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IMPACT OF ZIRCONIUM ON THE STRUCTURAL AND MECHANICAL PROPERTIES
OF COMMERCIAL AlSi10MgCu ALLOYS

The impact of small addition of zirconium in hypoeutectic commercial AlSi10MgCu alloys on their mechanical properties (hardness) in as cast and thermally treated conditions was investigated. Small addition of zirconium does not change significantly the as cast and heat-treated microstructure of investigated alloys except to reduce the SDAS and grain size of primary α-aluminium phases. Addition of zirconium up to 0.14 wt. percentage increases the hardness of investigated alloys in as cast conditions. The increase in the hardness of samples after various solid solution times can correlate very well with the formation of small needle like coherent Al$_3$Zr particles.

Keywords: zirconium, AlSi10MgCu alloy, hardness, solid solution treatment

1. Introduction

Aluminum-Silicon-Magnesium-Copper (AlSi10MgCu) hypoeutectic alloys are widely used cast alloys in automotive industry due to their good mechanical properties (moderate strength and elongation), thermos-physical properties (low density, low viscosity) and good corrosion resistance [1-3]. Magnesium and Copper are present as major alloying elements in these alloys with the main aim to increase their mechanical properties. [4]. Magnesium addition up to approximately 0.5 wt. percentage significantly increase the strength of these alloys in as cast and heat treated conditions [5]. Copper is in these alloys present in small concentration and does not contribute significantly to the improvement of mechanical properties of investigated alloys. The mechanical, thermo-physical and metallurgical properties of these alloys can be improved by alloying with zirconium. According to the available literature [6] it is well known that zirconium added to the aluminium-silicon-magnesium cast alloys (~up to 0.3 wt. percentage) precipitate during solid solution treatment in the small and coherent Al$_3$Zr phase. Because of zirconium low diffusivity and solubility in aluminium matrix, these fine particles are stable during solid solution and resistant to coarsening, increasing therefore the hardness and strength of cast AlSi10MgCu alloys. According to the literature [7] and recent investigations [8,9], the zirconium concentration in the investigated alloys needs to be between 0.08 wt. percentage [9] and 0.24 wt. percentage [8]. Higher concentration of zirconium in the aluminium-silicon alloys (~more than 0.20 wt. percentage according to literature [9] leads to the precipitation coarse primary Al$_3$Zr phase, which considerably reduce the mechanical properties of treated alloy. Additionally, mechanical properties of these alloys can be improved through various thermal treatments such as solid solution and aging. During solid solution, alloys are exposed to the maximal elevated temperature defined by their lower melting point in order to dissolve soluble phases (copper and magnesium rich phases in this particular case) in the α-aluminium matrix. Applying alloying practice and thermal treatment, the mechanical properties of aluminium cast alloys can be significantly improved. The strengthening of these alloys is achieved during artificial and/or natural aging by precipitation small, fine and coherent metastable phases. Therefore, the main objective of this study was to investigate the impact of small addition of zirconium on the hardness properties of hypoeutectic AlSi10MgCu alloys in as cast and thermal condition.

2. Experimental part

The material use in this work was hypoeutectic AlSi10MgCu commercial alloy without and with zirconium (0.08; 0.14 and 0.24 wt. percentage Zr) addition. The chemical composition of alloy is listed in Table 1 (for all elements in wt. percentage). The zirconium was added to the melt in the form of the Al10% Zr master alloy. The alloy was melted in the 700 kg capacity electric resistance furnace. The melt was degassed for 15 minutes using nitrogen gas. After degassing melt temperature was maintained at 760°C. The melt was poured in the steel mould to produced rounded samples with diameter of 25 mm and

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length of 100 mm. Those samples have been cut in small pieces and used for hardness measurement. As cast samples have been solution treated at 530°C at various time up to 24 hours in the electric furnace and quenched in the water at 60°C temperature. Standard metallographic techniques (sample preparation, Light Optical Microscope and Scanning Electron Microscope) have been applied in order to investigate the microstructure of treated samples. Hardness of as cast and heat-treated samples have been measured using Brinell hardness tester QNEES 3000 with load of 250 kN and a 5.0 mm diameter ball. From each specimen (25 mm in diameter and 25 mm in high), at least three hardness measurements have been taken and average value has been calculated.

