

Article

Effect of Modification on Microstructure and Properties of AZ91 Magnesium Alloy

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Abstract: Refinement of α -Mg solid solution grains has a significant influence on the improvement of mechanical properties of cast magnesium alloys. In the article, the effects of three modifiers on microstructure and properties of AZ91 magnesium alloy casted to a sand mould were described. Overheating, hexachloroethane and wax-CaF₂-carbon powder were applied. The research procedure comprised microstructure analysis by means of light microscopy, scanning electron microscopy and quantitative analysis with *AnalySIS Pro®* software and mechanical properties' investigation. The microstructure of AZ91 alloy in the as-cast condition consists of α -Mg solid solution with precipitates of Mg₁₇Al₁₂, Mg₂Si and Al₈Mn₅ phases. It was reported that all applied modifiers cause refinement of α -Mg solid solution grains and a decrease of the volume fraction of α -Mg+Mg₁₇Al₁₂ compound discontinuous precipitates. The best results were obtained in the case of wax-CaF₂-carbon powder.

Keywords: grain refinement; AZ91; overheating; hexachloroethane; wax-CaF₂-carbon; microstructure; heat treatment; mechanical properties

1. Introduction

Primary grain size is one of the elementary structural criteria in evaluation of the quality of cast magnesium alloys. Grain refinement results in improvement of mechanical properties of the alloy, e.g., wear resistance and corrosion resistance [1–3]. Cooling rate is relatively low in the case of sand casting, which causes the significant growth of solid solution grains and promotes the increase of volume fraction of intermetallic phases. Therefore, refinement of solid solution grains in gravity-casting requires modification.

In the case of Zr-containing magnesium alloys the main factors influencing the refinement of solid solution grains are the volume fraction of strengthening precipitates and the amount of zirconium or applied Mg–Zr master alloy [4], while in case of Mg–Al alloys the most common modification processes are:

- overheating of the molten alloy.
- Elfinal process—modification with iron (III) chloride.
- modification with carbon.

In industrial practice, most alloys should not be heated over the liquidus temperature more than necessary to homogenise the chemical composition. High overheating intensifies oxidation of the alloy, absorption of gases and causes the formation of coarse primary grain structure [5]. However, in the case of Mg–Al alloys the described treatment promotes the refinement of solid solution grains. The treatment comprises heating of the molten alloy 150–260 °C over liquidus, temperature arrest for

desired time and subsequent rapid cooling to pouring temperature with short hold at this temperature. Required temperature arrest time of overheated melt decreases with the increase of aluminium content, the amount of circulating scrap, crucible size and heating rate [6].

The Elfinal process is based on the concept of iron precipitates, acting as nucleation sites for magnesium grains [7]. Efficiency of Elfinal process is comparable to overheating process, which is efficient only in the case of Mg–Al alloys with the addition of manganese, which makes it different from other processes [8]. The method comprises rinsing the anhydrous FeCl_3 in molten metal at the temperature of approx. 760 °C and is efficient method of grain refinement in Mg–Al alloys and Mg–Zn alloys without Al addition [9]. The temperature applied during Elfinal process, which is lower than in case of overheating, makes this process more cost effective. Moreover, it enables holding the molten alloy at pouring temperature for at least one hour with no penalty to the efficiency of the grain refinement process [10]. However, the process has a limited application due to the harmful impact on the environment and negative effect of iron on the corrosion resistance of magnesium alloys [11].

Despite of the effectiveness of overheating and Elfinal processes in grain refinement, the problems connected with them caused the development of methods which apply the addition of carbon. These methods involve the introduction of carbon to molten magnesium alloy in the form of carbon gases (e.g., CO , CO_2 , CH_4), solid carbon (np. graphite, paraffin wax, Al_4C_3 and SiC carbides) and organic halides (e.g., hexachloroethane C_2Cl_6) [12]. To ensure the efficiency of solid solution grain refinement by the application of carbon, the content of approximately 0.5 wt. % of aluminium in the alloy is necessary, but the highest efficiency is achieved in alloys containing over 2 wt. % of aluminium [13]. Application of carbon gases is the easiest method of carbon introduction to the melt. The introduction of hexachloroethane C_2Cl_6 is not only an efficient method of grain refinement, but also degassing of the melt and is widely applied in the industry. Notwithstanding this, the emission of toxic gases determined the research of new modifiers, containing carbonaceous substances, which are less harmful to the environment. One of them is wax- CaF_2 -carbon powder, which is more eco-friendly and at the same time more effective in grain refinement [14].

2. Materials and Methods

The researches were conducted on AZ91 alloy after gravity casting to sand mould. The chemical composition of the alloy is presented in Table 1.

