

Effect of Titanium Alloying of Zn-Al-Cu Alloys for High Pressure Die Casting in Production Conditions

Łukasz Pasierb^{a*}, Jan Łakomski^a, Krzysztof Figurski^b 

^aSaga Poland, Guzowska 4, 96-515 Teresin, Poland

^bWarsaw University of Technology, Institute of Manufacturing Technology, Narbutta St. 85, 02-524 Warsaw, Poland

*e-mail: lpasierb@saga-mb.eu

© 2023 Authors. This is an open access publication, which can be used, distributed and reproduced in any medium according to the Creative Commons CC-BY 4.0 License requiring that the original work has been properly cited.

Received: 29 November 2023 / Accepted: 14 December 2023 / Published online: 15 December 2023.

This article is published with open access at AGH University of Science and Technology Journals.

Abstract

The paper presents the possibility of the industrial production of Zn4Al3Cu alloy with the addition of 0.41% Ti. Tests are described on the manner of introducing the ZnTi2 master alloy to the alloy, so that the chemical composition of the desirable elements proportion is obtained. The chemical persistence of the Zn4Al3CuTi was determined as low in the conditions of the long heating of the alloy before casting. Tests on the microstructure and mechanical properties of the obtained alloys were also conducted. The strength of the die-cast Zn4Al3Cu alloy was 265 MPa and, when measured on samples taken from the high pressure die-cast, it reached 369 MPa. It was determined that the addition of titanium to the Zn4Al3Cu alloy causes significant refinement of the structure and contributes to the formation of intermetallic phases.

Keywords:

HPDC, zinc alloys, titanium additives, microstructure, mechanical properties

1. INTRODUCTION

Owing to their favourable casting and utility properties, foundry zinc alloys are employed in a wide range of applications. They demonstrate a relatively low melting temperature and, consequently, a low casting temperature and good castability. They are used particularly frequently in pressure casting. In zinc alloys, the main alloying additives are aluminium and copper, with small quantities of magnesium, manganese, iron, nickel, zirconium and titanium.

The addition of titanium to zinc alloys produced by pressure casting may have a varying degree of influence on the properties of the alloy. Titanium may introduce a change in the mechanical properties, such as increased tensile strength, hardness, wear resistance of the die-cast zinc alloy [1]. Titanium may also contribute to the reduction of the alloy's susceptibility to hot cracking during solidification, improving its castability and reducing faults in the final product [1–4]. Additives of titanium may increase strength at high temperatures and the stability of die-cast zinc alloy, ensuring that it is more suitable for applications where higher temperatures are the problem.

In zinc alloys, titanium may also act as grain refiner. Grain refinement involves adding some elements, often in small amounts, in order to facilitate the creation of finer and evenly

spread grains in the alloy microstructure by heterogeneous nucleation. Titanium has a high preference to oxygen and easily forms titanium oxides. When titanium is added to the molten zinc alloy, those titanium oxides particles are the spots of heterogeneous nucleation. During the cooling process and solidification, these particles create spaces around which zinc solidifies. As solidification begins, multiple little grains compete for space, constraining the growth of other grains. Such competition additionally contributes to the formation of a fine-grained microstructure. Finer grains usually offer higher strength and increased wear resistance in comparison to larger ones. The effectiveness of titanium as a grain refiner may depend on various factors, including the concentration of titanium in an alloy, solidification speed, cooling rate, and the presence of other alloying elements. Proper control over those factors is essential for obtaining the desirable grain refinement effect. Additionally, the specific mechanism of grain refinement may differ depending on the alloy structure and interaction among titanium and other elements in the alloy. For example, in aluminium alloys, titanium forms certain intermetallic compounds that additionally serve as effective nucleation spots [2, 5–7]. Titanium additive to zinc alloys may be analysed with the use of the phase equilibrium systems. In pure zinc, at ambient temperatures, titanium solubility is negligible and amounts to

about 0.02% by weight (Fig. 1) [8]. At the eutectic point, at the temperature of 418.6°C, its maximum solubility is at the level of 0.2% by weight. The above condition means that the addition of titanium as an alloying element causes solid solution hardening and Zn-Ti intermetallic phases hardening. The increase of the alloying element concentration leads to the formation of primary precipitates which are increasingly richer in titanium.