TABLE 1

Chemical composition of investigated AlSi10MgCu alloy (wt.%)

Alloy	Si	Fe	Cu	Mg	Mn	Zn	Ti	Sr	Ni
AlSi10Mg Cu+Zr	9.19	0.38	0.27	0.39	0.31	0.13	0.13	0.015	0.008

Fig. 1. Microstructure of as cast AlSi10MgCuZr alloy obtained using light optical microscope

3. Results and discussions

The as cast microstructure of the AlSi10MgCu alloy, as Figure 1 illustrates is characterized by the presence of primary α-aluminium phase, modified aluminium-silicon eutectic (Al-Si) distributed between primary α-aluminium dendrites as well as Mg_2Si and zirconium – titan rich phases.

The zirconium-titan rich phase generally shows needle like form as it illustrated in Figure 2a. In the three dimensional view, as Figure 2b shows, those needles looks like plates. Literature [10] has documented that addition of 0.15 wt. percentage zirconium in the A319 alloy (AlSi5Cu3.8Mg0.26) does not change significantly as cast microstructure of investigated alloy except reduction in the size of the SDAS caused by grain refinement effect of zirconium. Our own recent investigation has confirmed
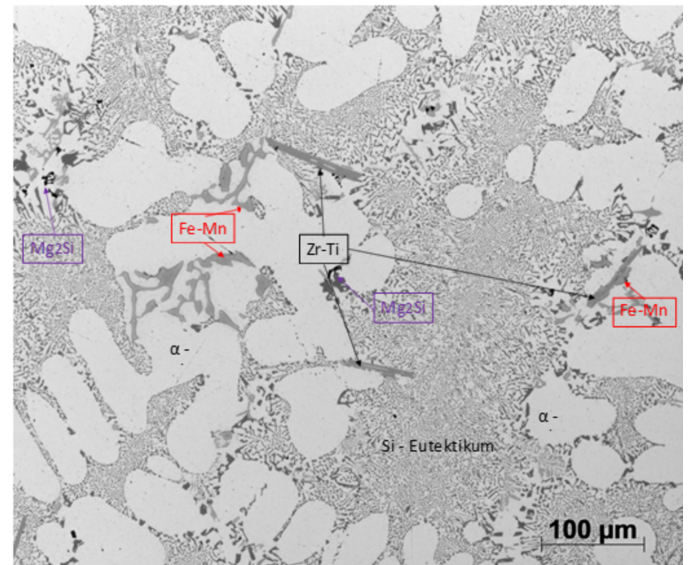
it, showing that addition of zirconium up to 0.24 wt. percentage reduced the SDAS from 57.3 µm to 50.4 µm and grain size from 3.6 mm to 1.2 mm.

