ARCHIVES
of
FOUNDRY ENGINEERING

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (1897-3310)
Volume 14
Special Issue
4/2014

77 – 82

16/4

Characteristic of Cast Zn-Al-Cu Alloy Microstructure after Modification

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Received 20.11.2014; accepted in revised form 12.12.2014

Abstract

Cast zinc alloys have similar properties to aluminium alloys. The differences are due to the lower melting point and higher density. Zinc has a density of 7.14 g/cm^3, a melting point of 419.5 °C and the boiling temperature of 906 º C. In the temperature range from 150 to 200 °C, zinc has good susceptibility to plastic deformation. It is also resistant to atmospheric factor influence, but is not resistant to acids. The main use of zinc alloy, is the production of thin-walled casts that require high precision. Zinc alloys are also used for die casting moulds, housings and covers as well as a variety of devices that are used in the precision industry, electrical engineering, automotive and construction industry.

Properly performed chemical modification leads to improve of properties of the produced castings. Therefore it is very important to know how the cast structure with the change of the chemical composition by adding metallic modifiers to the liquid metal.

In this work there was studied the effect of chemical modification of cast zinc alloy on the properties and microstructure of the alloys before and after modification. Modified alloys were prepared by adding modifiers in the range of 0.1% to 1% in form of Ti- Sr and B as aluminium master alloy and then cast into the metal moulds. Next the thermo-derivative analysis was performed of the modified Zn-Al-Cu alloy, the microstructure investigation was carried out using light microscopy and scanning electron microscopy with EDS X-ray microanalysis usage as well as hardness was measured of the modified Zn-Al-C alloys.

Keywords: Innovative cast materials and technologies, metallography, modification, cast zinc alloys, microstructure

1. Introduction

The main problems associated with zinc alloy production technology is their tendency for gassing and oxidation, and also the occurrence of a coarse-grained dendritic structure in slowly solidifying castings. Due to the occurrence of the phenomenon of dendritic microsegregation and the stability of the structure there is observed a heterogeneity of the obtained properties. In order to improve the quality of liquid metal, that provide after casting to the mould with no metallic precipitates and gas bubbles and the formation of the desired cast structure, ensures high and stable mechanical properties, there is applied special modification [1-5].

The main use of zinc alloy, is the production of thin-walled castings that require high precision. They have found its appliance also for die casting elements, housings and covers for a variety of devices that are used in the industry for precision elements, electrical engineering (computer panels, enclosures typewriters, automotive and construction industry (materials for building construction, solar panels). The application increases with development of the production and processing technology. Important advantage is receiving the material from scrap, during recycling, which is currently very important due to the increasing usage of natural resources. These alloys are characterized by a higher casting speed rate, which increases even 10 times the life of the moulds. Therefore zinc alloys are recognised as a material suitable for small volume production of castings. For manufacturing of cast zinc alloy there are usually used the technology of pressure die casting [1, 2, 3].

Copper is recognised as the main alloying addition of zinc alloy, which affects the increase of strength, hardness and corrosion resistance. The addition of Cu shifts the eutectic point in the Zn-Al-Cu system towards a higher Al content. Cu addition increases also the susceptibility of the Zn-Al alloys for aging and connected with this dimensional changes. This has little effect on the transformation of the eutectoid $\beta(\beta')$ phase and solubility changes in the solid state at low temperatures, but above all of the phase transitions in the solid state with the participation of the hexagonal η phase, with cubic face centred $\beta(\beta')$ phase, hexagonal ε ($CuZn_4$) phase and hexagonal τphase (intermetallic phase CuZn3). This transformation is the main reason for the dimensional changes. For occurrence of the τ phase there is necessary a content of 0.6-0.7% Cu in the alloy [1, 2, 5].

Investigations concerning the development of an optimum chemical composition and method for producing zinc - aluminium alloys modified with rare earth metals, having enhanced properties compared to elements produced using traditional methods and alloys, will contribute to a better understanding of the mechanisms underlying the improvement of functional properties of the newly developed alloys.

Currently there are used modified alloys with strontium and antimony, because these modifiers are the long-term acting. The effect of strontium is maintained after many remelting processes of the alloy, which enables to produce alloys, which modified are in-situ in foundries. There are also increasingly used also rare earth metals to modify the cast alloys investigated in this paper.

