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Effect of the Precipitation Hardening on the Structure of AlSi7Mg0.3Cu0.5 Alloy with Addition of Zr and Combination of Zr and Ti

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Abstract

The article focused primarily on comparing the achieved mechanical results for AlSi7Mg0.3Cu0.5Zr and AlSi7Mg0.3Cu0.5Zr0.15Ti experimental alloys. Experimental variants with the addition of Zr ≥ 0.05 wt. % demonstrated the ability of Zr to precipitate in the form of Al_3Zr or AlSiZr intermetallic phases. Zr precipitated in the form of long smooth needles with split ends. When evaluating the thermal analyses, the repeated peak was observed already with the initial addition of Zr in the range of approximately 630 °C. It was interesting to observe the increased interaction with other intermetallic phases. EDX analysis confirmed that the individual phases are based on Cu, Mg but also Fe. Similar phenomena were observed in experimental alloys with a constant addition of Zr and a gradual increase in Ti by 0.1 wt. %. A significant change occurred in the amount of precipitated Zr phases. A more significant increase in mechanical properties after heat treatment of AlSi7Mg0.3Cu0.5Zr experimental alloys was observed mainly above the Zr content ≥ 0.15 wt. % Zr. The improvement of yield and tensile strength over the AlSi7Mg0.3Cu0.5 reference alloy after heat treatment was minimal, not exceeding 1 %. A more significant improvement after heat treatment occurred in modulus of elongation with an increase by 6 %, and in hardness with an increase by 7 %. The most significant drop occurred in ductility where a decrease by 31 % was observed compared to the reference alloy. AlSi7Mg0.3Cu0.5Zr0.15Ti experimental alloys, characterized by varying Ti content, achieved a more significant improvement. The improvement in tensile strength over the AlSi7Mg0.3Cu0.5 reference alloy after heat treatment was minimal, not exceeding 1 %. A more significant improvement after heat treatment occurred in modulus of elongation with an increase by 12 %, in hardness with an increase by 12 % and the most significant improvement occurred in yield strength with a value of 18 %. The most significant decrease also occurred in ductility where, compared to the reference alloy, the ductility drop was by up to 67 %.

Key words AlSi7Mg0.3Cu0.5, Investment casting, Precipitation hardening, Improve mechanical properties, AlZr15

1. Introduction

The rate of increase in greenhouse gas concentrations is resulting in new measures being taken by governments around the world. For this reason, the foundry industry is also focused on more efficient production of individual components that are part of automobiles or aircraft. One of the possible ways is to develop new, more sophisticated Al alloys, with significantly better properties than the originally used Al alloys. If it is possible to create a new type of Al alloy that has much better properties than the reference Al alloy, then it is also possible to reduce the weight of the individual components. The result can be more efficient construction, fuel and energy savings, increased environmental friendliness of the vehicle or economic savings by reducing the amount of raw materials. Nowadays, companies in the automotive and aerospace sectors are replacing commercial Al-Si alloys with new types of Al alloys that either use a system other than Al-Si (e.g. AlCu7MnZr) or modify existing Al alloys by alloying with certain elements, which results in the improvement in selected properties (e.g. AlSi8Cu3, AlSi7MgCu0.5 or AlSi10Mg0.3Cu). In addition to alloying with major alloying elements such as Si, Mg or Cu, which are responsible for defining the microstructure and mechanical properties, by adding a smaller amount of additional alloying elements (e.g. Sr, Zr, Cr, Ni, Mn, Mo and V) it is possible to significantly change the method of solidification of the given Al alloys and thus improve the selected properties for the needs of the automotive and aerospace industries, for example. Developments in the field of electric vehicles (EVs) focuses on the development of stronger and more heat-resistant Al alloys, for example due to insufficient battery capacity (Fig. 1.). Thermal-physical properties and increased corrosion resistance are also important. Currently used heat treatment Al alloys make extensive use of Cu to increase strength. However, Cu reduces the corrosion resistance of aluminium alloys. The application of Cu-containing Al alloys can lead to an increase in the rate of corrosion on sealing elements in EVs and cause corrosion of electrical contacts [1-5].

