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The Influence of the Casting Process on Shaping the Primary Structure of Mg-Li Alloys

I. Bednarczyk 
 Silesian University of Technology, Department of Materials Technology
 40-019 Katowice ul. Krasińskiego 8, Poland

* Corresponding author: E-mail address: iwona.bednarczyk@polsl.pl

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Abstract

This paper presents the results of a study to determine the influence of casting parameters (cooling rate in the casting mould, casting temperature) on the primary structure of Mg-4%Li-1%Ca alloy ingots. The macro- and microstructure analysis of the Mg-4%Li-1%Ca alloy was performed using light and electron microscopy techniques. Microhardness measurements were made for the Mg-4%Li-1%Ca alloy and phase identification in the Mg-4%Li-1%Ca alloy was made using X-ray phase analysis.

Keywords: Casting, Mg-Li alloys, Microstructure, X-ray phase analysis

1. Introduction

1.1. Magnesium alloys, Mg-Li

Magnesium-based alloys are considered to be promising new-generation materials. This is due to their low density and high specific strength [1-2]. These alloys are used, inter alia, as lightweight materials in the space and transport industries, to produce computer cases and electronic elements. They are characterised by high rigidity and good deformability, which makes them capable of transferring static and dynamic loads, like in the case of aluminium and iron alloys, additionally providing good damping qualities [3-6]. The reduction of weight of the equipment while maintaining the high mechanical and functional properties of its components is an important technological and economic factor. In order to reduce the weight, magnesium-lithium alloys are used, as they show the lowest density among all metallic

engineering materials (approx. 1.75 g/cm³), high specific strength, good castability, machinability, high gas corrosion resistance and high vibration damping capacity. In recent years, a remarkable increase in demand for magnesium-lithium alloys has been observed. It is assumed that 1 wt.% of lithium reduces the density of magnesium alloys by approximately 3% [7-9]. Figure 1 presents the system of Mg-Li alloy phases equilibrium and the change in the Mg-Li alloy density with the change of lithium content [7-10].

The Mg-Li balance system shows that the hexagonal crystallographic lattice of magnesium (α - phase) does not change with a minor addition of lithium. The strength of Mg-Li alloys is satisfactory however, their plastic formability is low. A solid solution of magnesium with a higher lithium content changes the crystallographic structure into a cubic bcc (β - phase). This causes an increase in the plasticity of the alloy, while simultaneously decreasing its strength. A compromise between good plasticity (β phase) and satisfactory strength (α phase) is offered by two-phase alloys (α and β phase). Depending on the lithium content, the Mg-Li alloys may be divided into up to approx. 6 wt% Li – one-phase



alloy, α (hcp lattice), approx. 6-11 wt% Li – two-phase alloy, $\alpha + \beta$, above approx. 11 wt% Li – one-phase alloy, β (bcc lattice) [10-11].

The Mg-Li alloy group is characterised by good formability and rigidity. These properties are influenced by the presence of lithium in the chemical composition. Disadvantages of this group of materials are low strength and low corrosion resistance. In recent years, Mg-Li alloys have found applications in the medical industry due to their potential. An addition of Ca in the chemical composition of the Mg-Li-Ca alloy improves its strength and biocompatibility. It forms the intermetallic compound, Mg_2Ca , which improves the strength of the alloy. Calcium also reduces magnesium oxidation during melting and improves high-temperature strength. The most favourable Ca content in the alloys is between 0.8 and 1.0 wt.%, as the alloys have good biocompatibility and a good modulus of elasticity and strength. The Ca content in the chemical composition should not exceed 2 wt.%, as a higher content of this element causes brittleness of Mg-Li alloys [12-16]

