	
	nominal	measured	L <sub>0</sub>	L <sub>t</sub>	$\overline{Rm}$	A
	d					
	mm	mm	mm	mm	N/mm <sup>2</sup>	%
037	3.00	2.97	100	180	96	45
033		2.97			109	44
036		2.97			109	87
108		2.96			106	76

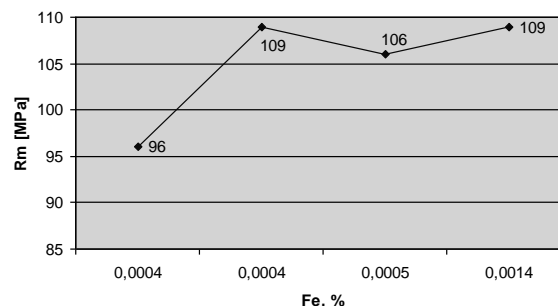
**Table 7.** Investigation results of the mechanical properties of ZnAl15 alloy

ZnAl15						
Cast	Sample dimensions				Mechanical properties	
	nominal	measured	L <sub>0</sub>	L <sub>t</sub>	$\overline{Rm}$	A
	d					
	mm	mm	mm	mm	N/mm <sup>2</sup>	%
609005	3.00	2.96	100	180	126	140
609006		2.96			100	200
609007		2.96			105	187
609007 <sup>1)</sup>		2.96			185	117

**Fig. 11:** Influence of the Mg addition on the yield strength ( $R_m$ ) of the zinc casts: 033 (96 MPa), 036 (109 MPa), 037 (106 MPa) i 108 (106 MPa).**Fig. 12:** Influence of the Al addition on the yield strength ( $R_m$ ) of the zinc casts: 033 (96 MPa), 036 (109 MPa), 037 (106 MPa) i 108 (106 MPa).



**Fig. 13:** Influence of the Cu addition on the yield strength (Rm) of the zinc casts: 033 (96 MPa), 036 (109 MPa), 037 (106 MPa) i 108 (106 MPa).



**Fig. 14:** Influence of the Fe addition on the yield strength (Rm) of the zinc casts: 033 (96 MPa), 036 (109 MPa), 037 (106 MPa) i 108 (106 MPa)

#### 4. CONCLUSIONS

The presented tests results carried out using light microscopy allowed the determination of the microstructures obtained after the production process of materials from pure zinc and selected zinc alloys. The observations made using the scanning electron microscope revealed that the decohesion after the static tensile strength test the investigated materials are characterized by a regular (circular) fracture. Pure zinc is characterized by the predominance of mixed fracture with the dominance of brittle fracture areas, whereas the zinc alloys reveals rather a ductile fracture. Based on the analysis of the chemical composition determined the chemical composition of the tested materials, stating their compliance with respect to the chemical composition included in the commercial standard [12-13]. The highest microhardness of the tested Zn and ZnAl15 reveals samples with the addition of Mg, Cu and Fe, further it was found that, in the tested Zn and ZnAl15 alloys there is a negative effect of Cd on the microhardness, revealing its decrease.

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