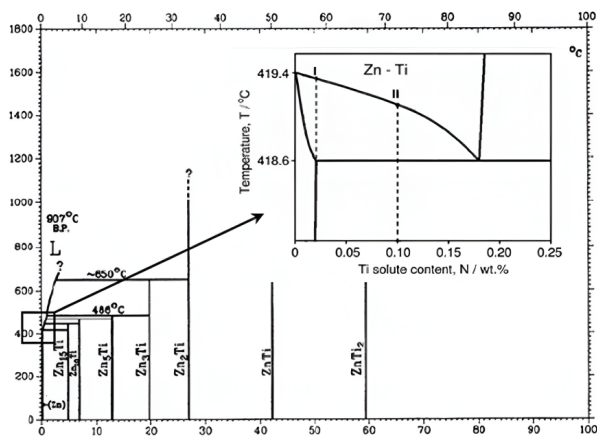


Fig. 1. Two-component Zn-Ti phase equilibrium system. The magnified part presents details of the zinc side [8]

Researchers have been interested in the Ti-Zn system for some years now, as Ti additives to Zn act as a grain refiner and they increase creep resistance in rolled alloys [9]. The solubility of Ti in Zn is estimated to be at 0.01% to 0.02% Ti at 300°C. It is assumed that the equilibrium phases are $Zn_{15}Ti$, $Zn_{10}Ti$, Zn_5Ti , Zn_3Ti , Zn_2Ti , $ZnTi$ and $ZnTi_2$. $Zn_{15}Ti$ phase is the richest Zn compound.

Adding titanium to a zinc alloy which includes Al and Cu in its composition gives a similar effect but the number of additional intermetallic phases formed is significantly higher. Taking into consideration the analysis of tables, including the standardised chemical composition of zinc alloys, in the tests Zn4Al3Cu alloy modified by titanium was taken into account due to, i.e., specialised literature available, where cases of such a modification are described. For example, in [10], what was tested was the influence of a modification on the change in the degree of refinement of the structure of zinc alloys of an average aluminium content. Tests were conducted on Zn alloy – 10% by weight of Al (ZnAl10), modified before casting to sand mould by an additive of modifying master alloy Zn – 3.2% by weight of Ti (ZnTi3.2). It was determined that the effect of a significant microstructure refinement is visible when titanium is added in the amount of 25 ppm, 50 ppm and 100 ppm. Modification by adding more titanium, i.e. 200 ppm and 400 ppm, does not result in the further refinement of α -dendrites (Al). In the paper [1], it was proven that the titanium additive is beneficial to distribution, strength, hot crack strength, and tightness of a two-component Zn-Al alloy (48% Al). Titanium causes the formation of $TiAl_3$ particles that form nuclei of crystallisation. However, too many $TiAl_3$ particles may result in segregation in the alloys and may reduce the effect of grain refinement. An analysis of the literature demonstrated that there were no structure modification tests conducted in commercial (multi-component) zinc alloys.

To sum up, adding titanium to zinc alloys may entail challenges in applications, both in terms of structures and properties obtained, as well as technological obstacles. Titanium has a higher melting point than zinc, so the alloy smelting characteristics may change. What is more, achieving the even distribution of titanium in the entire alloy may be difficult, and proper processing techniques are required to ensure such an even distribution. Additionally, typical alloying elements added to zinc, i.e., Al and Cu, also change the structure, nature and properties of the alloy. Therefore, precise benefits and results of titanium additives depend on particular composition, conditions of processing and designed application of the zinc alloy for die casting. It is absolutely crucial to carry out precise tests and analyses in order to optimise the alloy composition and processing parameters, particularly for industrial conditions.

2. ASSESSMENT OF ALLOYING POSSIBILITIES OF ZINC ALLOY FOR DIE CASTING

In order to conduct the tests, it was decided to prepare an Zn4Al3CuTi alloy that requires the addition of titanium to the alloy nominally 4% by weight of aluminium and 3% by weight of copper. Commercially available preliminary alloy ZnTi2 (master alloy) includes up to 2% of titanium by weight. Master alloys with a higher content of titanium are impossible to encounter due to the rapidly growing liquidus curve along the increase in titanium concentration. If the target titanium concentration in Zn4Al3CuTi alloy is 0.2 by weight, it approximately corresponds to the eutectic point. In order to achieve this scope, per each 10 kg of Zn4Al3Cu alloy, 1 kg of ZnTi2 master alloy needs to be added. This means the significant dilution of other alloy constituents down to values below the lower limit admissible by the standard. Within the tests, a procedure of preparation of liquid Zn4Al3Cu alloy with titanium additive was devised. The procedure is described below.