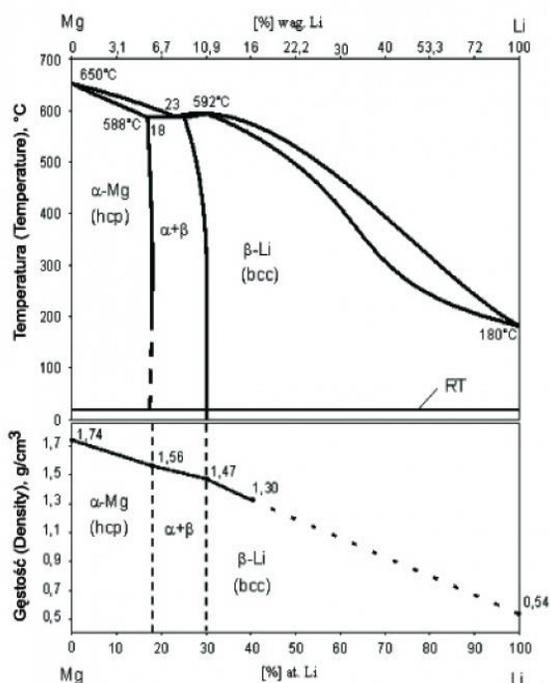


Fig. 1. The system of Mg-Li alloy phases equilibrium and the change in the Mg-Li alloy density with the change of lithium content [1]

1.2. Methods of melting and casting of Mg-Li alloys

Due to the high susceptibility to oxidation of their elements, Mg-Li alloys are melted only in a protective (oxygen-free) atmosphere or under a protective coating of refining slag. Vacuum furnaces are most commonly used for this purpose. In most cases, melting and casting processes are not conducted in vacuum but under neutral gas atmosphere, as melting in vacuum is connected with intense

vaporization of some of the alloying elements and an uncontrolled change in the chemical composition of the alloy. The quality of such alloys is generally higher than the quality of alloys melted in open furnaces, however, the melting and casting process is more expensive. Liquid magnesium alloys react with some ceramic materials of the crucible, especially with SiO_2 . As a result of the reaction, the liquid alloy becomes contaminated with silicon. For this reason, steel crucibles (so-called melting pots) are used for melting the alloys in question, in particular in open furnaces. Although iron is also soluble in magnesium, its presence in magnesium alloys is not as harmful as the presence of silicon. That is why particular attention is paid to thorough cleaning of the scrap from the moulding sand adhering to it, as the moulding sand may contain silica. Control of the melting and casting temperature of magnesium alloys using thermocouples with quartz tubes is also problematic. In that case, it is preferable to use shields made of, for example, Al_2O_3 . However, while casting alloys into sand moulds, protective components are added to the moulding sand which reduce reaction of the liquid metal with silica, or a moulding sand based on materials other than SiO_2 is used [17-18].

The research presented so far in scientific publications does not provide sufficient information on the influence of casting parameters on the formation of the primary structure of Mg-Li-Ca alloys. Therefore, this paper undertakes a study to evaluate the effect of casting parameters on the primary structure of Mg-4%Li-1%Ca alloy ingots. There is no detailed information in the literature on their manufacturing processes. The technology of melting and casting of Mg-Li-X alloys is relatively difficult because of their reactivity in contact with some ceramic materials, oxygen, nitrogen and carbon dioxide, and because of the evaporation of their main components (Mg, Li) while melting. The chemical composition of the Mg-4%Li-1%Ca alloy has been developed at the Department of Materials Engineering of the Silesian University of Technology and is under intensive study. The results obtained from the research will be used to develop casting technology for Mg-Li alloys.

2. Material and research methodology

2.1. Test material

The test material was the Mg-4%Li-1%Ca alloy. Magnesium of technical purity (min. 99.5% Mg), metallic lithium (99.9%Li) and calcium in the form of master alloy Mg-27.4%Ca, were used as charge components. The chemical composition of the Mg-4%Li-1%Ca alloy is presented in Table 1.

Table 1.

Chemical composition of magnesium alloy [mas %]

Alloy	Li	Ca	Mg
Mg-Li-Ca	4	1	rest

A Balzers laboratory vacuum induction furnace VSG 02 was used for melting and casting the Mg-4%Li-1%Ca alloy (Fig. 2).