Properly carried out chemical modification and the appropriate cooling of casts leads to improvement of the functional properties of the produced castings. Therefore it is very important to know how the cast structure changes according to the cooling rate or the change of chemical composition by adding modifiers to the liquid metal.

2. Material and investigation methodology

The zinc-aluminium-copper alloys were made with addition of the master Ti-B alloy and Sr. The mass concentration of aluminium is in the range from 8.04 to 11.27%, and this of copper in the range of 0.68 to 1.09%. The casts were made in a resistance furnace in chamotte - graphite crucibles. The casts were casted into metal moulds.

In order to investigate the mass concentrations of alloying elements Ti-B, chemical analyses of the investigated alloys was performed in accordance with the procedure ICP OES on the device ULTIMA 2 Jobin-YVON in a specialized laboratory for chemical analyses.

Material for investigations of the chemical composition was prepared in the form of chips produced from the material cast into the mould. The mass concentration of the various additives is in case of Ti - B in the range from 0.022 to 0.58%.

The samples for thermo-derivative analysis were prepared with a diameter of Ø30 mm and a height of 35mm. There have also been made holes for thermocouples, in the samples were the thermal node occurs for this type and arrangement of the sample geometry. The investigated samples were characterized with a mass of 160 g ± 3 g for this type of geometrical dimension.

The thermo-derivative analysis for the modified alloys was carried out in graphite crucibles (Fig. 1) using the metallurgical UMSA simulator (Universal Metallurgical Simulator and Analyzer) with software for control and calculations. Temperature measurement was performed using K-type thermocouples (Fig. 2, 3)

Fig. 1. a) Graphite crucible, b) Working chamber of the UMSA device: 1 –thermocouple, 2 – tested sample, 3 – induction coli, 4 – ceramic isolation

In order to determine the relationship between the crystallization kinetics of the alloy and the chemical composition and microstructure of cast zinc alloy Ti-modified B and Sr, the following investigations were performed:

- Thermo-derivative analysis using the UMSA device equipped with a computer-controlled cooling system, which allows to set flexible the cooling rate applied of the Zn-Al-Cu alloys.
- Microstructure and chemical composition investigations using EDS microanalysis on the scanning electron microscope Zeiss Supra 25.

- Alloy structure using MEF4A optical microscope supplied by Leica together with the image analysis software as well electron scanning microscope using Zeiss Supra 25 device within high resolution mode.
- The examinations of thin film's microstructure and phase identification were made on the high resolution transmission electron microscope Titan 80-300 from FEI with the scanning mode STEM.
- Hardness of the modified Zn-Al-Cu alloys - using the Rockwell hardness tester supplied by Zwick ZHR 4150,

4. Investigation results

Preliminary investigations have shown a beneficial effect of modifications on the microstructure and macrostructure of the alloy after modification. Addition of master alloy causes homogenisation of the structure (Fig. 4, 5). Investigations with the use of scanning electron microscopy using EDS X-ray microanalysis and confirmed the presence of Ti and Sr in the structure of the modified Zn-Al-Cu alloy. The results of diffraction investigations using a high resolution transmission microscope confirm the presence of the phase $(AlTi)_2B$ (Fig.4-7) and the presence of Al_2Sr phase (Fig. 7). On Figures 8 and 9 there are showed structure of the Al-Zn-Cu-Ti-B alloy in the bright and dark fields mode. In Figure 10 there is presented the solution of the diffraction pattern from Figure 11. Modification of the investigated alloy causes an increases of hardness of the Zn-Al-Cu-Ti-B alloy in comparison to the Zn-Al-Cu alloy (Fig. 13), which confirms the wear resistance investigation made using the ball on plate method.