Table 1. Chemical composition of AZ91.

Element	Al	Zn	Mn	Cu	Si	Fe	Ni	Mg
[%]	8.9	0.6	0.21	0.02	0.05	0.006	0.001	balance

The material was melted in gas crucible furnace under the protective atmosphere with the following composition: 20% argon, 20% CO_2 and 0.2% SF_6 . Sand casting was performed at 770 °C. Three types of modification were applied:

- overheating of 10 min. at 850 °C with subsequent rapid cooling to pouring temperature,
- application of hexachlorethane (commercial name DEGASAL C1/A), 1 kg/100 kg of the alloy at temperature of ~740 °C,
- application of wax- CaF_2 -carbon powder (commercial name NUCLEANT 5000), 0.3 kg/100 kg of the alloy at temperature of approx. 730 °C.

Then the heat treatment comprising solution treatment of 415 °C/25 h/water cooling and ageing treatment of 170 °C/8 h/air cooling was applied.

An Olympus GX71 light microscope (LM) and a HITACHI S-3400N scanning electron microscope (SEM) with a Thermo Noran energy-dispersive X-ray spectrometer (EDS) equipped with SYSTEM SIX were used for observations of microstructure. EDS analysis was performed with an accelerating voltage

of 15 keV. The specimens were prepared by the standard technique of grinding and polishing, followed by etching at 14.1 g CrO₃, 17.6 mL HNO₃, 100 mL H₂O. To evaluate the stereological parameters, *AnalySIS Pro®* software was used. To characterise the microstructure the following parameters were evaluated:

- volume fraction of intermetallic phases throughout the sample section, Vv [%],
- average area of solid solution grain cross-section \bar{A} [μm^2].

Conditions of phases detection and evaluation are presented in Figure 1.