Fig. 2. Laboratory vacuum induction furnace VSG 02 of Balzers company

It is a vacuum induction furnace designed for laboratory use, where the processes of melting and casting take place in one chamber. The charge is heated by eddy currents that are generated in an induction coil to which a current of 4 kHz is supplied, generated by a classic rotary generator. The melting took place in an Al_2O_3 crucible with dimensions of Φ 60x80 mm. Before commencing of the melting process, the chamber was pumped down to a pressure of approx. 10⁻² Torr, and then purged by refilling it with argon three times and pumping it out. The purging process was aimed at removing oxygen from the melting space. The melting was not performed in vacuum but instead, under neutral gas atmosphere (argon) in order to minimise evaporation of alloying elements. The melting temperature was ca. 640°C and was controlled by means of a PtRh10-Pt thermocouple placed in a special quartz casing coated with a barrier layer which protects the casing material from the aggressive action of the liquid alloy. The sand moulds were made of bentonite-quartz clay and were dried in a resistance furnace at a temperature of approx. 450°C prior to the casting process. Cooling of the sand moulds to ambient temperature took place in the furnace, which prevented them from moistness. The temperature of casting the Mg-4%Li-1%Ca alloy into sand moulds was approx. 640°C and approx. 690°C. The alloy was also

cast into a graphite mould, at a casting temperature of approx. 690°C.

The examination of the microstructure of the Mg-4%Li-1%Ca alloy was performed on the cross-section parallel to the axis of the sample. The samples were included in a conducting material and etched in a solution intended for etching magnesium alloys, containing: 5% nital (nitric acid, ethyl alcohol). The microstructure of the Mg-4%Li-1% alloy was analysed in the initial state using an Olympus GX71 light microscope in bright field mode. The analyses of the microstructures after casting were conducted with the use of light and scanning microscopy techniques - Hitachi S-3400N. An X-ray phase analysis was conducted on an X-ray diffractometer, JEOL JdX-7S, equipped with a copper anode tube ($\lambda\text{CuK}\alpha = 1.54178 \text{ \AA}$) and supplied with a current of 20 ma and voltage of 40 kV, and a graphite monochromator. The registration was conducted using the stepwise method with steps of 0.05° and a counting rate of 5 seconds in the range from 10 to 100° 2 θ . Tests were conducted on solid samples after casting and heat treatment processes. Measurements of HV0.2 microhardness were performed using a Zwick hardness tester in the initial state.

3. Test results

3.1. Analysis of the macrostructure of the Mg-4%Li-1%Ca alloy after casting

Figure 3 presents the appearance of an ingot with a diameter of 40 mm x 90 mm cast into a sand mould (Fig. 3 a-b) and a graphite mould (Fig. 3c) at a temperature range of 640-690°C. The examination of the Mg-4%Li-1%Ca alloy's macrostructure attempted to determine the influence of basic casting parameters (casting temperature, cooling rate in the sand mould) on the primary structure.

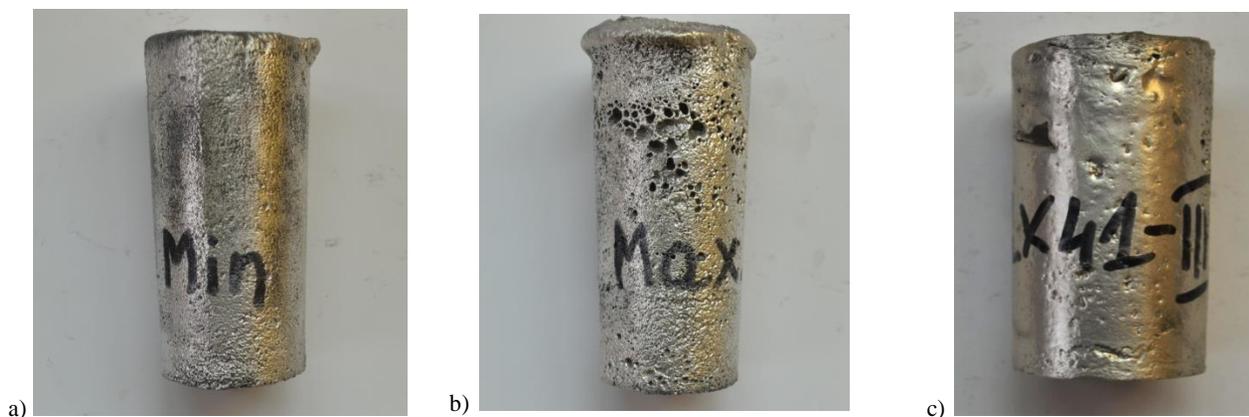


Fig. 3 Appearance of the Mg-4%Li-1%Ca alloy ingot: a) sand mould T=640°C, b) sand mould T=690°C, c) graphite mould T=690°C

