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The Effect of Zirconium as an Alloying Additive on the Microstructure and Properties of AlSi9Mg Alloy Cast in Sand Moulds

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Abstract

The aim of the study was to select the optimal content of zirconium introduced as an alloying additive to obtain the best strength properties of Al-Si alloy. A technically important disadvantage is the tendency of silumins to form a coarse-grained structure that adversely affects the mechanical properties of castings. To improve the structure, modification processes and alloying additives are used, both of which can effectively refine the structure and thus increase the mechanical properties. According to the Hall-Petch relationship, the finer is the structure, the higher are the mechanical properties of the alloy. The proposed addition of zirconium as an alloying element has a beneficial effect on the structure and properties of silumins, inhibiting the grain growth. The starting material was an aluminium-silicon casting alloy designated as EN AC-AlSi9Mg (AK9). Zirconium (Zr) was added to the alloy in an amount of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% by weight. From the modified alloy, after verification of the chemical composition, samples were cast into sand moulds based on a phenolic resin.
The first step in the research was testing the casting properties of alloys with the addition of Zr (castability, density, porosity). In the next step, the effect of zirconium addition on the structure and mechanical properties of castings was determined.

Keywords: Silumins, Precipitation hardening, Alloying additives, Microstructure examinations, Strength tests

1. Introduction

In the family of the currently used casting aluminium alloys, the most common are aluminium-silicon alloys, called silumins [1, 2]. Apart from silicon, silumins may contain the additions of copper, zinc, magnesium, nickel and manganese [3]. The use of silumins is mainly in the engineering industry - automotive, household, aviation, and in the precision-optical industry. Some of the silumins have quite specific features, which make them suitable for pistons and heads of internal combustion engines [4, 5].

The wide application range these alloys owe to their very good physical and technical characteristics. They are characterized by low density, a relatively low melting point, good thermal and electrical conductivity, high mechanical and casting properties (high castability and low shrinkage), good machinability and corrosion resistance. Some of the silumins are heat-treatable. From a technical point of view, a serious disadvantage is their tendency to form a coarse-grained structure that adversely affects the mechanical properties of castings. To improve the structure, modification with various elements is used. Appropriate modifiers and alloying additives can effectively refine the structure and thus increase the mechanical properties. According to the Hall-Petch relationship, the finer is the structure, the higher are the mechanical properties of the alloy. Obtaining different structures in silumins depends on the type of modifier/additive introduced into the alloy. The resulting structures include various forms of the eutectic, e.g., granular, lamellar, banded, and refined [6, 7].

The data in the technical literature [8-12] shows that zirconium (Zr) in aluminium alloys for plastic working inhibits the grain growth, allowing in this way for high electrical and mechanical properties to be obtained in the alloys. This is also the reason why zirconium is sometimes used as a modifier. Zirconium-containing alloys subjected to heat treatment (homogenization annealing, solution annealing or aging) are characterized by higher tensile strength and thermal resistance [13, 14]. The purpose of heat treatment is to produce in the alloy an appropriate amount of precipitates of the $MgZr_2$ and Al_2Cu intermetallic compounds and triple M and T type compounds, and to ensure that the matrix obtained contains some alloying additives dissolved in it. The grain growth can also be inhibited by suitable structural factors, such as e.g. the Al_3Zr-type dispersoids. During recrystallization, especially in the temperature range of 300-315°C, the state of intensive grain growth should be quickly exceeded [15]. Moreover, the addition of zirconium to aluminium alloys after the precipitation hardening process improves the alloy hardness [16]. The addition of zirconium leads to precipitation hardening through the formation of inclusions, which significantly improves the wear resistance of Al-Si alloys [17]. The authors of [18] focused their research on the effect of Ti, Zr and V additions on the microstructure and mechanical properties of the newly developed casting alloy for the automotive industry. Shrinkage porosity was observed in castings made from the tested alloys. The effect of Ti, Zr and V additions on the refinement of microstructure was insignificant and limited mainly to the formation of trialuminide inclusions. On the other hand, a much higher yield point and ultimate tensile strength were obtained, but with lower ductility compared to the conventional A356-T6 and 319-T6 alloys. Yuan and Liang [9] as well as Knych et al. [19] investigated the effect of zirconium on the electrical properties (change in resistivity) of aluminium alloys.