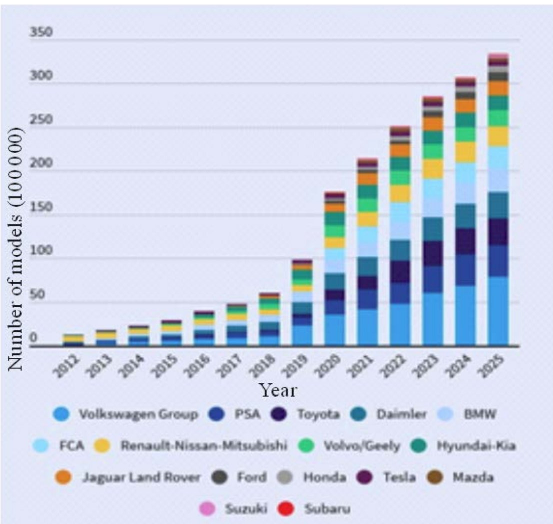

Fig. 1. Production of EVs by car manufacturers for the European market [9]

From this point of view, the application of additional alloying elements is also advantageous, where Zr is exactly the element that enables the development of more sophisticated aluminium alloys. Zirconium is introduced into the melt in order to improve certain, mainly mechanical properties of Al alloys. The strengthening effect is caused by the precipitation of Al_3Zr or AlSiZr intermetallic phases. It is preferably precipitated in particular in the form of Al_3Zr. Precipitation occurs during a peritectic reaction at Zr contents ≥ 0.10 wt. %, most frequently in the form of long smooth acicular formations with split ends. Zr phases are characterized by precipitation in different crystallographic morphologies, such as the DO_{23} tetragonal system, or the $L1_2$ cubic coherent metastable system (Fig. 2.). DO_{22} and DO_{23} tetragonal lattices have gained attention due to their high strength properties for construction materials. However, these phases are too fragile due to the low symmetry of the tetragonal lattice. More preferred is the L_{12} cubic coherent lattice, which better compensates for the negative aspect of DO_{22} and DO_{23} tetragonal lattices. Zirconium is also characterized by the lowest diffusion in Al compared to other transient elements such as Sc, V or Mn, where individual Zr atoms are characterized by high binding energy with unoccupied sites in the Al matrix. The advantages of precipitated intermetallic phases based on Al_3Zr include resistance to dissolution and coarsening, and regulation of the development of sub-grains and grains in the metal matrix of Al-Si alloys. The result is a metal matrix of Al alloys with increased strength, which is more stable even at higher temperatures. The influence of Zr on the Al alloy metal matrix is closely related in particular to the content of curing phases based on Mg and Cu. These elements are contained in aluminium alloys for the purpose of precipitation hardening, but their synergistic reaction with Zr increases the rate of "fragmentation" of Zr phases after heat treatment (HT). This results in the reduction in the strength properties even at higher temperatures (above 250 °C). The use of alloying elements of transition metals such as Zr is appropriate in combination with other elements such as Ti, Sr, Mn. These elements are standard in pre-inoculated and pre-modified aluminium alloys [3-9].

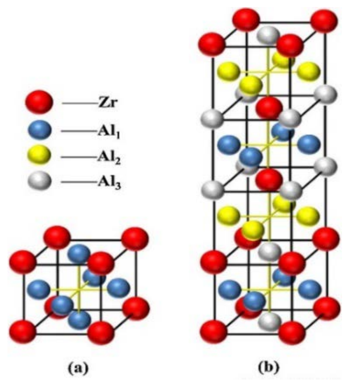

Fig. 2. Forms of the Al_3Zr intermetallic phase precipitation in the crystallographic lattice: a) $L1_2$ b) DO_{23} [10]

Ti is a grain refinement element in aluminium alloys. The combination of Zr and Ti significantly increases grain refinement and thus increases the strength characteristics of Al alloys. Ti precipitates in the form of Al_3Ti, which is active in the formation of nucleation nuclei. Ti precipitated in the form of Al_3Ti is characterized by a DO_{22} tetragonal crystal lattice, whose atomic distance of the nearest neighbour in the {1 1 2} plane is approximately 0.2826 nm, while in the {1 1 1} plane it is 0.2856 nm. The low permeability of the crystallographic lattice in the respective contact planes allows for a significant grain refinement in Al alloys. The combination of Zr and Ti can also serve in the formation of crystallization nuclei of precipitated Al_3Zr phases, it strengthens the refinement of grains and sub-grains and improves selected mechanical properties. However, the mean interatomic distance in the {1 1 4} plane indicates a significant reduction in the grain refinement effect when Zr and Ti were applied separately. The main objective of this paper is to verify the synergistic effect of Zr and Ti on the AlSi7Mg0.3Cu0.5 alloy with emphasis on obtaining an alloy with better mechanical properties and with a prediction of higher thermal conductivity of the investigated alloy [4-10].