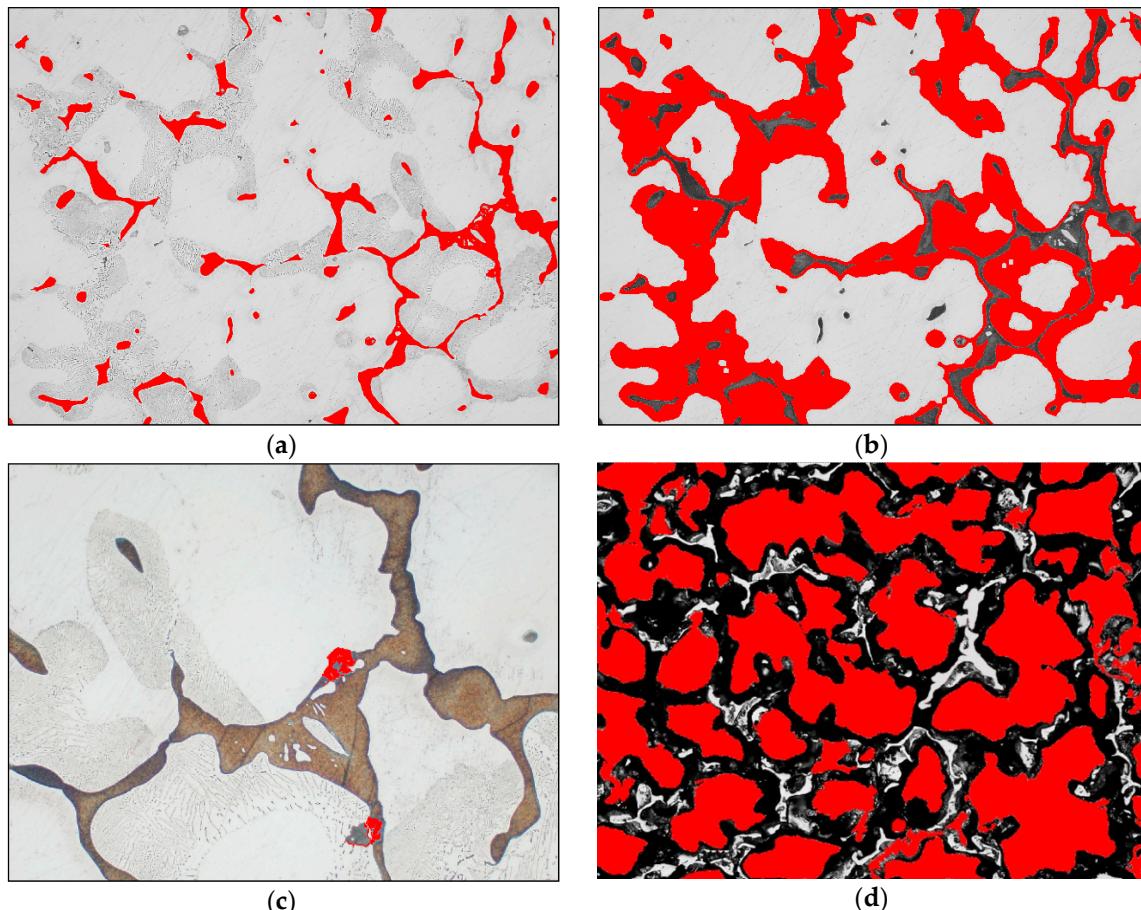


Figure 1. Conditions of phase detection: (a) continuous Mg₁₇Al₁₂, (b) discontinuous Mg₁₇Al₁₂, (c) Mg₂Si phase, (d) α -Mg solid solution.

Mechanical properties were evaluated according to ASTM B 557M standard [15] using an MTS-810 machine. Yield strength at 0.2% offset, elongation and ultimate tensile strength were averaged over three tensile samples.

3. Results and Discussion

3.1. As-Cast Condition

The microstructure of AZ91 alloy in as-cast condition is composed of α -Mg solid solution with precipitates of Mg₁₇Al₁₂ phase (Figure 2a). Two types of Mg₁₇Al₁₂ precipitates with different morphology were observed:

- continuous precipitates located mainly on grain boundaries of α -Mg solid solution;
- plate-like precipitates (discontinuous precipitates) formed in discontinuous diffusive transition creating the mixture of α -Mg and discontinuous precipitates of Mg₁₇Al₁₂ phase.

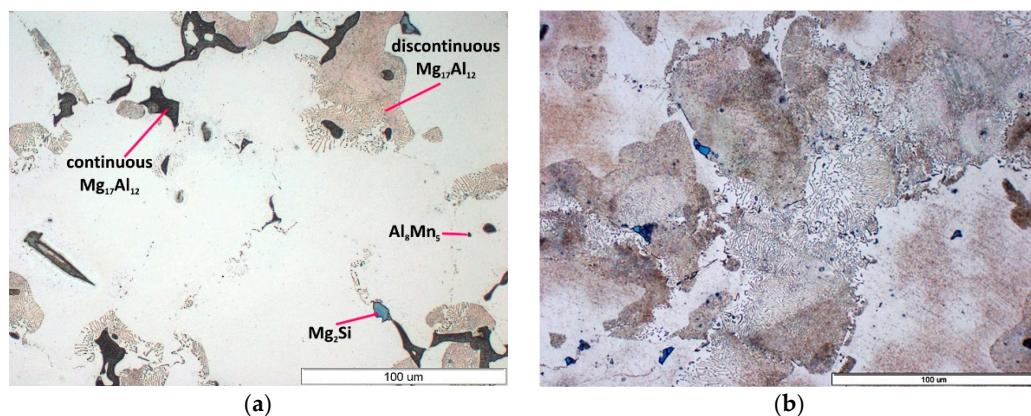


Figure 2. Microstructure of AZ91 alloy: (a) as-cast, (b) heat-treated.

The presence of α -Mg+Mg₁₇Al₁₂ discontinuous precipitates is a result of relatively slow solidification of the alloy in the sand mould. Moreover, the presence of Mg₂Si and Al₈Mn₅ phases in the microstructure of investigated alloy was reported [16].

Average area of solid solution grain cross-section was $\bar{A} = 1692 \mu\text{m}^2$ ($d = 43.6 \mu\text{m}$). The volume fraction of continuous precipitates of Mg₁₇Al₁₂ phase was estimated to $V_V = 4.9\%$, while in case of α -Mg+ Mg₁₇Al₁₂ discontinuous precipitates it was $V_V = 7.34\%$. Mg₂Si phase was inhomogeneously distributed in the structure of the alloy and its volume fraction was $V_V = 0.1\%$.

The applied heat treatment caused the disappearance of continuous precipitates of Mg₁₇Al₁₂ phase and significant increase of volume fraction of α -Mg+Mg₁₇Al₁₂ discontinuous precipitates up to $V_V = 31.55\%$ (Figure 2b).

3.2. Effect of Overheating

The microstructure of AZ91 alloy overheated at 850 °C is shown in Figure 3.