2. Materials and Methods

The starting test material was an AlSi9Mg (AK9) aluminium-silicon casting alloy. Zirconium addition to the alloy amounted to 0.1%, 0.2%, 0.3%, 0.4% and 0.5% by weight. It was introduced into the alloy in the form of a 15% Al-Zr master alloy. The melting procedure was carries out in resistance furnace in crucible with capacity of 25 kg charge, without a protective atmosphere. The metal charge of each melting was 20kg. During melting the alloying additives was introduced in the temperature of 720°C. The metal was stirred with a graphite rod to homogenize the alloy.

From the alloys, after verification of their chemical composition, samples were cast into sand moulds based on the SuperEko phenolic resin hardened with CO2. Sibelco silica sand classified as medium according to the PN-85/H-11001 Polish standard (main fraction 0.20/0.16/0.315) was used to make the sand mixtures.

The chemical composition of the alloys obtained was determined with a G.N.R. S3 MiniLab 300 emission spectrometer using the main database dedicated to Al-Si alloys.

The technological castability test was carried out in accordance with the BN-65/4051-08, industry standard by casting a spiral-shaped sample in metal mould.

Both density and porosity were determined on an ALU SPEED TESTER made by FMA. The density was determined from the difference in weight of the sample weighed in air and the sample weighed in water. The gas content in the tested samples, expressed as the gas number LG, was calculated from the quotient of the specific mass of the tested sample and the theoretical specific mass of the metal (without pores and shrinkage porosity). In the same way, the porosity of the casting was also determined. The density index, otherwise called the metal purity index, was determined from the differences in the density of the samples solidifying in the atmosphere and under a vacuum of 80 mbar. The hydrogen measurement was based on the first bubble principle. The Straube-Pfeiffer test and the Dross Test were also performed.

Microstructural studies were carried out using a Zeiss light microscope with an AxioObserver Zm10 program. The specimens were polished on a Struers grinding-polisher following the program for soft materials, i.e. using 220, 500 and 1000 papers and 9, 3, 1 and ¼ micron diamond pastes. The samples were then etched in a 1% HF solution in distilled water. The Secondary Dendritic Arm Spacing (SDAS) was measured with a ZEISS AxioVision software. Measurements were made on etched samples at 50x magnification using the secant method (10 oriented secants). Additionally, to identify the phases and determine the distribution of zirconium in castings, examinations were carried out on a HITACHI model TM-3000 scanning electron microscope (SEM) with the EDS analysis in micro-areas.

The static tensile test at ambient temperature was carried out in accordance with the PN-EN ISO 6892-1: 2016-09 Polish standard, Method B "Metallic materials. Tensile testing. Part 1: Method of test at room temperature”. An EU-20 testing machine with a maximum range of 200 kN was used for the tests. The increment in stress rate was 15.9 MPa/s. Standard samples according to the PN-EN ISO 6892-1: 2010 Polish standard (Metallic materials - Tensile Testing) were used in the tests.

The Brinell hardness test was carried out using a 2.5 mm diameter ball under a load of 62.5 N applied for 12 seconds.

3. Results

Chemical composition

Table 1 shows the chemical composition of the tested alloys. The Zr content in alloys was consistent with the assumed values. With the increasing Zr content in alloys, the content of Si was decreasing, mainly due to the presence of aluminium introduced along with zirconium into the alloy, but the content of this element was in line with the standard.

Table 1.
Chemical composition of the tested alloys

Chemical composition, %	Alloy designation					
	AK9	**AK9 + 0.1 Zr**	**AK9 + 0.2 Zr**	**AK9 + 0.3 Zr**	**AK9 + 0.4 Zr**	**AK9 + 0.5 Zr**
Si	**8.8587**	**8.7157**	**8.7155**	**8.3348**	**8.2269**	**7.9914**
Fe	0.2634	0.2400	0.3024	0.2507	0.3680	0.2973
Cu	0.1329	0.1152	0.1100	0.1350	0.0946	0.1017
Mn	0.2842	0.2288	0.2891	0.2676	0.2972	0.2757
Mg	0.3477	0.3458	0.3294	0.3584	0.3061	0.3259
Cr	0.0157	0.0192	0.0131	0.0138	0.0132	0.0128
Zn	0.0353	0.0678	0.1063	0.1170	0.1571	0.1749
Ti	0.0949	0.1085	0.0893	0.0962	0.0842	0.0918
Zr	**<0,003**	**0.1180**	**0.2013**	**0.3022**	**0.3952**	**0.5074**
Al	rest	rest	rest	rest	rest	rest