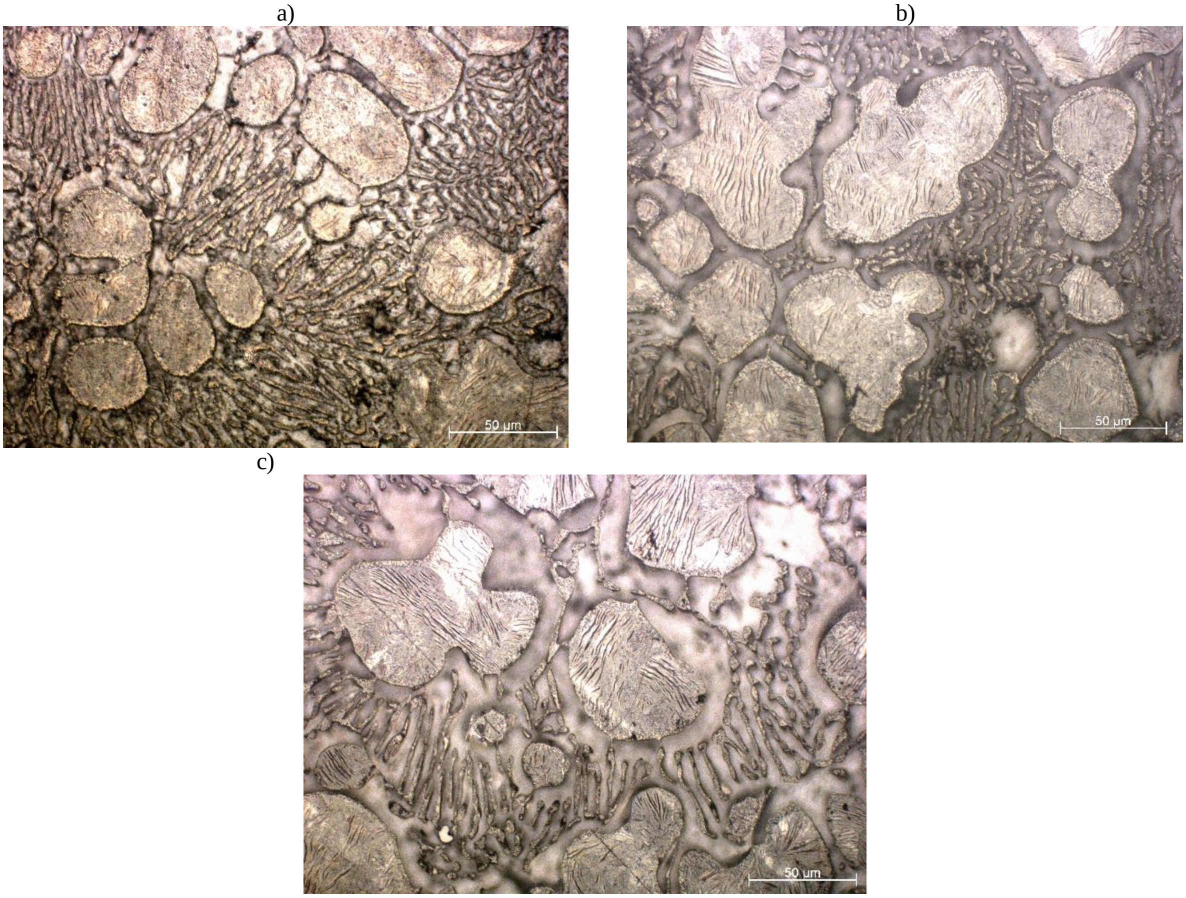
a)
b)
c)

Fig. 2. Microstructure of the Zn-Al-Cu alloy;a) alloy without modification, b) modified alloy with Ti-B,c) modified alloy with Sr