As the research has shown, the quality of ingots cast into sand moulds is significantly influenced by the temperature of casting of the alloy. A high casting temperature induces a reaction of the liquid alloy with the mould material, which is accompanied by emission of gaseous products of the reaction. The gasses get trapped in the near-wall layer of the ingot, forming clearly visible blisters on its surface (Fig. 3 a-b). Lowering the casting temperature to 640°C allows avoiding the gassing and obtaining an ingot with a surface of appropriate quality. In that case, the surface of the ingot is rough, with a surface texture matching the mould sand used. The use of graphite moulds in the casting process eliminates the risk of reaction of the mould material with the liquid alloy and allows avoiding the formation of gas defects on the surface of ingots. After the alloy was cast from a temperature of 690°C (overheating of approx. 100°C), only minor burrs and cold shots characteristic of rapid cooling of the ingot's near-wall layers occur on the surface of

the ingot (Fig. 3c). Figure 4 shows examples of macrostructures of the Mg-4%Li-1%Ca alloy after casting.

The observation of the macrostructure of the Mg-4%Li-1%Ca alloy ingots cast into sand moulds shows that these ingots have an unfavourable, heterogeneous and coarse-grained structure. Furthermore, the low melting and casting temperature prevented homogenisation of the liquid alloy and resulted in clearly visible areas of macrosegregation in the ingots (Fig. 4 a-b). On the entirety of the surface of the Mg-4%Li-1%Ca alloy cast into graphite moulds, only equiaxial grains are present (Fig. 4c). The macrostructure of the Mg-4%Li-1%Ca alloy does not contain any columnar grains, which may indicate that the Mg-4%Li-1%Ca alloy has a strong tendency towards volumetric crystallisation. The macrostructure consisting of equiaxed grains shows better plasticity. In the initial state, a microhardness of 41 HV0.2 was obtained.

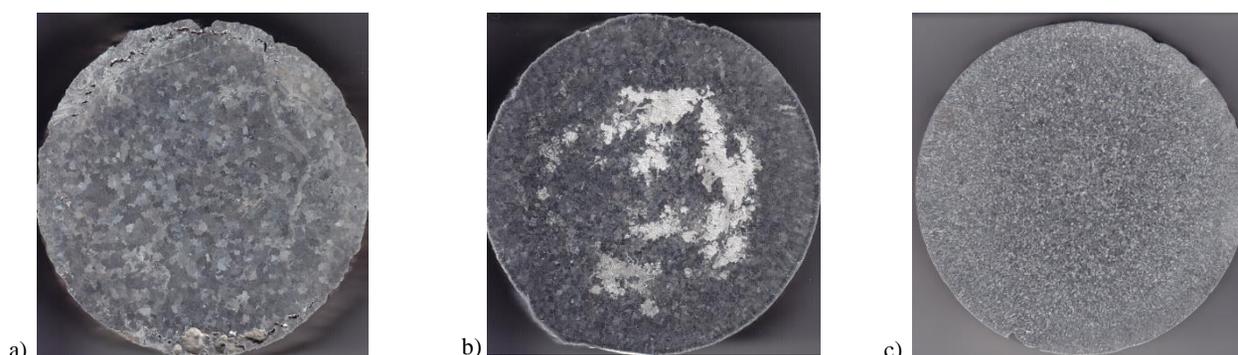


Fig. 4. The macrostructure of the Mg-4%Li-1%Ca alloy after casting: a) sand mould $T=640^{\circ}\text{C}$, b) sand mould $T=690^{\circ}\text{C}$, c) graphite mould $T=690^{\circ}\text{C}$

Figure 5 shows a diffraction pattern for the Mg-4%Li-1%Ca alloy. Analysis of the microstructure after casting for the Mg-4%Li-1%Ca alloy revealed the occurrence of a coarse-grained structure and the presence of eutectics ($\alpha\text{-Mg}$, Mg_2Ca) located at grain boundaries with an elongated or spherical shape. The identification of phase composition after casting was conducted with the use of an X-ray phase analysis. An example view of the X-ray diffraction pattern is shown in Fig. 5. Phase $\alpha\text{-Mg}$ (solid solution of lithium in magnesium) and phase Li_2Ca were identified.