In order to compensate the components, a commercially available AlCu50 master alloy was used, consisting of aluminium and copper in equal parts by weight. The liquidus temperature of this alloy is 600°C, and the solidus line at its lowest eutectic point is 545°C. This means that, in order to effectively dissolve AlCu50 master alloy, the alloy temperature should be increased over 550°C. Liquid material preparation time is crucial to ensure appropriate process productivity. The hot-chamber HPDC machine is the most expensive component of the system, and that is why its performance affects the viability of the entire casting process. The amount of the alloy prepared has to consider the ongoing continued parts production. To achieve minimal down-time of the HPDC machine, the assumption of creating a dedicated alloy mixing station was made. In terms to make the alloying procedure as fast as possible, the decision to use an induction furnace was conducted. Therefore, a special melting station was prepared, including the induction furnace with the specially made PLC-based controller equipped with thermocouples inserted directly into the furnace crucible, to allow a full control of an alloy temperature and minimize the risk of burning out alloy components. Additionally, the induction heating technology offers the important advantage of the ability to mix the

material occasioned by magnetic field and convection in liquid, something which is especially useful in making modification of the alloy composition.

Tests during the pressure die casting of Zn4Al3CuTi alloys were conducted on a dedicated, specially made 8-cavity die. In each case, the casting cycle lasted for 20 s. The weight of castings with intake pass-through systems in the most demanding case achieved 700 g meaning that, with the assumed time of injection, there is a need to ensure 125 kg of material per hour of the casting machine's operations. With the induction furnace volume being efficiently 250 kg of alloy, alloying time of Zn4Al3CuTi could not exceed 2 h. The first tests conducted in line with the original procedure showed that preparation of one batch of alloy (from the input of feedstock to tapping of alloy) took about 5.5 h, what was not a satisfactory result. During the next tests, the alloying procedure was modified by changing the time of feeding the furnace. During the first optimisation, the base alloy was divided into two parts – the first one, about 80% by weight, for the initial alloying and subject to overheating, and the second one, about 20% of feedstock, to be added at the moment the dissolving of AlCu50 master alloy is over. This procedure results in a very rapid reduction of temperature from 550°C to the required level of 450°C, reducing the alloying time to about 4 h. The most time-consuming stage of the alloying procedure is the period of the overheating of the alloy and the dissolution of AlCu50 master alloy.

During the next technological tests, attempts were taken to obtain the alloy at a temperature not higher than 450°C. With the use of the casting machine furnace, tests of the rate of AlCu50 master alloy dissolution in 450°C were conducted. This time span may be shortened by using small fragments of the master alloy and the agitation of the alloy. During the tests, 2 cm × 2 cm × 4 cm pieces were used and an additional agitator operating at 0.5 r.p.s. was applied. The described conditions were: temperature of 450°C coupled with intense agitation enabled dissolution of added master alloy lumps within the time range of 2 h to 2.5 h. From the technological point of view, the time span is too long and it prevents the casting machine from operating in a continuous cycle. In order to accelerate the kinetics of the master alloy dissolution, its modification with the use of ZnTi2-AlCu50 alloy was proposed. Using an additional furnace, another pre-alloy was prepared, consisting of 50% by weight of ZnTi2 and 50% by weight of AlCu50. An exemplary photograph of the cast master alloy is presented in Figure 2.

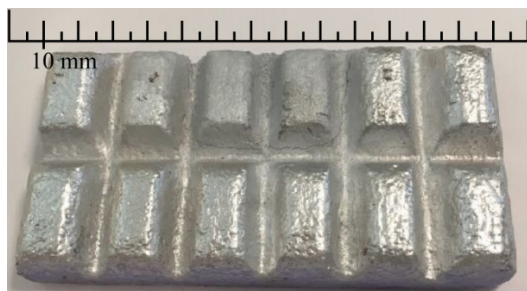


Fig. 2. Castings made of master alloy with chemical composition: 50% by weight of AlCu50 + 50% by weight of ZnTi2

Once again, the tests of alloying at the temperature of 450°C and with intense agitation began. The master alloy dissolved

within the time not exceeding 10 min, what translates into tenfold acceleration of the process. The above experiments were repeated at the tests with the use of the dedicated induction furnace, during preparation of Zn4Al3CuTi alloy. ZnTi2-AlCu50 master alloy was added already at the stage of the first furnace feeding, which means that at the moment of achieving the correct temperature and readiness to tap – it was already dissolved. The condition of agitation was also met during melting in the induction furnace, where intense movement of the alloy was occasioned by magnetic field and convection in liquid.