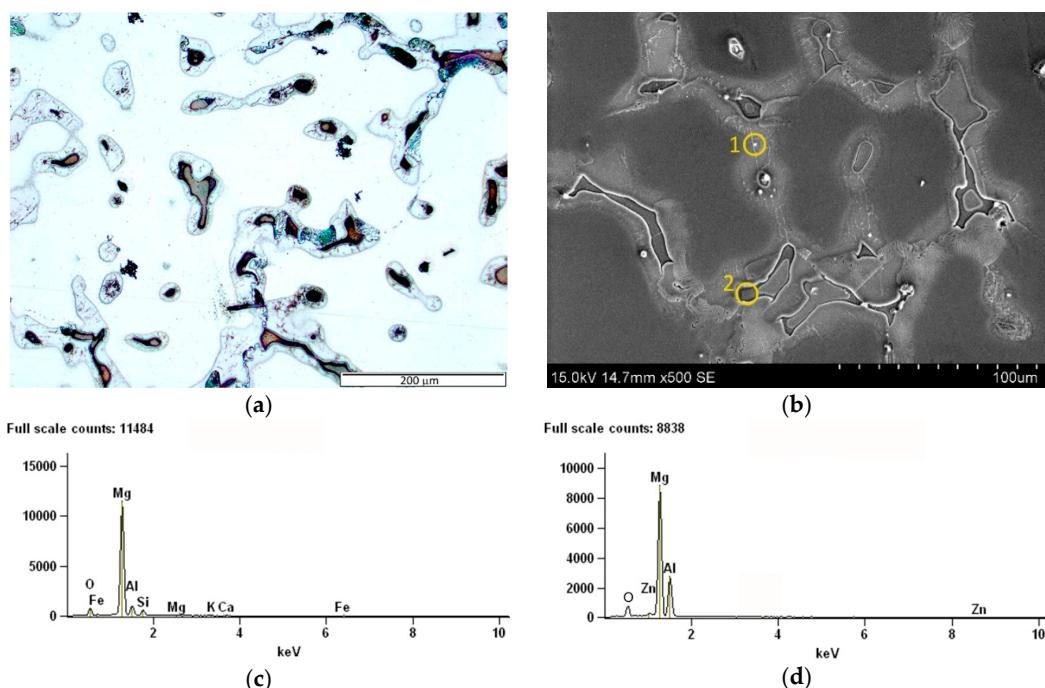


Figure 3. Microstructure of AZ91 alloy overheated at 850 °C: (a) light microscope (LM), (b) scanning electron microscope (SEM) (c) energy-dispersive X-ray spectroscopy (EDS) spectrum obtained from Fe-containing particles (point 1), (d) EDS spectrum obtained from oxidised areas (point 2).

Overheating of the alloy resulted in an approximate 7% decrease of average area of solid solution grain cross-section to $\bar{A} = 1585 \mu\text{m}^2$ ($d = 40.2 \mu\text{m}$) in comparison to as-cast condition. No significant changes in volume fraction of continuous precipitates of $\text{Mg}_{17}\text{Al}_{12}$ ($V_V = 5.28\%$) and Mg_2Si ($V_V = 0.08\%$) phases were observed. However, significant change was observed in the case of $\alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ areas (decrease to $V_V = 2.15\%$, approximately 70% in comparison to as-cast condition). Moreover, the presence of particles containing iron, as well as calcium and potassium, was reported (Figure 3b, c—points 1 and 2), whereas aluminium oxides were observed in the vicinity of $\text{Mg}_{17}\text{Al}_{12}$ phase precipitates (Figure 3b,d—point 3 and Figure 4).

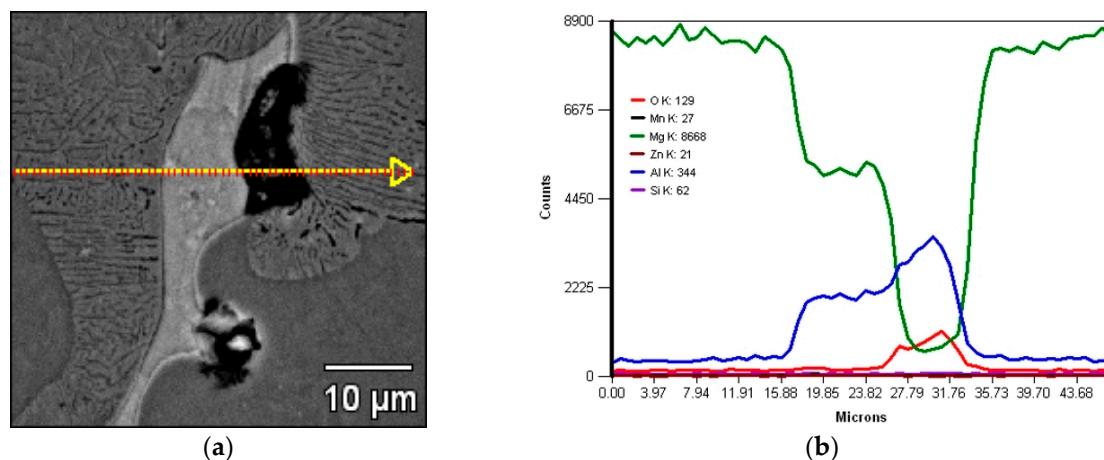


Figure 4. Aluminium oxides in AZ91 alloy overheated at 850 °C: (a) SEM, (b) line EDS analysis of chemical composition.