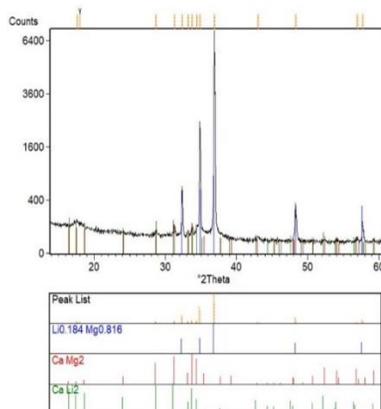


Fig. 5. X-ray diffraction pattern after casting process

3.2. Analysis of the microstructure of the Mg-4%Li-1%Ca alloy after casting

Figure 6 and 7 presents examples of the Mg-4%Li-1%Ca alloy microstructure after casting. The microstructural analysis showed the presence of a residual dendritic structure (Fig. 6, 7). At grain boundaries, in interdendritic regions, a lamellar eutectic structure, which is a mixture of $\alpha\text{-Mg}$ and Mg_2Ca phases, can be noticed. The morphology of the eutectics is visible in the microstructure of the Mg-4%Li-1%Ca alloy cast into graphite moulds (Fig. 6c-d, Fig. 7c-d).

Analysis of the chemical composition in the micro-areas of the alloy under examination showed that calcium is mainly concentrated in the eutectic areas (Fig. 8). This may be due to the fact that the higher cooling rate of alloys in graphite moulds results in partial supersaturation of the calcium-containing phases in the alloy matrix, rather than in the interdendritic regions only. In the Mg-4%Li-1%Ca alloy, the distribution of calcium is uniform throughout the analysed area. Limitations resulting from the test method used did not allow identification of areas with the presence of lithium in the alloys tested.

The presence of lithium in the individual of the tested alloys cannot be confirmed using the EDS technique. EDS detector is equipped with a window made of Norvar, which is characterized by virtually zero transmittance for characteristic X-rays with

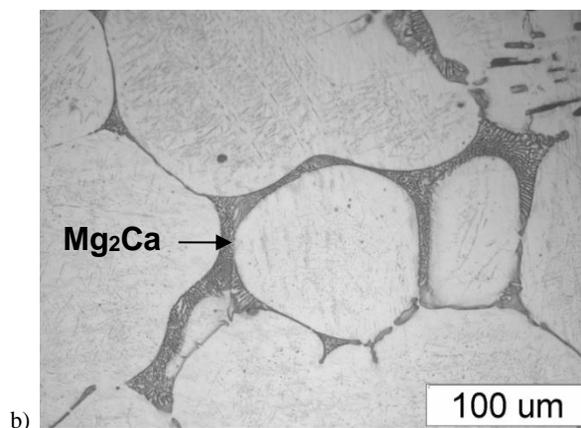
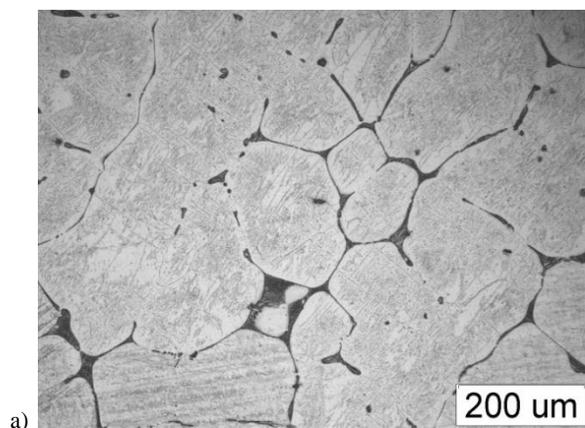
energy less than 150 eV (while the energy of $K\alpha$ line of lithium is 50eV).

When analysing the chemical composition of the Mg-4%Li-1%Ca alloy, the presence of Mg and Ca was identified in some micro-areas.