Tests conducted with the modified AlCu50 master alloy showed a significant possibility to shorten the alloying time. It was achieved by the modification of the master alloy and the complete elimination of the overheating stage. This solution shortened the total time of the alloy preparation to about 2 h, increasing productivity and at the same time simplifying the entire procedure of the Zn4Al3CuTi alloy preparation. The achieved total alloying time is also sufficient for ensuring the continuous supply of liquid alloy to a hot chamber casting machine, and by this its uninterrupted operation. Continuity of the process is essential element of the high-pressure die casting technology that enables achieving high performance and repeatability of casting parameters. An important aspect is also the elimination of alloy overheating and the excessive oxidation such overheating entails.

3. CHEMICAL COMPOSITION TESTS

Experimental smeltings of base alloy – Zn4Al3Cu – with the addition of titanium, were carried out. In order to increase the hardness of the alloy, copper was introduced in a form of AlCu50 master alloy and titanium was introduced in a form of ZnTi2 master alloy, in various weight proportions. Tests on the chemical composition of the experimental smeltings were conducted with the use of a Solar M6 atomic absorption spectrophotometer, with the results presented in Table 1.

Table 1
Chemical composition of testing smeltings of Zn4Al3Cu and Zn4Al3CuTi alloys

Alloy	Al	Cu	Ti	Zn
Zn4Al3Cu	4.91	2.78	0.005	Re
Zn4Al3CuTi	4.28	2.77	0.410	Re

The analysis of chemical composition of the material was carried out. The material had the form of samples taken after a specified period of time from a pre-heating furnace where the alloy with Ti additives was prepared. The diagram in Figure 3 shows that over time the content of essential alloying elements diminishes [11]. Additional protection against the oxidation of the metal bath should be taken into consideration. A particularly adverse effect may be caused by the fluctuations in copper and titanium alloy, as those elements are responsible for hardness and the stabilisation of mechanical properties while soaking castings during possible subsequent technological operations, e.g. cathodic coating.

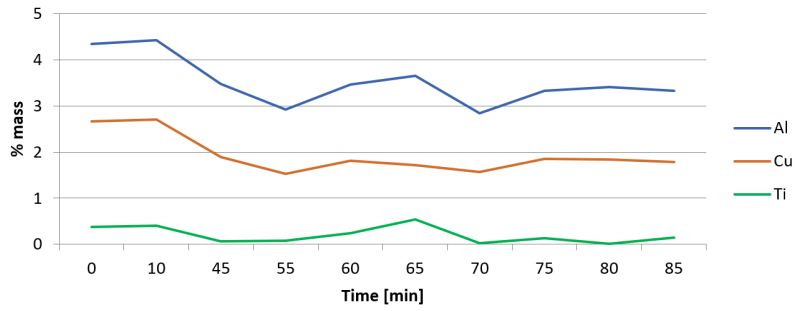


Fig. 3. Change in the content of selected elements in Zn4Al3Cu alloy over the time in a pre-heating furnace

4. MICROSTRUCTURE ANALYSIS

Tests of macrostructure, microstructure and phase composition were carried out on samples cut out of ingots of chemical composition of Zn4Al3Cu and of a pressure die-cast of Zn4Al3CuTi chemical composition. The tests were carried out with the use of a FEI Scios FEG high-resolution scanning electron microscope equipped with a thermal field-emission

electron gun and with additional X-ray microanalysis system (EDS) and electron backscatter diffraction system (EBDS). At this stage of testing, none of the particular microstructure components were characterised. Only a significant influence of titanium as a structure refining element was determined. The microstructures obtained during the tests are shown in the Figure 4.