Solid solution grain refinement by overheating in the case of investigated alloy results from the occurrence of two different mechanisms of nucleation. First, a significant amount of aluminium oxides acting as effective nucleation sites for $\alpha\text{-Mg}$ solid solution was observed. The presence of these oxides results from excessively high overheating temperature, which increased the solubility of gases and in consequence the number of impurities formed [10,17]. The second mechanism relates to the presence of iron in the alloy. At 850 °C, iron diffused from the mild steel crucible to the melt and formed highly dispersive Al–Fe intermetallic phases. These phases acted as nucleation sites for solid solution. At the same time, the decrease of volume fraction of $\alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ areas was an effect of higher supercooling and in consequence higher solidification rate, which significantly decreased the possibility of discontinuous diffusive transition occurrence [6].

3.3. Effect of Hexachloroethane Refiner

The application of hexachloroethane caused the decrease of the average area of $\alpha\text{-Mg}$ solid solution grain cross-section to $\bar{A} = 1513 \mu\text{m}^2$ ($d = 38.7 \mu\text{m}$). That value was slightly (~5%) lower than after the overheating process (Figure 5a).

No significant change in volume fraction of continuous precipitates of $\text{Mg}_{17}\text{Al}_{12}$ ($V_V = 5.56\%$) and Mg_2Si ($V_V = 0.1\%$) phases were observed in comparison to as-cast alloy. However, as in the case of overheating, significant decrease of the volume fraction of $\alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ areas to $V_V = 1.97\%$ (approximately 75% in comparison to as-cast condition) was reported. Apart from precipitates typical for this alloy, the particles of the Al_8Mn_5 phase containing carbon were observed (Figure 6). No continuous precipitates of the $\text{Mg}_{17}\text{Al}_{12}$ phase were observed in the alloy after age-hardening treatment as in case of non-modified alloy. However, a significant increase of volume fraction of $\alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ discontinuous precipitates to $V_V = 36.45\%$ (approximately 15% in comparison to non-modified alloy after heat treatment) was reported.

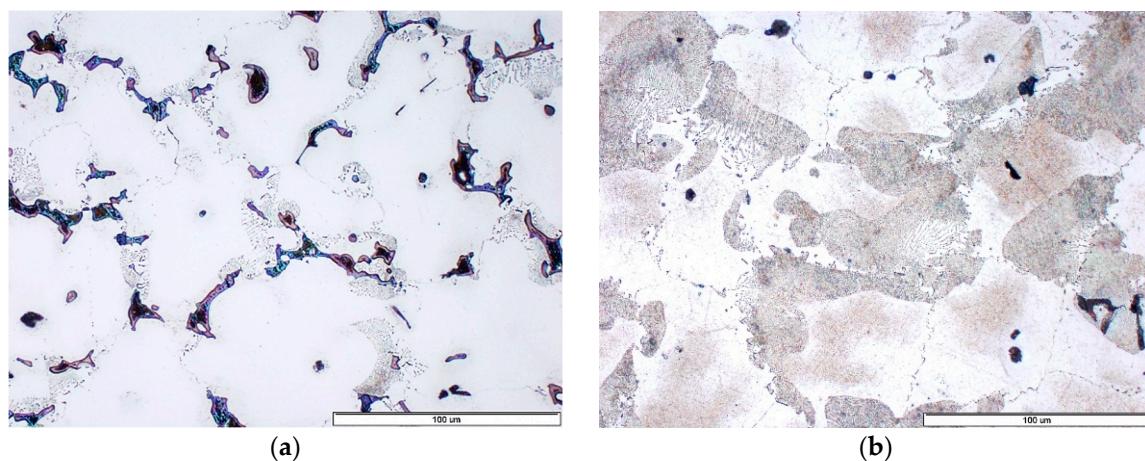


Figure 5. Microstructure of AZ91 alloy after modification with hexachloroethane: (a) as-cast, (b) heat-treated.