4. Summary

The research object was the Mg-4%Li-1%Ca alloy, a new-generation lightweight engineering material with prospects of being widely used e.g. in aviation, automotive industry and medicine. When investigating the melting process of the alloy under discussion, it was found that it was relatively easy to introduce calcium into its chemical composition in the form of a master alloy Mg-27.4%Ca. This form of calcium carrier poses no major technological problems in terms of storage, dosing into the alloy, scrap disposal and waste disposal. Pure calcium is easily oxidised and for this reason it is not a suitable component for melting of the alloy, even if a furnace with protective atmosphere is used. Calcium introduced into magnesium-lithium alloys in an amount of 1 wt.% results in a lamellar eutectic in the structure of this alloy, distributed along grain boundaries. According to literature data, eutectic with a hard Mg_2Ca phase should strengthen the grain boundaries and improve mechanical properties. Calcium also increases the biocompatibility of the alloys, which is particularly important for their use in medical applications [11-12]. When analysing the casting process of the Mg-4%Li-1%Ca alloy, two types of casting moulds were used: sand moulds based on bentonite-quartz clay and graphite moulds. It was found that sand

moulds are not suitable for casting magnesium-lithium alloys and should be used only as an exception, including for casting of customised or large-size products without thin-walled elements. The prerequisite for obtaining products (castings or ingots) with a high-quality surface is the application of relatively low casting temperatures. Casting from a temperature of approximately 640°C brought a positive result. However, such a temperature does not guarantee homogenisation of the liquid alloy prior to casting and may not be sufficient to ensure adequate alloy castability when casting thin-walled elements. Increasing the casting temperature to 690°C extends the contact time between the liquid alloy and the bentonite-quartz clay, which is accompanied by a chemical reaction with the emission of gases. Numerous gas defects (open and closed blisters, porosity) form on the surface and in the subsurface zone of the ingots, which practically disqualifies the ingots and castings as full-value products. Regardless of the casting temperature used, the macrostructure of ingots cast into sand moulds is not favourable. Although only a zone of equiaxial grains is present, these grains are heterogeneous in size and relatively large. A more fine-grained structure is observed in the case of ingots cast into graphite moulds. Moreover, the use of a high casting temperature (690°C) for graphite moulds does not result in grain growth. Surface quality of the ingots cast into these moulds is also adequate. There are only minor surface defects (burrs, cold shots) here, typical of permanent moulds, which can be easily removed if necessary, e.g. by machining. Investigations of the primary structure and chemical composition of the Mg-4%Li-1%Ca alloy in the micro-areas showed that the alloy has high homogeneity and purity. The high purity of the Mg-4%Li-1%Ca alloy is due to its melting in a vacuum induction furnace under argon gas and the use of high-quality Al_2O_3 sintered crucibles.