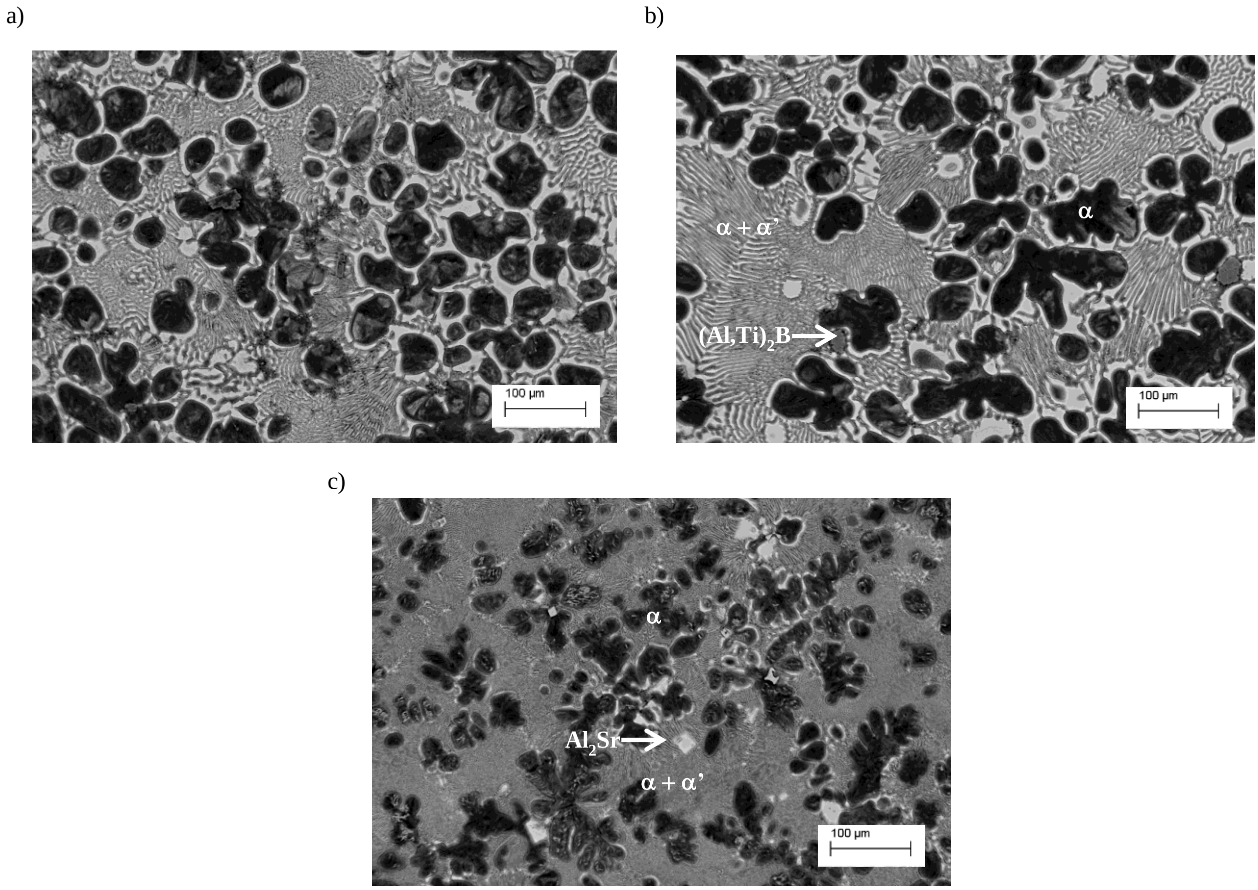

Fig. 3. Microstructure of the Zn-Al-Cu alloy; a) alloy without modification, b) modified alloy with Ti-B, c) modified alloy with Sr