Castability test

The castability test was performed to determine the alloy ability to fill the mould cavity and reproduce its shape at a given pouring temperature and chemical composition. The castability test temperature was 720°C and 200°C for metal and die, respectively. The castability test results are shown in Figure 1. Alloy dependent phenomena that determine castability are porosity. The addition of Zr in an amount of up to 0.3% improved the alloy castability, which is related to the reduction of gas content in the liquid metal (porosity). While at 0.5% Zr, the alloy castability was reduced by 10% compared to the base alloy. For AK9 alloys with the addition of 0.1-0.3% Zr, the porosity is at a similar, low level (approx. 1.46%). For the addition of 0.5% of Zr the porosity rise up to 1.57%.

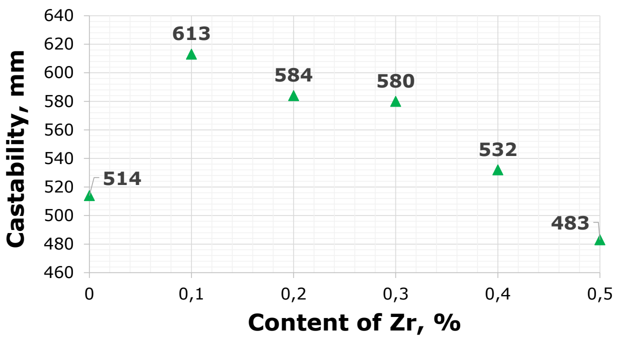


Fig. 1. The castability of alloys

Determination of density and porosity

The results of studies of the density, porosity and hydrogen content in alloys are summarized in Table 2. The addition of zirconium in an amount from 0.1 to 0.3% reduced both porosity and density index with the resulting increase in alloy density. The presence of zirconium in an amount even as low as 0.3% sharply increased the hydrogen content in the alloy.

The Dross test and the Straube-Pfeiffer test were also performed. Images of the tested samples are shown in Figure 2. The dross test allows for quick and cheap classification of non-metallic inclusions. During sample solidification under a vacuum below 10 mbar, the non-metallic inclusions flow out along with gas bubbles to the surface. The Straube-Pfeiffer test is an additional method for the determination of gas inclusions in metal that solidifies under a vacuum of 30-50 mbar. After solidification, the sample is cut through and the shape, size and position of pores give information about the gas content. Both tests have confirmed a significant increase in the gas content in metal with the zirconium content in alloy at the level of 0.3% and higher. The precipitation of non-metallic inclusions was not observed on the surface of the samples.

Table 2.
The results of the density, porosity, and hydrogen content measurements

Parameter	Alloy designation					
	AK9	**AK9 + 0,1 Zr**	**AK9 + 0,2 Zr**	**AK9 + 0,3 Zr**	**AK9 + 0,4 Zr**	**AK9 + 0,5 Zr**
Density index DI, %	3.414	2.655	1.744	3.212	5.218	7.917
Density ρ_{pr}, g/cm^3	2.636	2.637	2.638	2.638	2.628	2.621
Porosity P, %	1.495	1.465	1.464	1.464	1.554	1.572
Gas number LG	0.985	0.985	0.983	0.985	0.983	0.983
Hydrogen content, cm^3/100g	0.145	0.140	0.135	0.190	0.190	0.240

Alloy designation	Dross test	Straube-Pfeiffer test
AK9		
AK9 + 0.1 Zr		
AK9 + 0.2 Zr		
AK9 + 0.3 Zr		
AK9 + 0.4 Zr		
AK9 + 0.5 Zr		