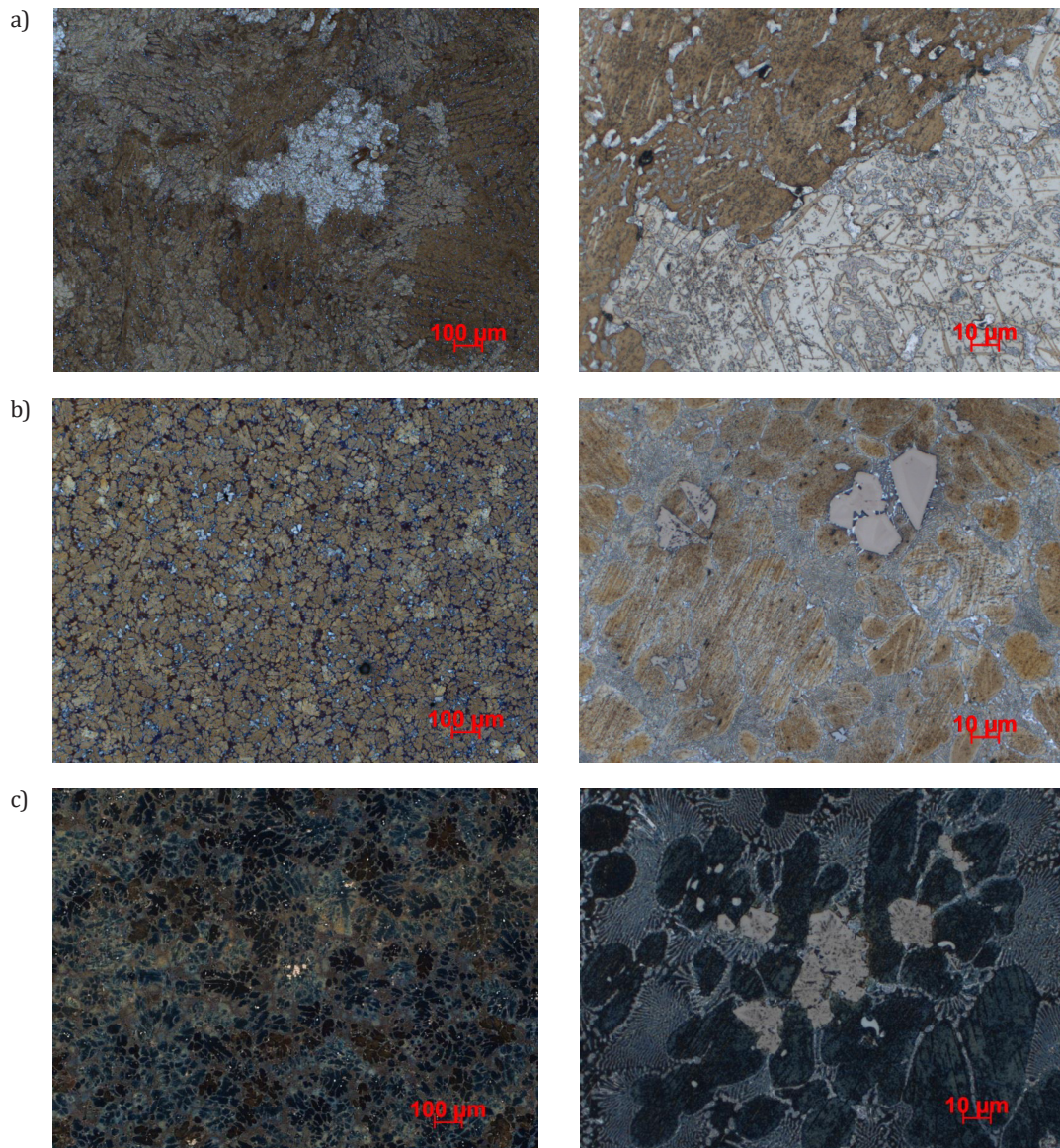


Fig. 4. Microstructures of testing castings: a) ingot surface; b) die-casting surface; c) high-pressure casting surface

The microstructure of the Zn4Al3Cu alloy includes dendrites of a solid solution based on zinc and eutectic based on zinc and aluminium (Fig. 5). It is a typical and distinctive microstructure of Zn-Al alloys. Due to its high cooling rate during casting, zinc is oversaturated into alloying additive for copper, which, by the mechanism of solid-solution hardening, significantly increases the mechanical parameters of the alloy. The titanium additive caused the formation of additional intermetallic phases. Their detailed description may be found in the publication [12]. Typically, already in a liquid form at the casting temperature of 450°C, an intermetallic phase forms, here denoted with the symbol T (Fig. 6). Its chemical composition may vary and may reach a wide range of various concentrations of zinc, aluminium, and titanium. Three-component phase T positions itself outside the eutectic or at the grain boundaries. T phase at the grain boundaries may inhibit growth of the primary phase η . Therefore, adding Ti to the zinc alloys may reduce the volume of the primary phase η . With Ti content in the Zn alloy above 0.05% by weight, coarse-grained phase T causes a decrease in the mechanical properties of the alloy [13].