The Brinell hardness of investigated samples in as cast condition is presented in Figure 3. It can be noticed that hardness of investigated alloys increase by increasing zirconium content up to 0.14 wt. percentage). Further addition of zirconium, up to 0.24 wt. percentage in the AlSi10MgCu alloy, decrease hardness of this alloy. According to Mahmudi [10] and Seperband [11] minor addition of zirconium (up to 0.15 wt. percentage) to the AlSi6Cu4 alloy results in an 8% to 10% increase in hardness in all investigated alloys in both as cast and heat treated conditions. Voncina at al [7], found that addition of 0.202 wt. percentage zirconium to the AlSi9Cu3(Fe) alloy did not impact considerably the hardness of the die cast alloys (hardness barely increase after
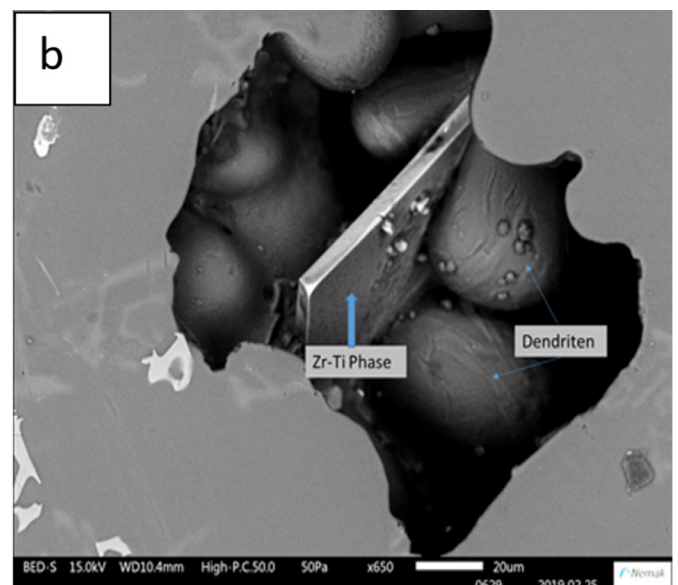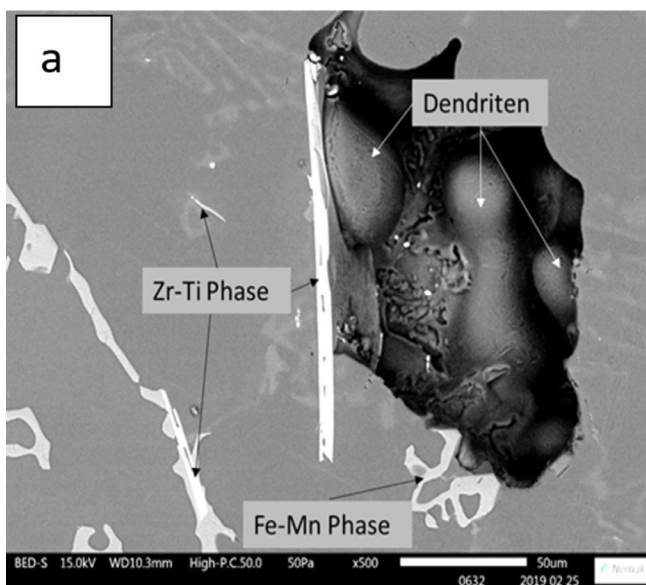

Fig. 2. Microstructure of zirconium-titan rectangular phases in as cast conditions obtained using scanning electron microscope

addition of zirconium from 84 to 85 HV). Based on our own investigation presented in Figure 3, it is worth noting to add more than 0.14 wt. percentage zirconium in the as cast AlSi10MgCu alloy in order to improve its hardness.
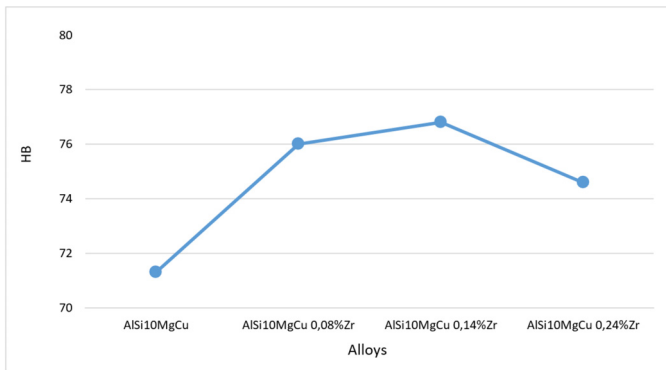

Fig. 3. Impact of zirconium content on the hardness of as cast Ali 10MgCu alloy

Alloys may not possess all the desired properties in as cast conditions. Therefore, heat treatment is extensively used for controlling their properties. During the heat treatment process, the microstructures of treated alloys are modified, resulting in improved mechanical properties like strength, ductility, toughness, hardness and wear resistance. In order to improve the hardness of the AlSi10MgCuZr alloy as cast structure of selected samples have been thermally treated applying solid solution process. A recent study run by Sepehrband et al. [11] has shown that small addition of zirconium change the optimum solid solution time of the AlSi5Cu3.8Mg0.28 (A319) and AlSi5Cu3.8Mg0.28Zr0.15 (A319Zr) alloys. Both alloys were solid solution treated at 503°C from 4 to 36 hours. As Figure 4 shows the hardness of two alloys with and without zirconium drop down deeply with increasing solid solution time up to 8 hours.