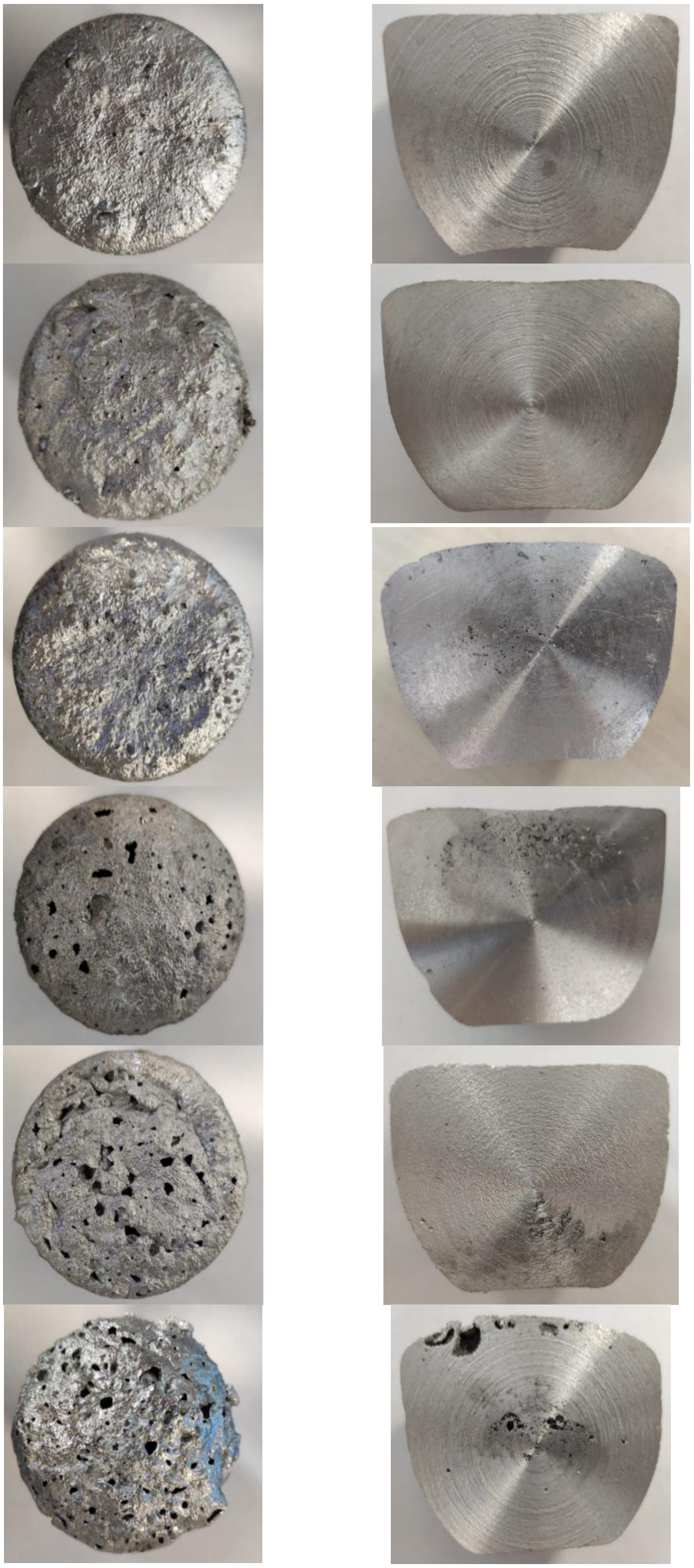


Fig. 2. Samples after Dross test and Straube-Pfeiffer test

Microstructural studies

To determine the effect of zirconium on the structure of castings, microscopic examinations were carried out. The secondary dendritic arm spacing (SDAS) was determined for all the tested alloys. Figures 3-8 show the dispersion of casting structure on both non-etched specimen sections at 50x magnification and HF etched specimen sections at 1000x magnification. In the AK9 alloy, the addition of zirconium causes grain growth. The dendritic arm spacing increases from 87 μm for pure alloy to 116 μm for alloy containing 0.5 wt%. Zr. For zirconium content in the range of 0.2-0.5%, the secondary dendritic arm spacing is constant (about 115 μm).