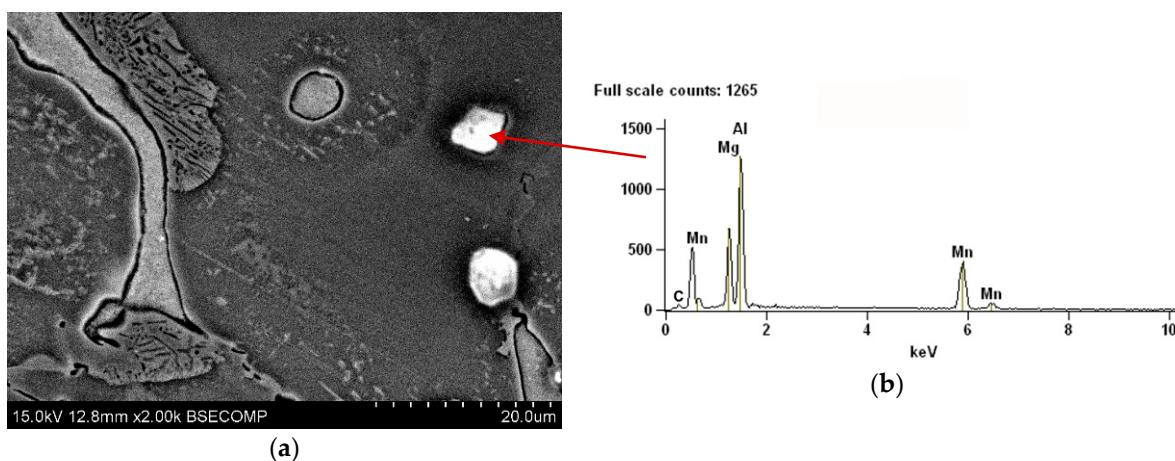


Figure 6. Carbon in Al_8Mn_5 precipitates: (a) SEM, (b) EDS.

The presence of particles containing carbon may result from the formation of numerous Al_4C_3 phase particles in the reaction of aluminium with the C_2Cl_6 phase during the mixing of the melt. Al_4C_3 particles act as sites for heterogenic nucleation of α -Mg solid solution. Effective refinement is associated with the same type of crystalline structure. Both Al_4C_3 phase and α -Mg solid solution have hexagonal unit cell with similar lattice parameters ($a = 0.333 \text{ nm}$, $c = 0.49900 \text{ nm}$ in Al_4C_3 and $a = 0.32030 \text{ nm}$, $c = 0.52002 \text{ nm}$ in α -Mg). Because the presence of carbon was observed mainly within Al_8Mn_5 precipitates (Figure 6), more complex mechanism of α -Mg solid solution grain refinement is very probable. In the first stage, Al_4C_3 particle is formed. On its surface, the Al_8Mn_5 phase forms and then the α -Mg solid solution grain nucleates on it [18].

Carbon hexachloride was effective both in grain refinement and in degassing of the melt. Nevertheless, its application is limited due to emission of toxic gases, like hydrocarbon chlorates, which cause severe pollution of the environment [19].

3.4. Effect of Wax- CaF_2 -Carbon Refiner

In the first stage of the process (addition of 0.2 kg of modifier per 100 kg of the alloy), it was reported that the applied modification had no significant influence on the size of solid solution grains and did not cause the increase of mechanical properties of the casting, which was caused by improper amount of modifier being added, inappropriate technology of its introduction to the melt, and insufficient temperature of the modification process (720°C). Therefore, in the second stage the

amount of modifier was increased from 0.2 kg to 0.4 kg per 100 kg of the alloy. The technology of introduction of modifier to the melt was changed as well. The technology utilised in the first stage comprised the introduction of the modifier on the surface of molten metal with subsequent intensive mixing, which resulted in the modifier burnout. Hence, in the second stage the modifier powder was wrapped in aluminium foil and introduced to the bottom of the crucible. Simultaneously the temperature of the process was raised to 740°C to increase the reactivity of the modifier. The change of the modification process parameters and increased reactivity of the modifier resulted in solid solution grain refinement. The average area of solid solution grain cross-section decreased to $\bar{A} = 1457 \mu\text{m}^2$ ($d = 37.5 \mu\text{m}$) and was reported to be the lowest among all investigated smelts (Figure 7a).