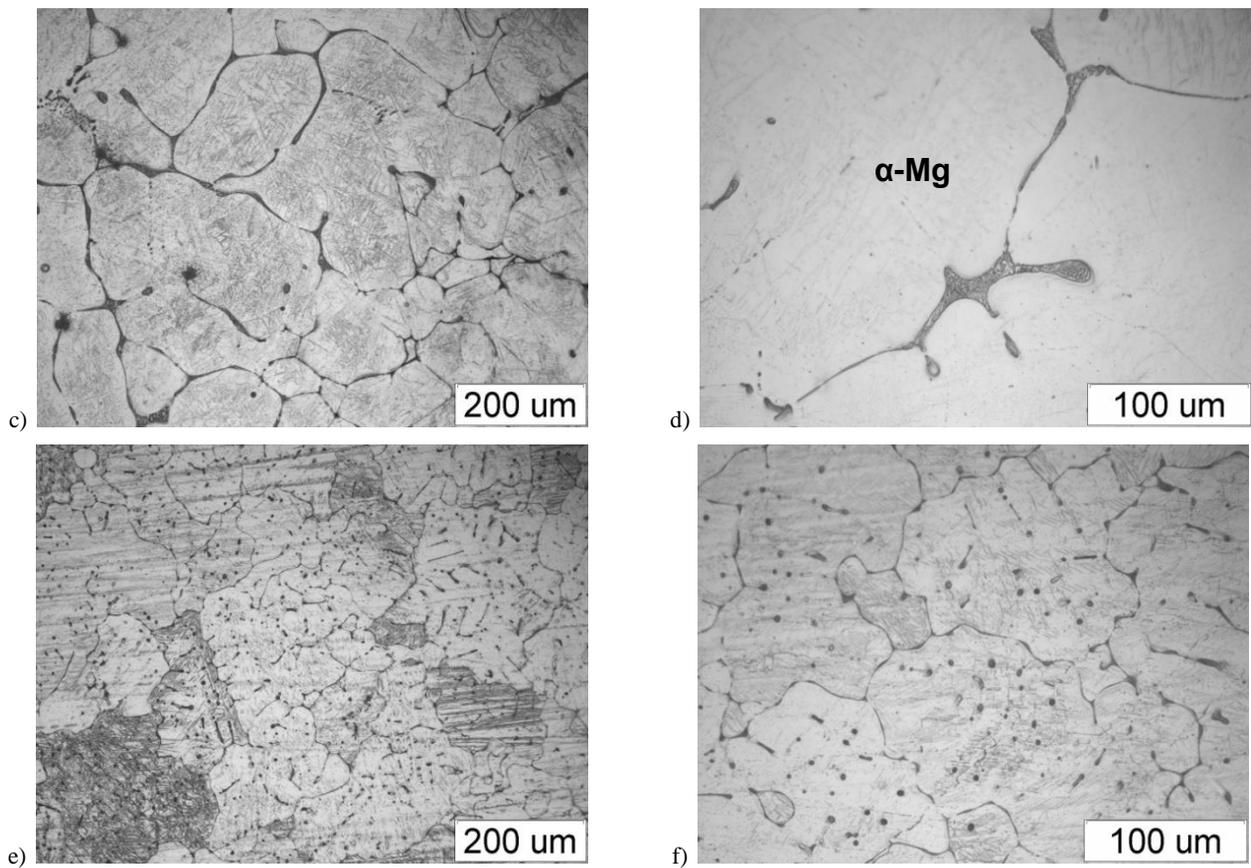
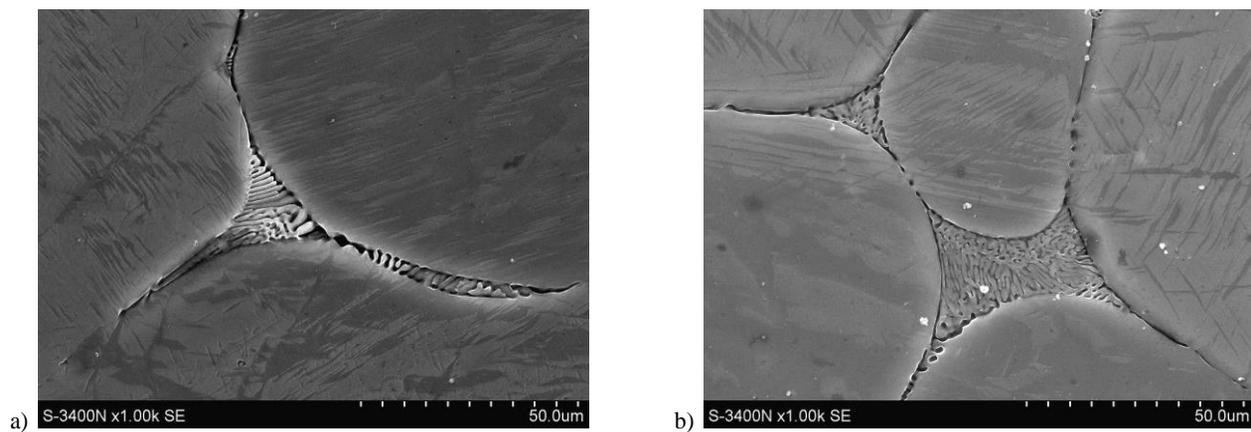


Fig. 6. Microstructure of the Mg-4%Li-1%Ca alloy after casting: a-b) sand mould $T=640^{\circ}\text{C}$, c-d) sand mould $T=690^{\circ}\text{C}$, e-f) graphite mould $T=690^{\circ}\text{C}$, magnification 20x- 200 μm and 50x-100 μm