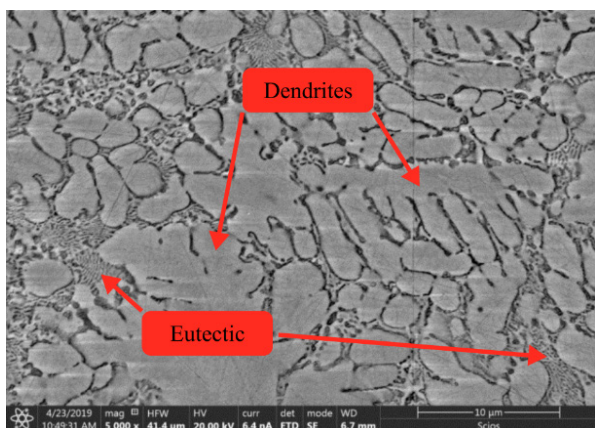


Fig. 5. Microstructure of Zn4Al3Cu alloy observed with the use of a scanning electron microscope with a BSE (back scattered electrons) detector

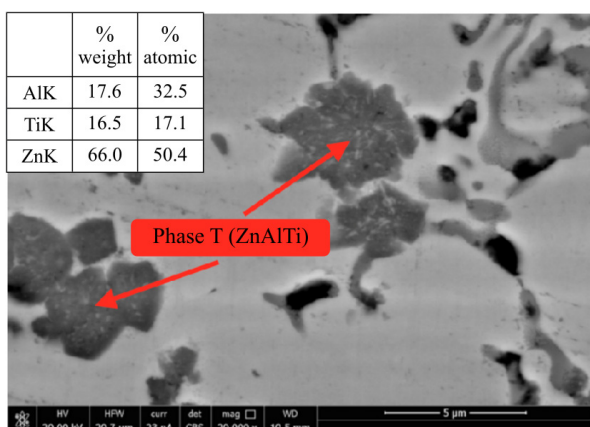


Fig. 6. Microstructure of Zn4Al3CuTi alloy observed with the use of a scanning electron microscope with back scattered electrons BSE detector

During the analysis, intermetallic phase based on iron was additionally identified. It is the result of contaminants coming mainly from the steel lining of the casting machine furnace.

The following structural components were defined:

- dendrites of zinc-based solid solution containing copper and aluminium,
- eutectic Al-Zn,
- phase T – ZnAlTi intermetallic phase,
- $Al_{13}Fe_4$ intermetallic phase.

5. TESTING OF MECHANICAL PROPERTIES

Statistical tensile tests were conducted in compliance with the PN-EN 10002-1 standard. The shape and dimensions of the samples are presented in Figure 7.

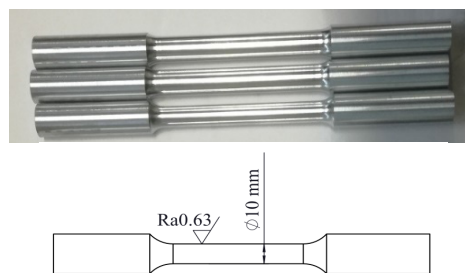


Fig. 7. Shape and dimensions of the samples for tensile strength tests

The details cast in the new technology were subjected to a series of mechanical tests. At first, the tests with the samples cast in semi-industrial conditions in a steel ingot mould were conducted. The alloy was prepared in a resistance furnace with mechanical agitation. In order to dissolve the AlCu50 master alloy, overheating of the alloy up to 550°C was employed. The final titanium content in the alloy was 0.41% by weight. The endurance of the die-cast Zn4Al3Cu alloy was 265 ± 29 MPa and yield strength of 250 ± 15 MPa. Significant spreads in the results and different natures of the stress-strain curves are caused by high porosity of castings made by gravity die casting. High-pressure casting is characterised by significantly different conditions of the alloy crystallisation, in effect giving completely different mechanical parameters of the finished detail. Moreover, the casts made in the discussed technology are usually thin-walled, something which is favourable for the better removal of heat, quicker crystallisation, and, in effect, refinement of the alloy microstructure. We should, therefore, expect considerably better strength parameters. The resulting cast has a complex shape with walls of various thickness in its cross-section. As the test shows, the porosity is mainly positioned in the central part of the material (Fig. 8). The additional problem during the tests concerned a small size of the discussed detail, giving little freedom when preparing the sample for the mechanical tests.