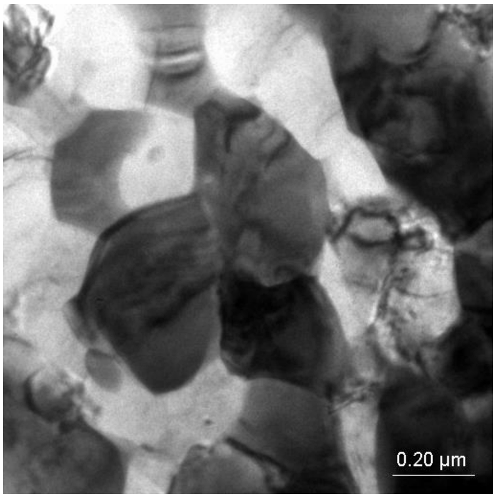

Fig. 4. Structure of the cast alloy Zn-Al-Cu-Ti-B, bright field image, TEM

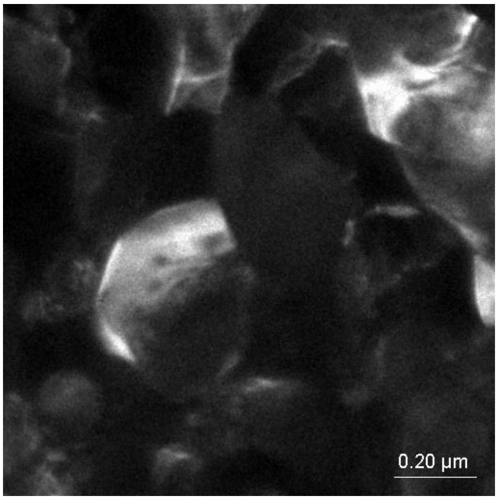

Fig. 5. Structure of the cast alloy Zn-Al-Cu-Ti-B, dark field image, TEM

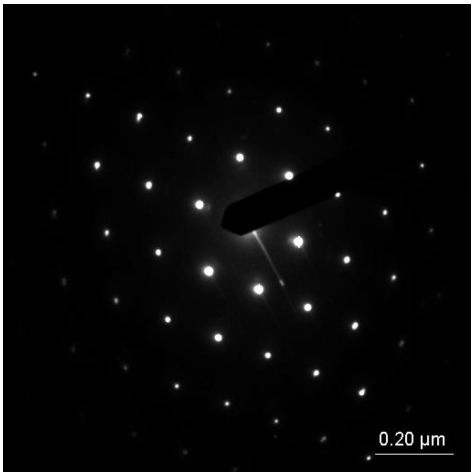

Fig. 6.Diffraction pattern from Fig. 4

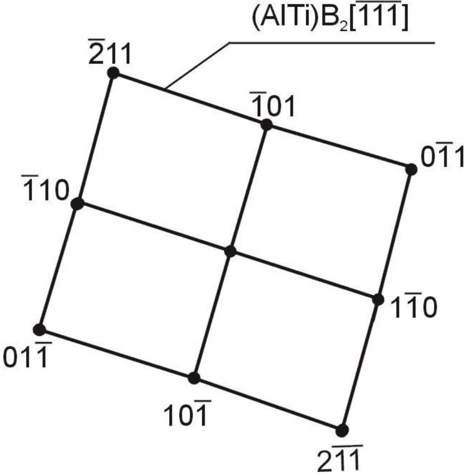

Fig. 7. Solution of the diffraction pattern from Fig. 6

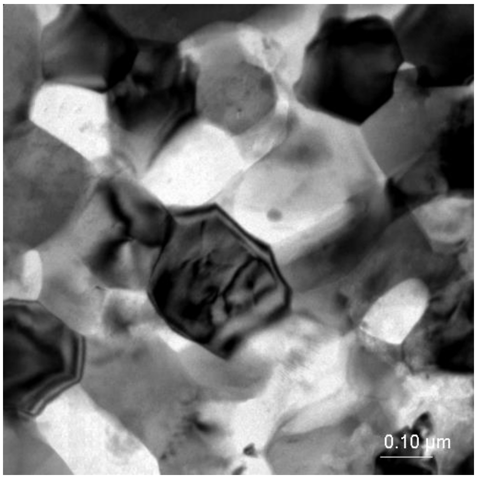

Fig.8. ZnAlCuSr alloy, bright field, TEM

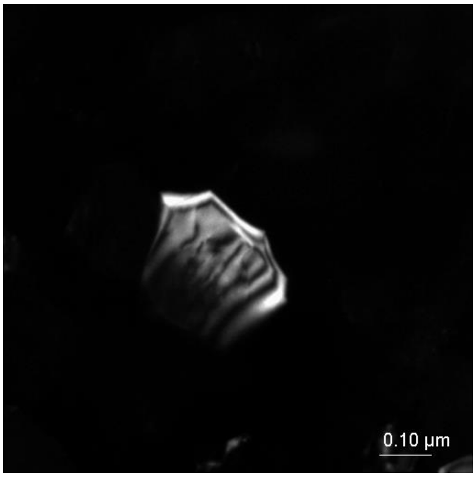

Fig. 9. ZnAlCuSr alloy, dark field, TEM

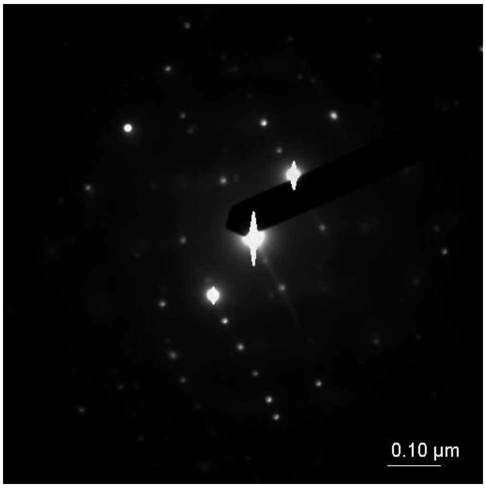

Fig. 10. Diffraction pattern of Fig 8

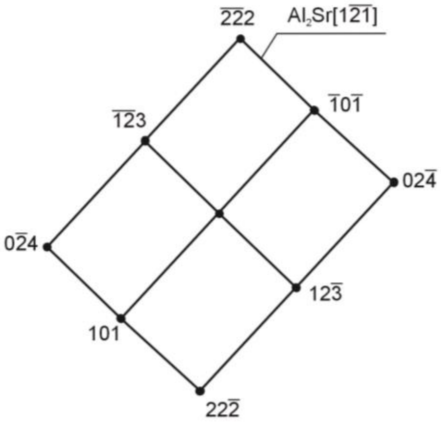

Fig. 11. Solution of the diffraction pattern of Fig.10

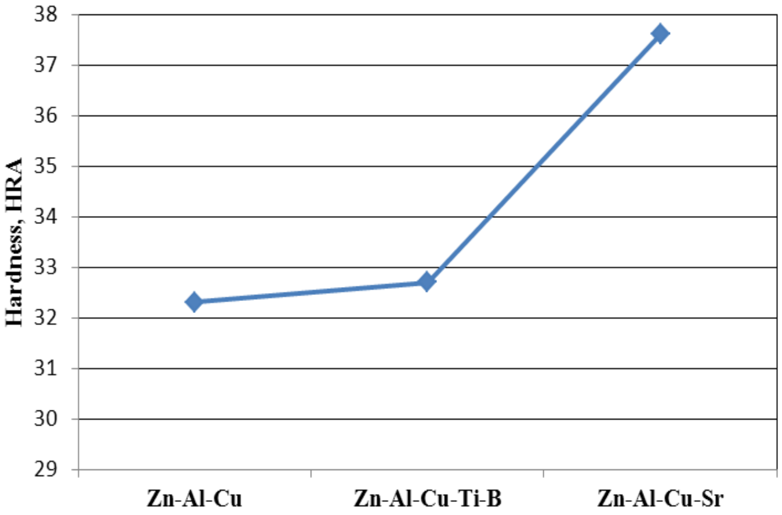

Fig. 12. Results of the hardness measurement of the base alloy Zn-Al-Cu, modified with Zn-Al-Cu-Ti-B and Zn-Al-Cu-Sr

5. Conclusions

The addition of Ti-B and Sr to the alloy Zn-Al-Cu causes modification of the structure (by its modification of grains and subgrains refinement, what is consistent with the available literature data). There are also visible changes in the morphology of Al dendrites, which before modification have expanded second row arms, and in their neighbourhood there appear precipitations.

Based on the performed transmission electron microscope investigations it was found that the microstructure reveal crystallites of the size of ca 100nm which are closely placed even to smaller ones. Investigations using the transmission electron microscopy