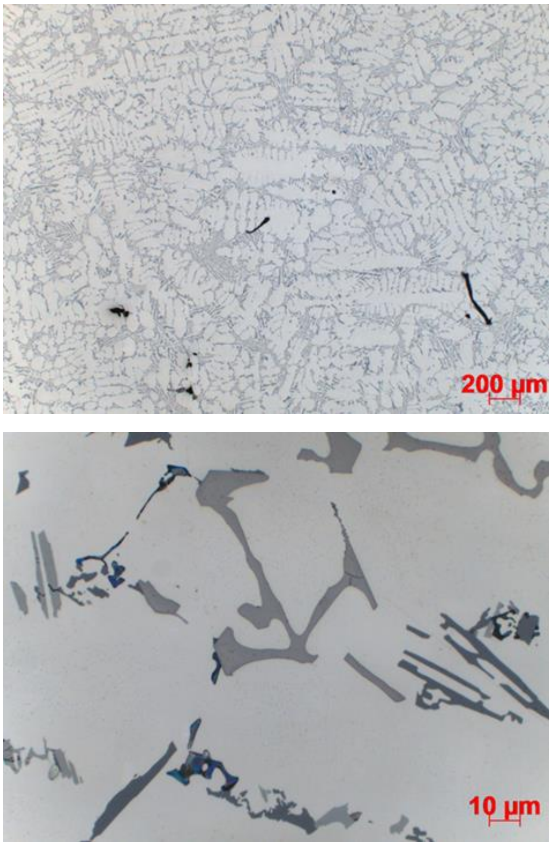


Fig. 3. Microstructure of pure AK9 alloy casting at various magnifications, SDAS - 87 μm

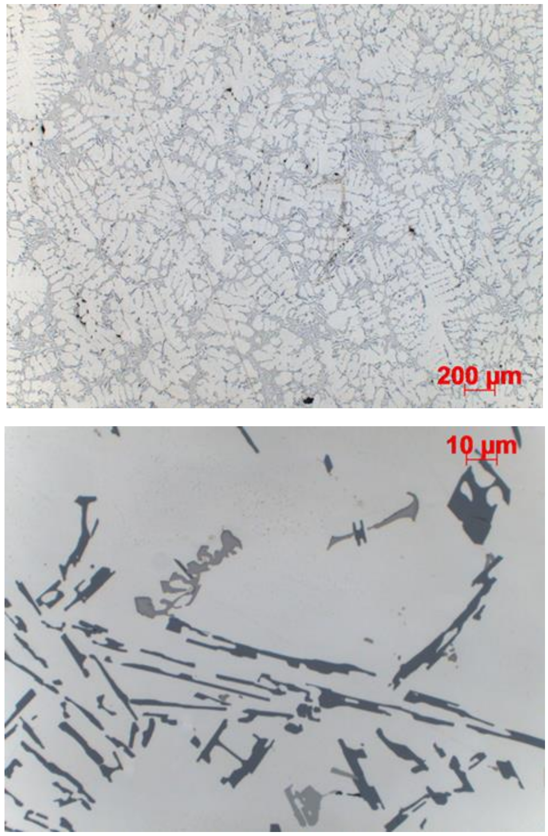
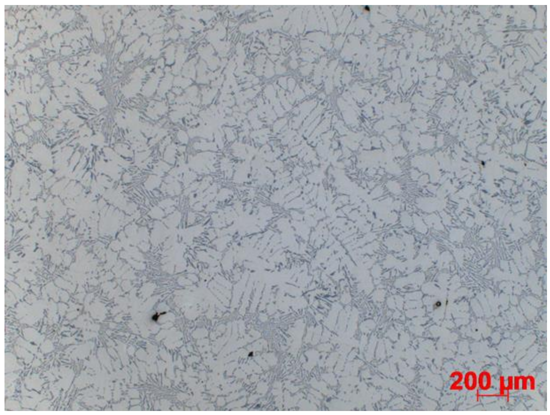


Fig. 4. Microstructure of AK9 alloy casting with the addition of 0.1% Zr at various magnifications, SDAS - 98 μm



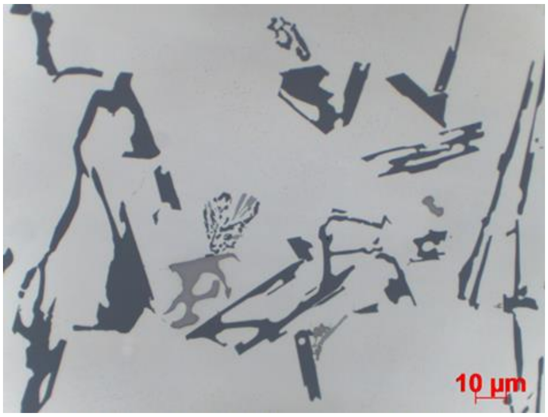


Fig. 5. Microstructure of AK9 alloy casting with the addition of 0.2% Zr at various magnifications, SDAS - 115 µm