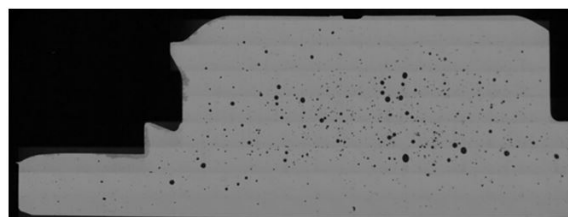


Fig. 8. Macro photographs of cross-section of the Zn4Al3CuTi alloy details

A method for cutting out the samples for tensile strength tests was suggested, i.e. cutting out of a material piece of thickness corresponding to half of the thickness of the cast detail. Thus, the influence of the spot of the collection of the sample (surface, centre of the cast) on material strength was determined. Exemplary samples for tests are presented in Figure 9. For the purpose of comparison, a photograph of the 33.5 mm-diameter detail is also attached. All the tests were conducted on Zn4Al3CuTi alloy of titanium content of 0.41% by weight. The discussed tests were carried out with the samples collected from the stabilised part of the casting process, i.e. after the thirtieth injection (smelting without alloy overheating).

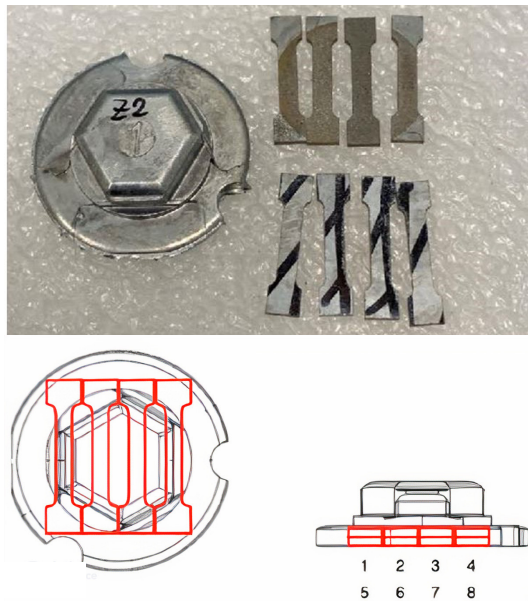


Fig. 9. Pattern of cutting out the samples for mechanical tests and photographs of those samples

The results of the tensile strength tests are given in Figure 10, comparing endurance qualities of the material taken from the surface and from the area closer to the details centre. Additionally, in the table attached to the figure, average values of yield strength, tensile strength, and total strain are presented. The best mechanical parameters were obtained on the samples cut out from the flat external part of the casting (samples 5, 6, 7, 8 – Fig. 9). Average yield strength $R_{0.2}$ and tensile strength R_m amounted to approx. 320 MPa and 370 MPa, respectively. Samples taken from the central part of the casting had slightly lower mechanical parameters, namely: $R_{0.2} = 270$ MPa and $R_m = 330$ MPa, and substantially worse plasticity. Lower endurance was the effect of higher porosity in the casting centre, but also of the conditions for slower crystallisation during the casting process. Differences in the porosity were already visually apparent at the moment of comparing the two sets of samples. The results clearly show significantly higher tensile strength and pre-arranged yield strength for both the samples cut of the centre and those cut out from the casting surface, in comparison to the properties of the die-cast casting samples. Even in the worst case, the tested material has better strength than the material cast by gravity casting, which could be also found in other alloys used in high pressure casting techniques [14].

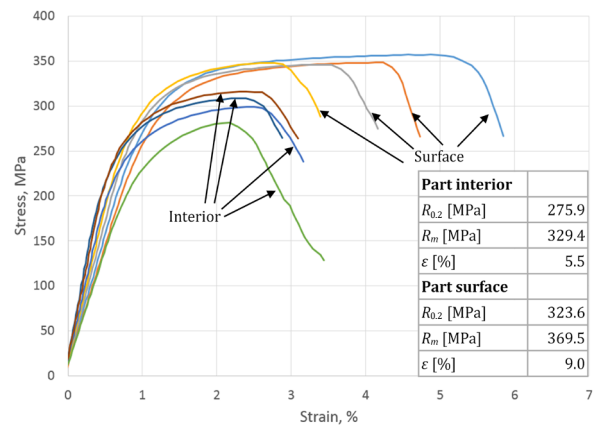


Fig. 10. Juxtaposition of tensile test curves for samples taken from the surface and from the centre of the detail

6. CONCLUSIONS

Based on the tests and analyses conducted, it was determined that:

1. The alloying procedure for Zn4Al3Cu alloy containing up to 0.41% of titanium in the form of die-casts and high-pressure castings was developed and tested in manufacturing conditions.
2. The chemical composition of an alloy demonstrating mechanical properties that exceed the properties identified for die-cast Zn4Al3Cu alloy was proposed.
3. Significant refinement of grain by means of the addition of 0.41% of titanium to the Zn4Al3Cu alloy cast by gravity casting was determined, as well as by high-pressure casting to a metal mould.
4. A change in chemical composition during the smelting process of the test alloy, Zn4Al3CuTi, was determined, requiring adjustments in the content of particular elements during the period when the metal is held in the melting furnace.