confirmed also the occurrence of $(AlTi)_2B$ and the presence of Al_2Sr phase, what was proved especially based on the diffraction techniques, where the zone axis was determined as [111] for the $(AlTi)_2B$ phase and [1-2-1] for the Al_2Sr phase.

Modification of the investigated Zn-Al-Cu alloy causes an hardness increase. In Figure 12 there is showed the change in hardness of the unmodified Zn-Al-Cu alloy as well as modified Zn-Al-Cu-Ti-B and Zn-Al-Cu-Sr alloy. The calculated hardness average value based on the particular investigation results, is also characterized by a lower value of the standard deviation for the Zn-Al-Cu alloy modified with Ti-B and Sr.

Acknowledgements

The research was funded by the National Science Centre No. 2640/B/T02/2011/40 headed by Dr. Beata Krupińska.

References

[1] Skrzypek, S.J., Przybyłowich, K. (2012). *Engineering metals and their alloys*, Publisher AGH, Cracow

[2] Górny, Z., Sobczak J. (2005). *Non-ferrous metals based novel materials in foundry practice*, ZA-PIS, Cracow

[3] Krupińska, B., Labisz, K., Rdzawski, Z. (2012). *Light and electron microscope investigations of cast Zn-Al alloys*. Arch. Mater. Sci. Eng. vol. 55, nr 1, s. 29-36

[4] Krupińska, B., Labisz, K., Rdzawski, Z. (2011). *Crystallisation kinetics of the Zn-Al alloys modified with lanthanum and cerium*. -J. Achiev. Mater. Manuf. Eng. vol. 46 iss. 2, s. 154-160

[5] Krajewski, W. (2001). *Shaping the structure of Zn-Al alloys by doping with Zn-Ti master alloy*, St. Staszic University of Mining and Metallurgy, Faculty of Foundry Engineering, Cracow