2. Methods and goals

The experimental work focused on comparing the effect of Zr and the combination of Zr and Ti after heat treatment on the resulting mechanical properties of the AlSi7Mg0.3Cu0.5 reference alloy (P alloy). The P reference alloy was cast into ceramic moulds created by investment casting technology. The ceramic mould consisted of three layers (contact, insulating and reinforcing casing). The wax pattern melting and the ceramic mould resting for at least 24 hours were followed by the process of ceramic mould burn-off. Burn-of took place at a temperature of 750 ± 10 °C for 1.5 hours. Burn-off was completed by removing the ceramic mould from the furnace and casting experimental alloys (F1 - F6, E1 - E3). The temperature of the ceramic mould reached from 510 to 540 °C. The casting temperature of the alloys was 750 ± 10 °C, the casting height from the inlet well was 200 mm and the casting rate was 0.6 kg.s^{-1}. After casting, the ceramic mould was cooled in air for 1 h. The AlSi7Mg0.3Cu0.5 reference alloy is currently a non-standardized alloy used mainly in the automotive industry. Said alloy was modified from AlSi7Mg0.3 alloy as defined by technical standard STN EN 1706. AlSi7Mg0.3Cu0.5 alloy was delivered by the manufacturer in pre-modified and pre-inoculation conditions. Six experimental melts were cast for variants with only Zr added (0.05 - 0.3 wt. %), and three with constant addition of Zr (0.15 wt. %) and gradually increasing addition of Ti (0.1 - 0.3 wt. %). Zr was added in the form of AlZr15 pre-alloy and Ti in the form of AlTi5B pre-alloy. The heat treatment (HT) process was performed by T6 precipitation hardening. From each experimental variant, half of the samples (Fig. 3.) were heat treated (5 pieces out of the 10 pieces of cast experimental samples from each variant).

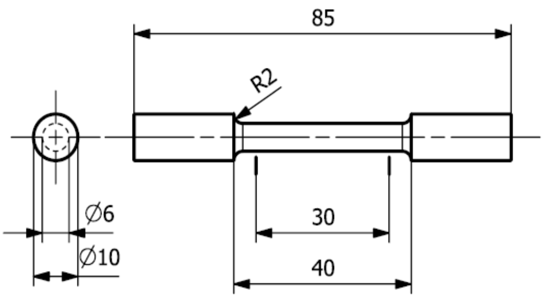

Fig. 3. Scheme of the testing sample (dimensions in mm)

Mechanical tests were performed on an Inspekt table 50 kN bursting device according to EN ISO 6892-1. Samples that reached the highest values of mechanical properties were selected to evaluate the microstructure before and after heat treatment. Samples were prepared by standard metallographic procedures. To distinguish the Zr phases, the samples were etched with H_2SO_4 etchant. The results of the mechanical properties were confronted with the values of the P reference alloy. Experimental alloys F1 to F6 were alloys for which the optimal addition of Zr was defined for the best possible mechanical properties in range from 0.05 wt. % to 0.3 wt. % Zr. Experimental alloys E1 to E3 were alloys with a constant addition of Zr (0.15 wt. %) and with a gradually increasing Ti content in the range of 0.2 wt. % to 0.3 wt. % Ti.

Table 1.
Chemical composition of P, F1-F6, E1-E3 alloys (wt. %)

Variant	Si	Fe	Cu	Mn	Mg	Sr	Ti	Zr
P	6.88	0.12	0.54	0.07	0.37	0.01	0.13	-
F1	7.02	0.12	0.55	0.07	0.40	0.01	0.15	0.04
F2	6.90	0.11	0.54	0.07	0.37	0.01	0.16	0.09
F3	6.86	0.12	0.55	0.07	0.37	0.01	0.16	0.13
F4	6.76	0.12	0.54	0.07	0.37	0.01	0.15	0.18
F5	6.79	0.12	0.54	0.07	0.37	0.01	0.14	0.20
F6	6.80	0.12	0.54	0.07	0.36	0.01	0.13	0.26
E1	6.96	0.13	0.55	0.07	0.37	0.01	0.23	0.12
E2	6.68	0.13	0.54	0.07	0.35	0.01	0.28	0.14
E3	6.51	0.13	0.52	0.07	0.34	0.01	0.37	0.13