Acknowledgements

The presented results of R&D works were obtained by SAGA Poland sp. z o.o. as a result of the project called "Development and implementation of a production programme for auto glazing positioners equipment along with palletising process automation based on an innovative zinc alloy of improved thermal and mechanical resistance parameters" co-financed by the ERDF under the measure 1.2. SGOP 2014-2020 "Sectoral R&D programmes" agreement no. POIR.01.02.00-00-0229/16.

REFERENCES

- [1] Yan Shu-qing, Xie Jing-pei Wang Wen-yan & Li Ji-wen (2009). Microstructure and tensile property of Zn-Al alloy reinforced with titanium produced by electrolysis. *Advanced Materials Research*, 79–82, 1415–1418. Doi: <https://doi.org/10.4028/www.scientific.net/AMR.79-82.1415>.
- [2] Wang Jianhua, Wang Xiande, Tu Hao & Su Xuping (2011). Effects of titanium on microstructure and mechanical properties of ZnAl4Y alloy. *China Foundry*, 4, 397–400.
- [3] *Engineering in Zinc, Today's Answer* (2019). Retrieved from <https://www.zinc.org/engineering-in-zinc-todays-answer/> [accessed: 14.12.2023].

- [4] Jemielewski J. (1970). *Odlewnictwo metali nieżelaznych*. Wydawnictwa Naukowo-Techniczne, Warszawa.
- [5] Zyska A., Konopka Z., Łągiewka M., Nadolski M. & Chojnacki A. (2009). High-aluminium zinc alloy (ZnAl27Cu2) modified with titanium and boron. *Archives of Foundry Engineering*, 9(4), 237–240.
- [6] Krajewski W. (1996). Phases of heterogeneous nucleation in the ZnAl25 alloy modified by ZnTi and AlTi master alloys. *Materials Research and Advanced Techniques*, 87(8), 645651.
- [7] Leis-Speaker W. & Kallien L. (2013). Ageing and creep behaviour of Zinc-Diecasting-Alloys. International Zinc Diecasting Conference "Tradition & Innovation", Prague, Czech Republic, 13–14 June 2013. Retrieved from <https://www.yumpu.com/en/document/view/40575985/ageing-and-creep-behaviour-of-zinc-diecasting-alloys-international-> [accessed: 14.12.2023].
- [8] Von W. Heine & U. Zwicker (1962). Untersuchungen an Legierungen des Systems Zink-Titan. *International Journal of Materials Research, Zeitschrift für Metallkunde*, 53(6), 380–385. Doi: <https://doi.org/10.1515/ijmr-1962-530607>.
- [9] Sailin Fan, Changjun Wu, Ya Liu, Hao Tu, Xuping Su & Jianhua Wang (2017). 600 and 450°C isothermal sections of the Zn-Ce-Ti system. *Journal of Alloys and Compounds*, 709, 842–849. Doi: <https://doi.org/10.1016/j.jallcom.2017.03.215>.
- [10] Piwowski G., Buraś J. & Krajewski W.K. (2013). Wpływ zabiegu modyfikowania zaprawą ZnTi3,2 na mikrostrukturę stopu ZnAl10. *Archives of Foundry Engineering*, 13(spec. iss. 3), 129–132.
- [11] Kallien L.H. & Leis W. (2011). Ageing of Zinc Alloys. *International Foundry Research*, 64(1), 1–23.
- [12] Sui Yang, Xuping Su, Jianhua Wang, Fucheng Yin, Zhi Li, Hao Tu & Haoping Peng (2010). The Zn-rich corner of the Zn-Al-Ti system at 723 K. *Journal of Alloys and Compounds*, 499(2), 194–199. Doi: <https://doi.org/10.1016/j.jallcom.2010.03.148>.
- [13] Krupińska B., Rdzawski Z. & Labisz K. (2011). Crystallisation kinetics of the Zn-Al alloys modified with lanthanum and cerium. *Journal of Achievements of Materials and Manufacturing Engineering*, 46(2), 154–160.
- [14] Pastirčák R., Brůna M., Matejka M. & Bolibruchová D. (2023). Effect of input parameters on the structure and properties of castings obtained via crystallization under pressure. *Metals*, 13(8), 1424. Doi: <https://doi.org/10.3390/met13081424>.