Longer solutionizing time has different impact on these two alloys. At standard 319 alloy longer solid solution time decrease slightly hardness while 319 alloy with zirconium content gain hardness. Authors concluded that the observed decrease in the hardness by 319 alloy without zirconium can be attributed to the dissolution of precipitates formed during solidification. An increase in the hardness of the 319 alloy with zirconium is related to the optimal solid solution temperature range for formation of
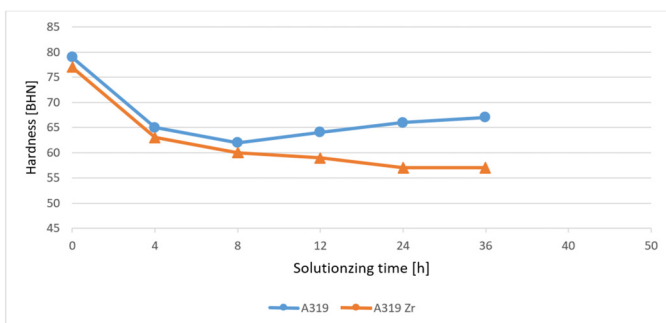

Fig. 4. Hardness of the A319 and A319Zr alloys after different time of solid solution [11]

fine Al_3Zr phase as well as longer period of soaking time may lead to formation of this coherent phase, resulting in the greater hardness of investigated alloys.

The present work was aimed at determining the optimal solid solution time for the AlSi10MgCu alloy with (0.14 wt. percentage Zr) and without (0 wt. percentage Zr) zirconium addition that would generate the development of increased hardness. Solid solution time was scheduled to be: 0; 5.5; 7.0; 8.5; 10.0, 11.5 and 24 hours at 530°C. The Figure 5 shows the impact of zirconium and selected solid solution times on the hardness of the AlSi10MgCu and the AlSi10MgCuZr alloys.
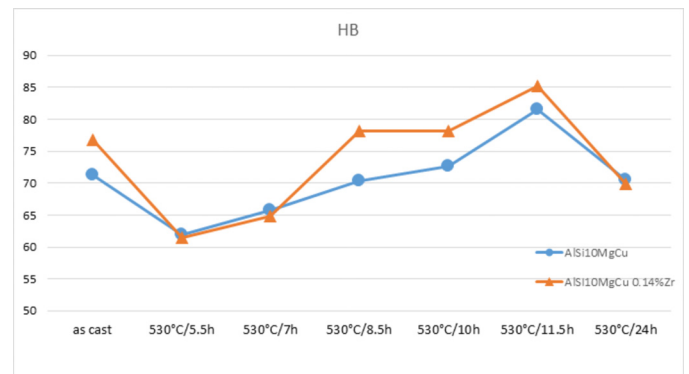

Fig. 5. Effect of zirconium (0 and 0.14 wt. %) and various solid solution time on the hardness of AlSi10MgCu alloys