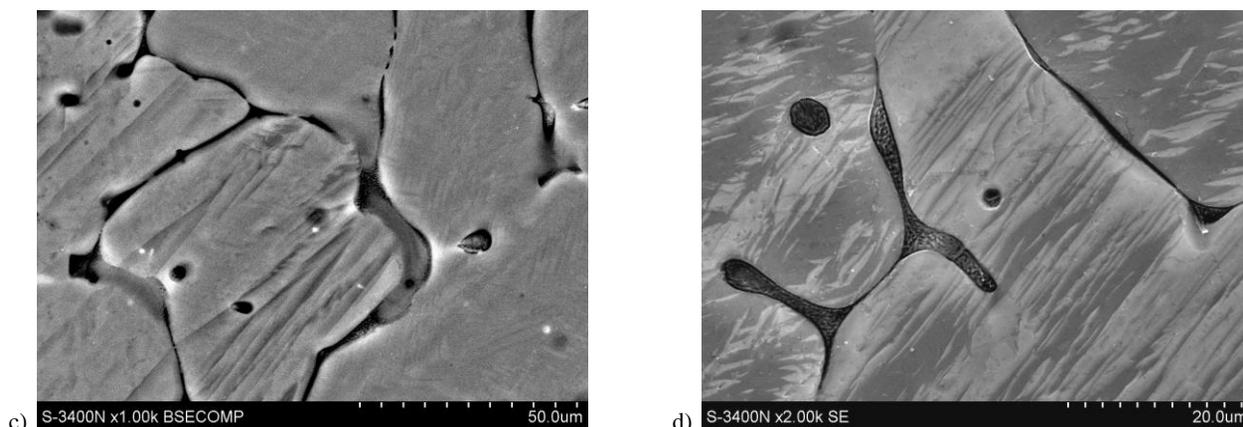


Fig. 7. Microstructure of the Mg-4%Li-1%Ca alloy after casting:

a) sand mould T=640°C, b) sand mould T=690°C, c-d) graphite mould T=690°C, eutectics in the interdendritic regions - SEM

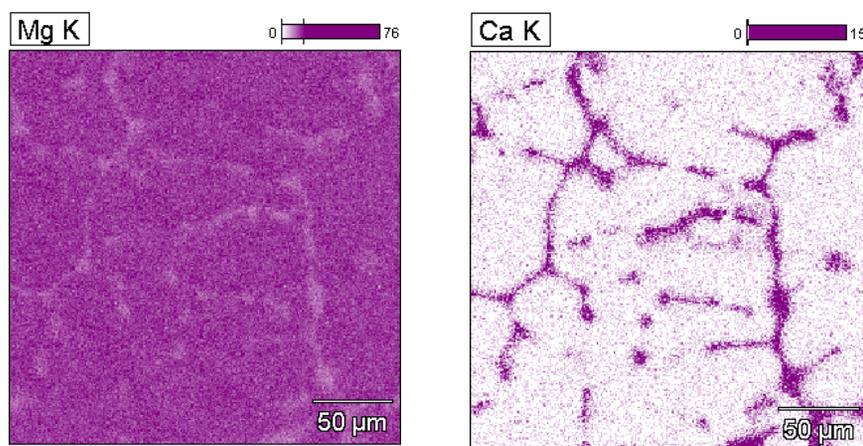


Fig. 8. Surface distribution of Mg and Ca elements in the Mg-4%Li-1%Ca alloy graphite mould T=690°C

5. Conclusions

1. The applied technology of melting in a vacuum induction furnace allows obtaining a Mg-Li alloy of the Mg-4%Li-1%Ca type with high homogeneity and purity.
2. The introduction of 1 wt.% of calcium into the alloy results in the formation of a lamellar eutectic α -Mg+Mg₂Ca, distributed at the grain boundaries. According to literature data, the eutectic causes, among other things, an increase in the mechanical properties of the alloy.
3. The Mg-4%Li-1%Ca alloy should be cast into permanent moulds, as casting into sand moulds causes a reduction in the surface quality of the ingots due to their action of the moulding sand with the liquid alloy.
4. In the case where the Mg-4%Li-1%Ca alloy was cast into moulds that heat up quickly (permanent moulds), the use of a high casting temperature (690°C; overheating of approx.

100°C) does not result in a significant grain growth in the ingots.

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