P- reference alloy AlSi7Mg0.3Cu without addition of Zr and Ti; F1 - F6, experimental alloys AlSi7Mg0.3Cu with graduated addition of Zr 0.05 wt. %; E1 - E3 experimental alloys AlSi7Mg0.3Cu with constant addition of Zr 0.15 wt. % and graduated addition of Ti 0.1 wt. %

3. Experimental part

3.1 Thermal analysis

The effect of Zr phase precipitation in the metal matrix of experimental alloys was monitored by thermal analysis. A recurring peak was observed in the temperature range from 610 to 630 °C (Fig. 4.) with a gradual increase in the amount of Zr in the F1 - F6 experimental alloys.

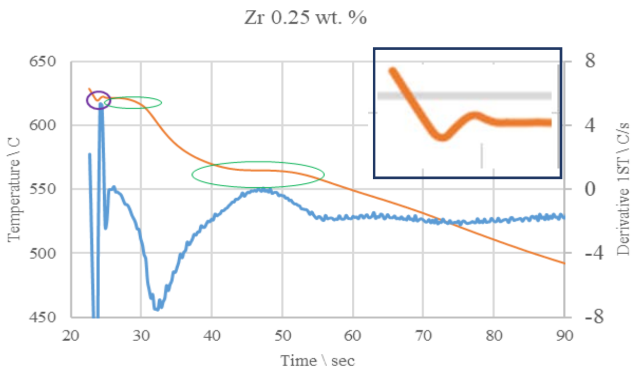

Fig. 4. Thermal analysis of F5 AlSi7Mg0.3Cu0.5 experimental alloy with the addition of 0.25 wt. % Zr

Precipitation of a new phase was observed in the areas indicated by the purple ellipses because a recurring peak in the P reference alloy was not observed (compare Fig. 5a. and Fig 5b.). No significant change was observed in the precipitation of the basic components of the metal matrix of the AlSi7Mg0.3Cu0.5 reference alloy with the addition of Zr and Zr with Ti. The eutectic precipitated at a temperature of 555 ± 5 °C, precipitation of hardening phases, for example Mg_2Si, occurred at 550 ± 5 °C. A synergistic effect of Zr and Ti treatment was not observed at different precipitation temperatures, but a different size of the subcooling curve was identified (Fig. 5b.). For this reason, which was confirmed by observing the microstructure, a larger number of Zr phases precipitated. This fact points to the effect of Ti as an element positively supporting the formation of nucleation nuclei of future Zr phases.

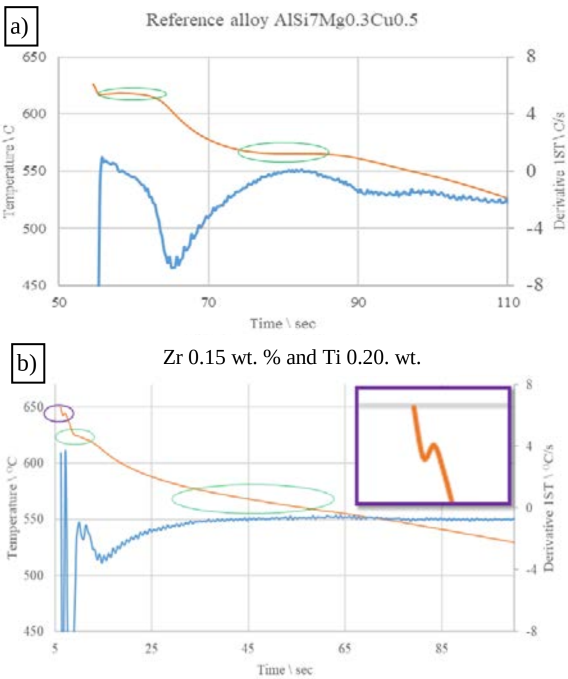

Fig. 5. a) Thermal analysis of the P reference alloy; b, E2 AlSi7Mg0.3Cu0.5Zr0.15 experimental alloy