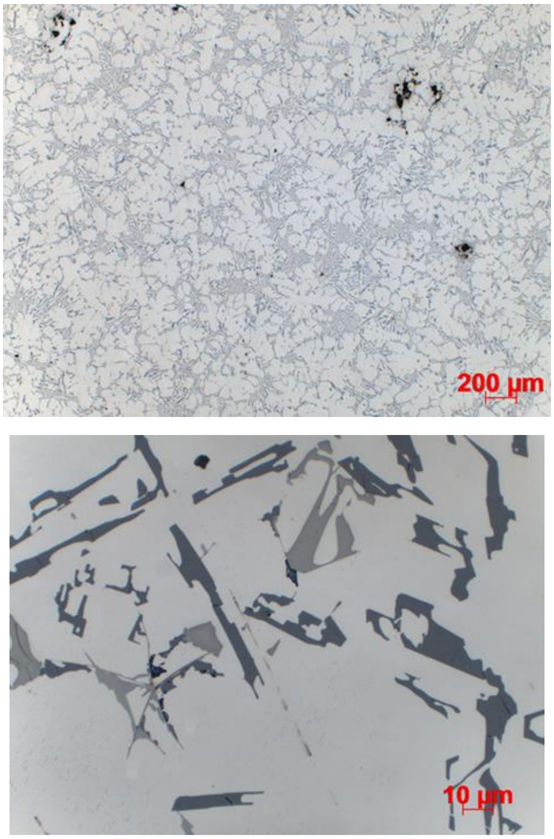


Fig. 6. Microstructure of AK9 alloy casting with the addition of 0.3% Zr at various magnifications, SDAS - 115 µm

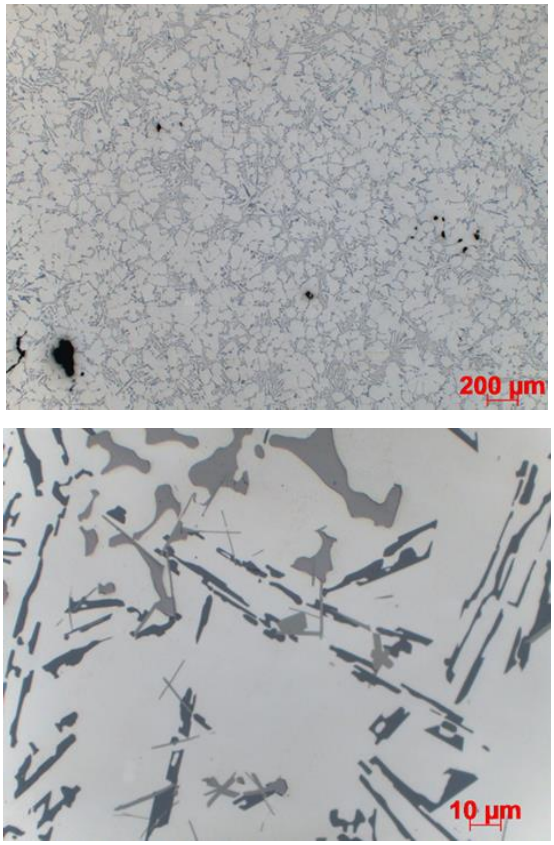
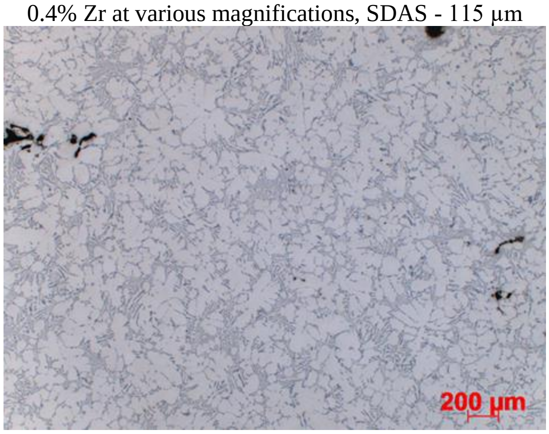


Fig. 7. Microstructure of AK9 alloy casting with the addition of 0.4% Zr at various magnifications, SDAS - 115 µm