According to Figures 3 and 5, small addition of zirconium (0.14 wt. percentage) increases the hardness of the AlSi10MgCu alloys in the as cast conditions. As Figure 5 indicates, the hardness of both materials, with and without zirconium, firstly drop with increasing solution time up to 5.5 hours. The decrease of hardness for both alloys is significant (20% for the AlSi10MgCuZr alloy and 14% for the AlSi10MgCu alloy), being slightly stronger for alloy with zirconium. By longer solution time (up to ~24 hours), however, alloys with and without zirconium show similar trend and slightly different behaviour. The hardness of alloy with zirconium shows a stronger increase reaching the highest value of 85 HB, while material without zirconium reach maximal value of 82 HB after 11.5 hours solid solution time. The detected effect seems to correlate very well with formation of coherent small Al_3Zr intermetallics. Due to low interface energy with matrix α-aluminium, slow diffusion coefficient and low solubility the additional hardening effect of Al_3Zr has been recognized after 7 hours solid solution treatment. As Figure 5 indicates, the longer solid solution time than 11.5 hours (up to 24 hours) resulted in a completely different trend decreasing the hardness of both alloys significantly. The hardness of both alloys (with and without zirconium) after 24 hours solid solution treatment reached almost the same value of 70 HB. The main reason for such behaviour can be find in different diffusion coefficients of magnesium, and zirconium elements into aluminium matrix. Magnesium has the higher diffusion coefficient compare to zirconium (Mg = 10^{-7} cm²/s; Zr = 10^{-19} cm²/s). Therefore, it is clear that zirconium needs more
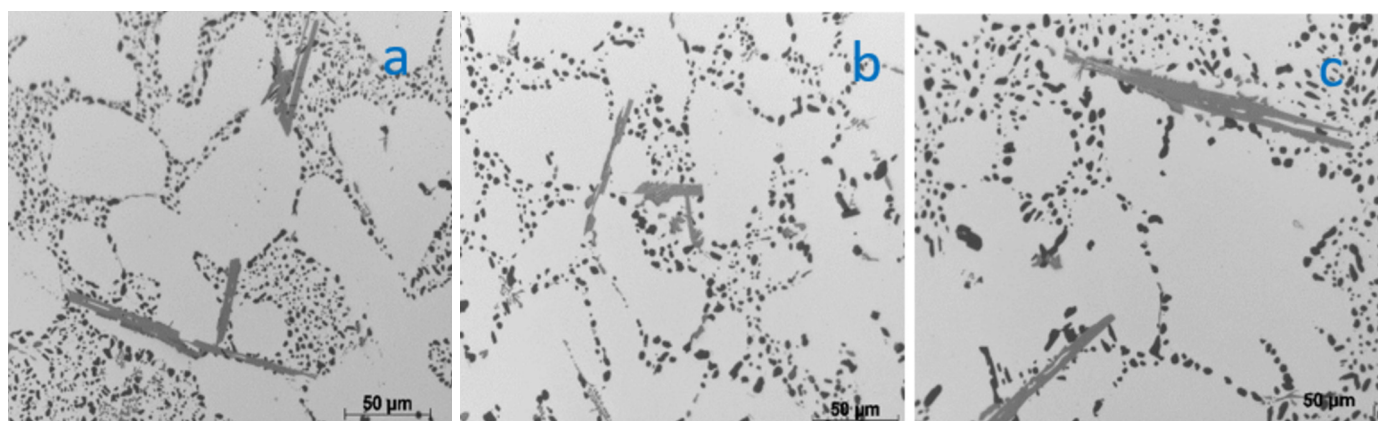
Fig. 6. Coarsening silicon parties as a function of various solid solution time; (a) solid solution time after 7 h; (b) solid solution after 10 h and (c) solid solution after 24 h. Note the presence of ZrTi rich phases after various solid solution time without any considerable changes

time to be dissolved during solid solution in α-aluminium matrix. During longer solid solution time (up to 11.5 hours) zirconium is precipitating in the small Al₃Zr particles (in nanoscale ~48 nm) [12] which caused the slightly higher hardness of thermally treated alloy with zirconium. Hardness of alloy without zirconium increase due to precipitation of the Mg_2Si particles. At longer solid solution time (>11.5 hours) the coarsening of both precipitated particles (Al_3Zr and Mg_2Si) is one of the reason that in both observed alloys hardness decreased. The second reason for hardness decrease can be attributed to the coarsening effect of silicon particles. As Figure 6 illustrates, it is evident that at longer solid solution time silicon particles are getting coarser causing the decrease in the hardness value by both alloys.

4. Conclusions

In this paper it has been analysed the effect of the small addition of zirconium in the AlSi10MgCu alloy on its structural and mechanical (hardness) properties. By alloying the standard commercial alloy with zirconium, the rich ZrTi intermetallic phase has been formed nearby iron-manganese rich phases. Small addition of zirconium to the AlSi10MgCu cast alloy improves the hardness in both as cast and as thermally treated condition. Optimal hardness of as cast AlSi10MgCu alloy has been achieved by adding 0.14 wt. percentage zirconium. Combined zirconium addition (0.14 wt. percentage) and thermal treatment (solid solution 530°C / 11.5 hours) are needed to achieve the maximal increase in the hardness of investigated alloys. The optimal hardness increases in approximately 18% in comparison to the base alloy without zirconium and thermal treatment. Longer solid solution time leads to decrease in the hardness of alloys with and without zirconium content due to coarsening of fine precipitated phases (Al_3Zr and Mg_2Si) as well as silicon phases. During solid solution time, up to 24 hours it has not been recognized any significant changes in the shape and form of the ZrTi rich phases.

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