3.2 Mechanical properties

Experimental alloys F1 to F6 alloyed only with Zr show a partial increase in the evaluated mechanical properties compared to the P reference alloy. When evaluating the agreed yield strength ($Rp_{0.2}$) after heat treatment, a more significant increase of values occurs only with the addition of Zr ≥ 0.15 wt. % (Fig. 6a.). The highest increase of values is achieved in alloy F3 with an increase in $Rp_{0.2}$ values compared to the P reference alloy by 3.5 %. $Rp_{0.2}$ is much higher in the case of experimental alloys E1 to E, which are characterized by a constant addition of 0.15 wt. % Zr and the addition 0.1 wt. % Ti. The obtained values exceed the mechanical values of experimental alloys of variants F1 to F6 especially after heat treatment (HT). The highest values after HT were achieved with the E3 experimental alloy (237 MPa). This represents an increase of $Rp_{0.2}$ over the P reference alloy by almost 15 %. The increase in the alloy with the addition of 0.15 wt. % Zr (F3) is by 14.5 %. When evaluating the yield strength (R_m), alloys F1 to F3 did not reach a significant increase (Fig. 6a.). A slight increase was observed before heat treatment, but no significant changes occurred after HT. The change occurred in E1, E2 and E3 alloys. Here, R_m slightly increased, especially in the E1 variants. The increase in R_m compared to the P alloy and the alloy with the best obtained mechanical properties (F5) with the addition of only Zr is only by 1.5 %. The improvement of the investigated properties was observed in the evaluation of the modulus of elasticity (elongation) (E) and hardness (HBW) after heat treatment. For alloys F3 to F6, an increase in E was observed (Fig. 6b.), while the highest values were reached for F4 samples (approx. 82 MPa). The improvement over the P reference alloy was by 6.8 %. The synergistic effect of the combination of Zr and Ti was reaffirmed, when the experimental alloys E1 and E3 reached much higher mechanical properties values than the original variant with the addition of only Zr. The increase of the values of E3 experimental samples compared to the P reference alloy is by almost 27 %.

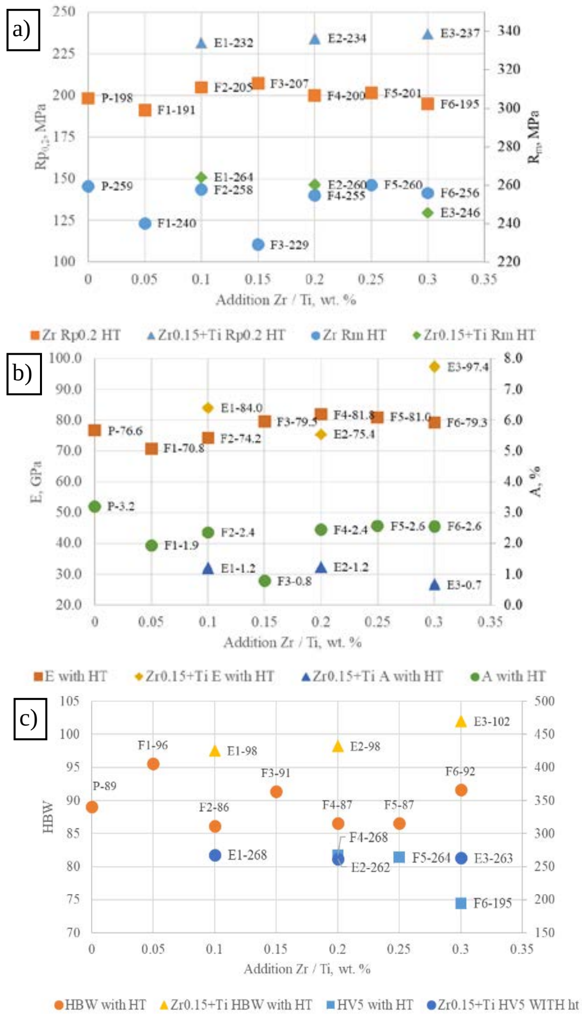

Fig. 6 Dependence of R_m, $Rp_{0,2}$, E, A, and HBW after heat treatment and HV5 Zr phases before heat treatment for P alloy and experimental F1- F6 and E1 - E3 alloys