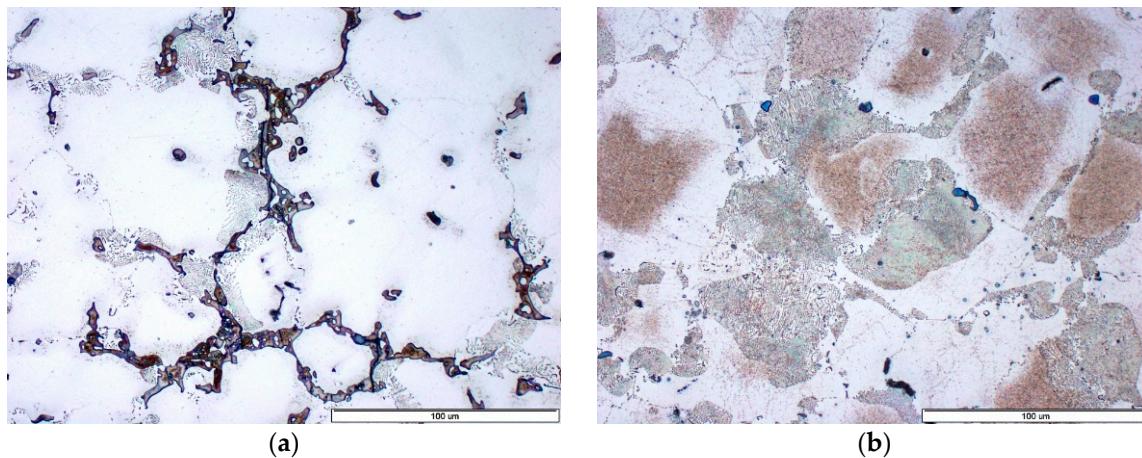


Figure 7. Microstructure of AZ91 alloy after modification with wax-CaF₂-carbon powder: (a) as-cast, (b) heat-treated.

After modification with wax-CaF₂-carbon (as in the case of modification with carbon hexachloroethane) the volume fraction of continuous precipitates of Mg₁₇Al₁₂ phase ($V_V = 5.13\%$) and Mg₂Si phase ($V_V = 0.09\%$) remained unchanged in comparison to as-cast alloy, whereas the volume fraction of α -Mg+Mg₁₇Al₁₂ areas was decreased by approximately 80% to $V_V = 1.54\%$ (the most significant change among all applied modifiers). Precipitates containing carbon were observed in the microstructure of the alloy, in the vicinity of Al₈Mn₅ phase (Figure 8a,b), as in the case of modification with carbon hexachloride. Moreover, the presence of precipitates containing carbon, calcium and fluorine was reported (Figure 8a,c). In this case no continuous precipitates of Mg₁₇Al₁₂ phase were observed after heat treatment as well (Figure 7b). However, the volume fraction of α -Mg+Mg₁₇Al₁₂ discontinuous precipitates was the largest, $V_V = 42.39\%$.

In the case of this modifier, the mechanism of grain refinement is complex. First mechanism comprises the formation of Al₄C₃ phase particles, which act as nucleation sites for the α -Mg solid solution, while the second is a result of the presence of calcium, which forms Al₂Ca phase with aluminium. Al₂Ca phase promotes nucleation, increases supercooling, and limits the grain growth [20].

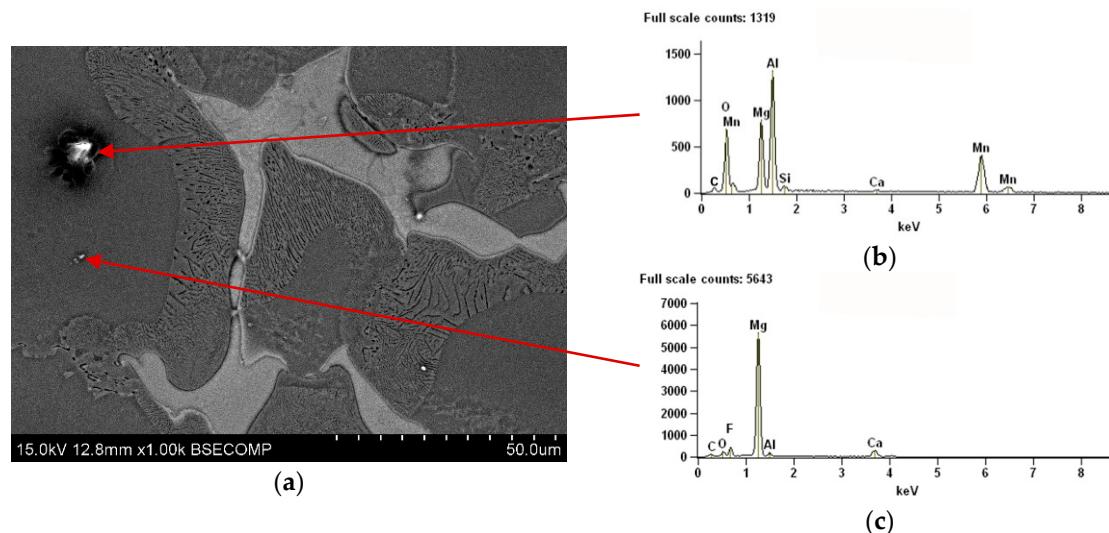


Figure 8. Precipitates containing carbon and calcium in alloy after modification with wax-CaF₂-carbon powder: (a) SEM, (b,c) EDS.