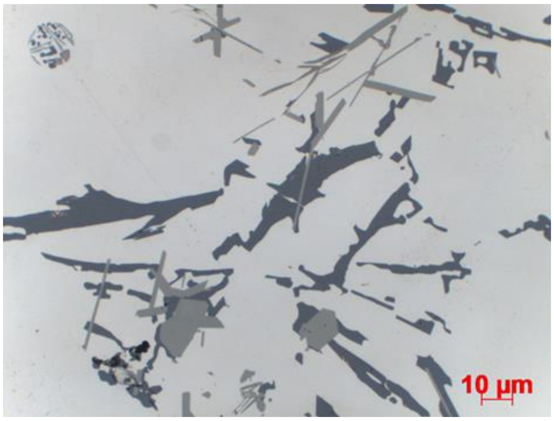


Fig. 8. Microstructure of AK9 alloy casting with the addition of 0.5% Zr at various magnifications, SDAS - 116 µm

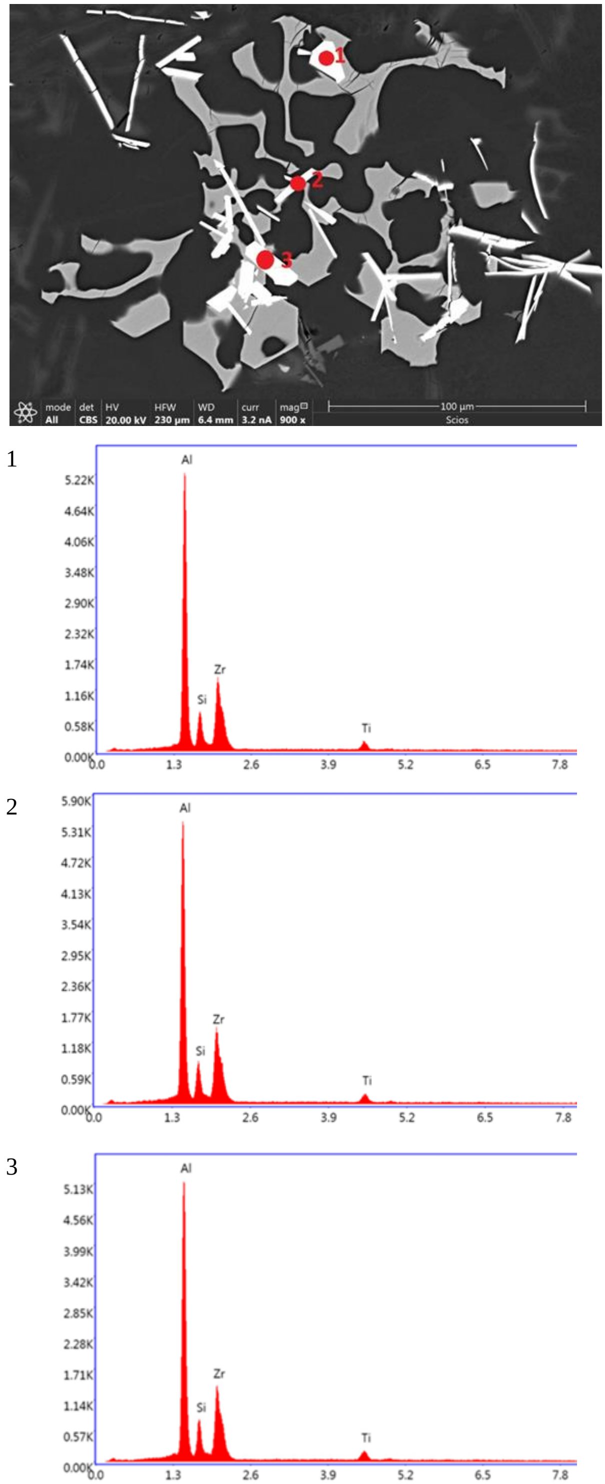


Fig. 9. The structure of AK9 alloy with the addition of 0.5% Zr and the results of microanalysis of the local chemical composition

In the structure of castings containing 0.4 and 0.5% Zr, some additional phases were observed to occur. To identify these phases and determine the distribution of zirconium in alloys, EDS studies of the local chemical composition in micro-areas were carried out and maps of the distribution of elements were drawn. In alloys containing up to 0.3% Zr, zirconium was distributed in the solution, resulting in alloy hardening. For Zr contents of 0.4 and 0.5%, it was also present in the form of fine, coherent precipitates, intermetallic phases of the Al_3Zr or AlSiZr type. The Zr-based particles are derived from insufficient dissolved AlZr15 master alloy. The results of microanalysis of the chemical composition of the alloy with the addition of 0.5% Zr are shown in Figure 9.