An increase by 20 % was achieved in comparison with the F4 experimental alloy with the best obtained properties with the addition of 0.2 wt. % Zr. Based on the given parameters, it can be stated that the investigated samples are likely to be able to withstand higher operating stress during the operation of the device. By increasing $Rp_{0.2}$ and E, AlSi7Mg0.3Cu alloy is obtained capable of withstanding the same or higher operating loads even when the functional cross-sections of the casting walls (e.g. cylinder heads) are narrowed. The most significant decrease in mechanical properties was observed in ductility (A). Ductility decreased by 20 to 25 % (Fig. 6b.) in the experimental alloys from F1 to F6. Samples E1 to E3 showed a decrease in ductility by up to 63 %. This is a significant decrease that can negatively affect the application possibilities, especially for automotive components. In the case of reduced ductility, such components, for example engine cylinders, would not be able to react flexibly and plastically to the required extent during the temperature change in the combustion chamber. This would reduce the life of the internal combustion engine. Although the dispersed shorter Zr phases in the metal matrix of the AlSi7Mg0.3Cu0.5 alloy increased strength, the sharp ends initiate trans-crystalline cleavage (splitting) and thus a decrease in A. When evaluating HBW hardness, the highest values in the investigated alloys from F1 to F6 were measured in the F1 alloy (Fig. 6c.). In other cases, the values obtained were similar to the P reference alloy. The improvement after heat treatment was 7 % for the F1 experimental alloy compared to the P reference alloy. The synergistic effect of Zr and Ti in E1, E2 and E3 alloys caused a more significant increase in HBW. The highest values were measured for E3 samples (102 HBW). The increase over the P reference alloy was by 15 %.

3.3 Microhardness and EDX analysis

The microhardness of the Zr phases was evaluated as the arithmetic mean of 10 test punctures, the value obtained being around 260 HM 5 (Fig. 6c.). The microhardness of the Zr phases is in the hardness range of, for example, Al_4Ca or Al_6CuMg phases, which are characterized by microhardness in the range of 200 to 300 HM 5. In the microhardness evaluation, a decrease was observed in Zr phases in interaction with other phases, for example those based on Mg and Fe. In contrast, microhardness increased in Zr phases without interaction with other phases. Based on the chemical composition and evaluation of the microstructures, it is possible to define the reference and experimental alloys as pre-modified and pre-inoculated sub-eutectic alloys, containing primary α-phase dendrites and a globular eutectic. In addition to the basic phases, the structure of the metal matrix also contained hardening (curing) Al_2Cu and Mg_2Si phases. Fe-based intermetallic phases in the form of "Chinese letters" have also been identified. Visible precipitation of Zr phases in the alloy occurs above the content of 0.10 wt. % Zr in the form of long needles (acicular formations) with slightly split ends. With increasing Zr content, there was an increase in the length of precipitated Zr phases. After heat treatment, it was possible to observe an increased rate of decay of precipitated Zr phases (Fig. 7a.) especially in Zr content higher than 0.20 wt. %.

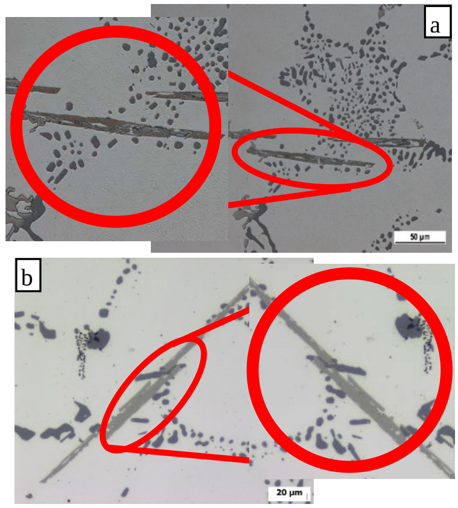

Fig. 7. a) Microstructure of the F4 experimental alloy after heat treatment, b) Microstructure of the E1 experimental alloy after heat treatment

This results in a reduced degree of stability of the thus precipitated Zr phases. The synergistic action of Zr and Ti increased the stability of Zr phases (Fig. 7b.) especially before heat treatment, and at the same time the increase of precipitated Zr phases was observed in microstructures, as can be seen in Figure 8 where Zr phases are marked in red (Fig. 8.).