3.5. Influence of Modification on Mechanical Properties

Basing on the conducted research it was reported that the type of modifier does not have a significant influence on the mechanical properties of AZ91 alloy in as-cast condition (Figure 9a).

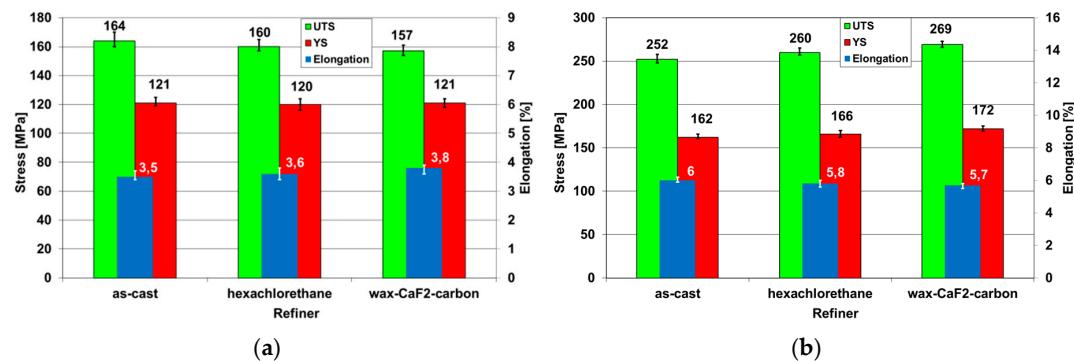


Figure 9. Influence of modifiers on mechanical properties of AZ91 alloy: (a) as-cast, (b) heat-treated.

A slight (~5%) decrease of ultimate tensile strength was observed and was attributed to the decrease of the volume fraction of α -Mg+Mg₁₇Al₁₂ discontinuous precipitates areas. The strengthening effect resulting from the grain refinement was relatively insignificant in this case. On the other hand, the effect of grain refinement was noticeable after heat treatment (Figure 9b). Grain boundaries act as nucleation sites for discontinuous Mg₁₇Al₁₂ precipitates, and the more grain boundaries, the higher volume fraction of the Mg₁₇Al₁₂ phase. The highest volume fraction of α -Mg+Mg₁₇Al₁₂ discontinuous precipitates ($V_V = 42.39\%$) was reported after modification with wax-CaF₂-carbon powder, while the lowest was in non-modified alloy ($V_V = 31.55\%$). This results in the highest ultimate tensile strength of the alloy after wax-CaF₂-carbon powder modification (UTS = 269 MPa), whereas the lowest ultimate tensile strength was reported in the case of non-modified alloy (UTS = 252 MPa).

4. Conclusions

In the article the effect of three methods of modification on microstructure and properties of gravity-casted and heat-treated AZ91 alloy were presented. The most important outcomes are the following:

- (1) Microstructure of AZ91 alloy in as-cast condition consists of α -Mg solid solution with continuous precipitates of $Mg_{17}Al_{12}$ phase, discontinuous precipitates of α -Mg+ $Mg_{17}Al_{12}$ compound, and the particles of Mg_2Si and Al_8Mn_5 phases.
- (2) Overheating of the alloy caused the decrease of the average area of α -Mg solid solution grain cross-section and the increase of the volume fraction of α -Mg+ $Mg_{17}Al_{12}$ areas. Numerous aluminium oxides and iron diffused from the crucible acted as the nucleation sites. Their presence was effective in grain refinement but had a negative effect on the quality and mechanical properties of the castings.
- (3) Carbon hexachloride turned out to be highly effective both in grain refinement and degassing of the melt. Al_4C_3 phase and Al_8Mn_5 phase nucleating on the surface of Al_4C_3 acted as nucleation sites. Unfortunately, the application of carbon hexachloride is limited due to the emission of toxic gases, which cause severe environment pollution.
- (4) Wax- CaF_2 -carbon was the most effective modifier. The mechanism of grain refinement was complex. In the first stage, as in the case of carbon hexachloride, the precipitates of Al_4C_3 phase were formed, while the second stage comprised the formation of Al_2Ca phase, which promotes nucleation and increases the supercooling.
- (5) The type of applied modifier does not influence the mechanical properties of AZ91 alloy in the as-cast condition. A slight decrease of ultimate tensile strength resulted from the decrease of the volume fraction of α -Mg+ $Mg_{17}Al_{12}$ discontinuous precipitates' areas. After age-hardening treatment, the increase of mechanical properties with the grain refinement was observed and was attributed to the nucleation of discontinuous precipitates of $Mg_{17}Al_{12}$ phase on the grain boundaries.

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Conflicts of Interest: The authors declare no conflict of interest.

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