The Al_3Zr dispersoids tend to produce a homogeneous distribution in the centre of the dendrites, where the supersaturation with zirconium assumes high values [12]. The effect of this phase on casting properties is still not fully explained. According to the authors of [20, 21], this phase inhibits the migration of grain boundaries, taking place in the processes of recrystallization and grain growth, i.e. during heat treatment. On the other hand, the research conducted by Voorhees and Knipling [22, 23] has shown that the Al_3Zr phase is a tetragonal phase with no significant effect on the refinement of aluminium alloys.

In the case of the AlSi9Mg cast alloy, the Al_3Zr phase causes a significant reduction in the mechanical properties of the castings. Due to the fact that the decrease in strength properties is not caused by the grain growth of the alloy structure (SDAS at a similar level for the Zr content in the range of 0.2-0.5%), the matrix microhardness and Al_3Zr phase were tested. The research has shown that the α-Al phase is characterized by a microhardness at the level of 81HV 0.003, while the Al_3Zr phase at the level of 520-750HV 0.003. The high microhardness of the Al_3Zr phase indicates that it is a brittle phase, which negatively affects the strength values of castings.

Strength testing

The mechanical properties tested on samples taken from the castings are presented in Table 3. The results are also shown in Figure 10. The static tensile test at ambient temperature was performed on standard Φ10mm diameter samples. The highest values of the tensile strength and hardness were obtained for the alloy containing 0.1 and 0.3% Zr. The addition of zirconium had an adverse effect on the remaining mechanical properties. The deterioration of the mechanical properties observed in castings containing more than 0.4% Zr was the result of the formation of a coherent Al_3Zr phase and increased casting porosity (Table 2).

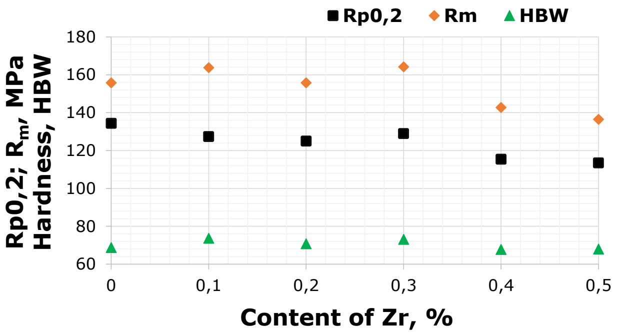


Fig. 10. Selected strength properties of castings

Table 3.
Strength testing of castings

Properties tested	Alloy designation					
	AK9	**AK9 + 0.1 Zr**	**AK9 + 0.2 Zr**	**AK9 + 0.3 Zr**	**AK9 + 0.4 Zr**	**AK9 + 0.5 Zr**
$R_{p0.2}$, MPa	134.4	127.4	125.0	129.0	115.4	113.5
R_m, MPa	155.8	**163.8**	155.8	**164.2**	142.8	136.5
A, %	2.0	1.6	1.6	1.6	1.5	1.6
Z, %	2.2	2.0	1.8	1.8	1.5	1.2
Hardness, HBW	68.8	**73.7**	70.8	**73.1**	67.8	68.0

4. Conclusions

There is no information in the available scientific literature on the effect of zirconium addition on the casting properties of Al-Si alloys. Research in this area concerns mainly alloys for plastic working. However, some preliminary results show that:

- properly selected addition of Zr introduced to the AlSi9Mg alloy improves the alloy castability, reduces porosity and increases the density,
- zirconium in Al-Si casting alloys increases the size of dendrite,
- even distribution of zirconium in the solution (up to 0.3%) strengthens the casting structure with a positive effect on both tensile strength and hardness,
- the deterioration of mechanical properties observed in castings containing more than 0.4% Zr is most likely due to the formation of a coherent Al_3Zr phase.

Further studies will concern the heat treatment and its impact on the microstructure and mechanical properties of castings as well as the resistance of alloys to thermal shocks.

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