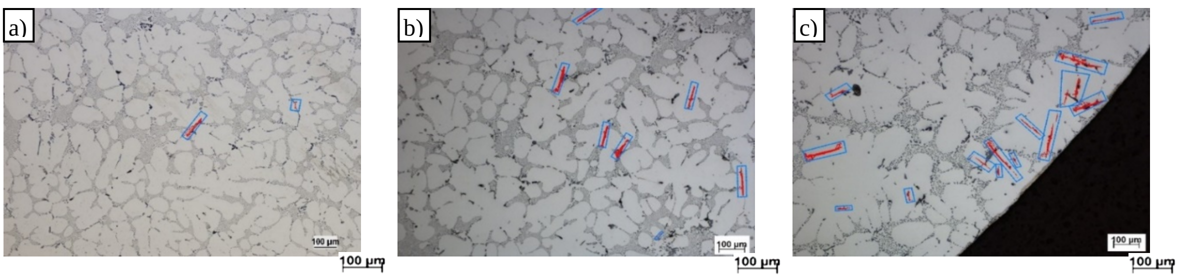

Fig. 8. Microstructure of primary and experimental alloys before HT a) R alloy, b) E1 alloy, c) E2 alloy, etchant H_2SO_4

There was an increase in Zr phases in the metal matrix of the investigated alloys by about 40 % with increasing Ti content in the alloys. Subsequent heat treatment did not cause significant decay of the precipitated Zr phases. It can be stated that the precipitation of smaller but much more stable Zr phases allows a sharp improvement of selected mechanical properties. When evaluating the microstructure of experimental alloys with the addition of Zr and Zr together with Ti, an increased interaction between Zr phases and other phases was observed, most often based on Mg, Cu but also Fe. It is also possible to confirm the positive effect of Zr as a corrector for the negative effect of iron phases, i.e. the acicular form is transformed into a less negative form of Chinese letters. It is also possible to assume an increase in the stability of the Al_2Cu and Mg_2Si curing phases (Fig. 9.). At the same time, the presence of Ti in the Zr phases was identified, which indicates the influence of Ti as a nucleating element in the formation of nuclei of future Zr phases.

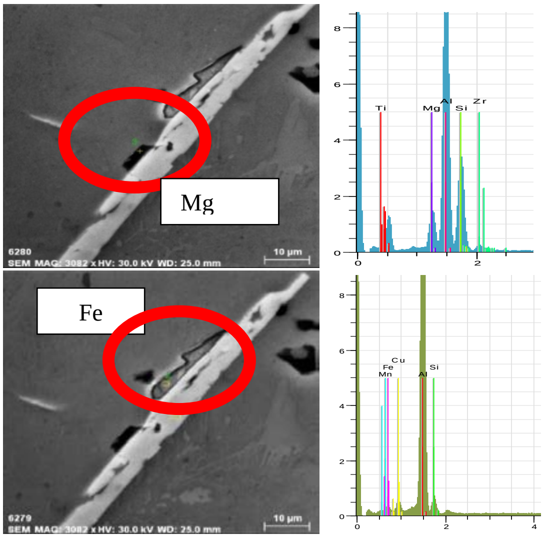

Fig. 9. EDX analysis of Zr phases and phase morphology in its interaction in the F4 experimental alloy

4. Evaluation

The synergistic effect of Zr and Ti indicates a positive effect in increasing $Rp_{0,2}$, E, HBW and partly also RF_m. However, the synergistic effect of Zr and Ti significantly reduces A in alloys E1 to E3. Visible precipitation of Zr phases occurs above the content of 0.1 wt. %, in the form of long smooth needles, with slightly split ends. The size of the Zr phases increases as the content of Zr in the alloy increases. After heat treatment, Zr phases were visible at contents $\geq$ 0.15 wt. % Zr, however, these were significantly more fragmented than in alloys containing Zr and Ti. The synergistic effect of Zr and Ti increases the number of precipitated Zr phases in the metal matrix of the experimental alloy as well as their stability after heat treatment compared to alloys alloyed only with Zr. By increasing Ti content by 0.1 wt. % was observed an increase in the number of precipitated Zr phases by approximately 40 %, which confirms the assumed fact that Ti acts in the alloy as a significant nucleation element in the formation of nuclei of Zr phases. With an increasing Zr content in the investigated alloy, there was an increase in the interaction of Zr phases with other phases based on Mg, Cu and Fe. This fact points to the ability of Zr phases to increase the stability of curing (hardening) phases at higher temperatures and also has a corrective effect on the negative intermetallic Fe phases in the investigated Al alloy.

5. Conclusion

The use of the synergistic effect of Zr with other elements points to a possible path in the development of new, more sophisticated alloys for the automotive and aerospace industries. It can be stated that for the investigated AlSi7Mg0.3Cu0.5 alloy cast in a ceramic mould, the content of 0.15 to 0.20 wt. % Zr and 0.20 to 0.30 wt. % Ti appears to be the most advantageous combination.

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