

SUITABILITY OF MOULDING MATERIALS FOR Al-Li ALLOY CASTING

PRIMERENOST FORMARSKIH MATERIALOV ZA LITJE Al-Li ZLITIN

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The paper describes the production of an AlSi7Mg cast alloy with Li additions and the reactions of the melt with different moulding materials. It is known that Li is very reactive and tends to form various reaction products such as oxides, gases, etc., which can influence the casting quality. The aim of the research was to find a suitable way to produce such an alloy and to describe the reaction products that are formed between the melt and the moulding material and thus to find a suitable moulding material for processing Al cast alloys with Li additions. The melt was produced in an induction furnace under an inert atmosphere. After melting, 1 w% Li was added and the melt was cast into five different mould materials consisting of graphite, steel, a CO₂ sand mixture, Croning mixture and calcium silicate materials. In the last three cases, various alcohol-based coatings were also used, such as graphite, zirconium oxide-graphite coating and aluminate-graphite filler coating. The results showed that the reaction products in the form of powder on the casting surfaces and the gas porosity in the castings occurred in the cast of a calcium silicate mould and sand mould mixtures. In the case of graphite and steel moulds, the casting surfaces were not oxidised, with no reaction products, and no gas porosity.

Keywords: aluminium lithium alloy, reaction products, moulding materials

Delo predstavlja izdelavo aluminijeve livarske zlitine z dodatki litija ter reakcije med talino in različnimi formarskimi materiali. Znano je, da je Li zelo reaktivna kovina in je nagnjena k tvorbi različnih reakcijskih produktov kot so oksidi, plini itd., ki lahko vplivajo na kvaliteto ulitkov. Cilj raziskave je bil ugotoviti primeren način izdelave zlitine z Li in preučiti reakcijske produkte, ki nastajajo med talino in formarskimi materiali. Na ta način bi se ugotovil najbolj ustrezen formarski material. Talina je bila pripravljena v indukcijski peči v zaščitni atmosferi. V talino je bil dodan 1 w% Li. Tako pripravljena talina je bila ulita v forme iz petih različnih formarskih materialov, kot so Croning peščena mešanica, CO₂ peščena mešanica, silikatna opeka, grafit in jeklo. Na tri forme iz prvih treh naštetih materialov, so bili nanešeni premazi na alkoholni osnovi (grafitni, cirkonov-grafitni in aluminatni-grafitni premaz). Rezultati so pokazali, da v primeru peščenih mešanic na ulitkih nastane veliko reakcijskih produktov v prašnati obliki. V ulitkih pa nastane veliko plinske poroznosti. Pri uporabi grafitne in jeklene forme, površine ulitkov niso oksidirane in so brez reakcijskih produktov. Ulitki so v tem primeru brez poroznosti.

Ključne besede: aluminij litijeve zlitine, reakcijski produkti, formarski materiali

1 INTRODUCTION

Aluminium alloys containing lithium show promise in the aerospace industry, as the addition of lithium can reduce the density and increase the mechanical properties. The melting and casting of aluminium alloys with lithium has proven to be problematic, due to the high reactivity of lithium with oxygen and nitrogen. In order for these alloys to be selected for the aerospace industry, e.g., in helicopters and aeroplanes, their performance in terms of other properties must be better than those of the alloys commonly used, particularly in terms of reactions between the moulds and the liquid alloy. Lithium reacts with dry oxygen to form Li₂O at temperatures as low as 100 °C. Similarly, it reacts with water vapour to form Li₂O and H₂. Although MgO has been reported to be thermodynamically more stable than Li₂O, the higher mobility and higher atomic fraction of Li favours the

early formation of Li₂O compared to other compounds in Al-Li-Mg alloys.¹⁻³

Possible reactions of Al-Li alloys are also reported in literature,⁴ and the Gibbs free formation energies (ΔG) for temperatures of 800 K and 1000 K are given in **Table 1**. The mentioned reaction products are mainly oxides, hydroxides, and carbonates. The calculated free energies show that Li and Mg are reactive in contact with oxygen and water and form lithium aluminate and magnesium oxide, while lithium carbonate can be formed from Li or Li₂O in combination with CO₂.⁴

The presence of water vapour and carbon dioxide in the atmosphere of the melting furnace can cause the formation of LiOH and LiOH·H₂O.⁴ Molten lithium reacts strongly with nitrogen to form a black coloured hygroscopic nitride, Li₃N. At a temperature of 500–800 °C, lithium can react with hydrogen to form lithium hydride, which is relatively stable and has a melting point of 690.8 °C. In the presence of molten aluminium, the compound Li₃AlH₆ can be formed.⁴⁻⁶

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Due to the lithium reactivity, the crucible materials used for aluminium melting are not stable enough for melting Al-Li alloys. However, stainless steels crucibles (304L, 321 and 347) have been proven to be very resistant to the reactivity of lithium.⁷⁻⁹ In certain cases, even steels with 2.5 w% (Cr) and 1.0 w% (Mo) had better corrosion resistance than stainless steel grades. HSLA steels have also shown high resistance to lithium reactivity. Pure iron also shows good resistance to lithium but is practically unusable due to its low strength. When aluminium is melted in the same crucible as lithium, it turns out that Fe and Ni begin to dissolve in liquid aluminium when stainless steel is used.¹⁰⁻¹² Researchers proposed using tantalum, which has good resistance to molten aluminium and molten lithium, but is not economically justified due to its price. However, tantalum also becomes less resistant to aluminium when the oxygen concentration in tantalum exceeds 100 ppm.¹⁰ Research shows that third-generation Al-Li alloys cause fewer problems (less than 2 w% Li) because the lithium content exponentially increases all the hazards and problems associated with the production of lithium alloys.^{1,12}

The graphite crucible is widely used in which aluminium is melted because no impurities are precipitated from it.⁹ Graphite is proving to be a good material for melting Al-Li alloys when an inert atmosphere is used. In a normal atmosphere, the use of a graphite crucible is questionable because lithium reacts with carbonaceous molecules in the air. Crucibles whose graphite is bonded with clay have been shown to be compatible with melts containing up to 1.5 w% Li.^{1,2}

Table 1: Reactions at Al-Li alloys at two different temperatures⁴

| React. no. | Reaction | ΔG (kJ) / 800 K | ΔG (kJ) / 1000 K |
|------------|--|-------------------------|--------------------------|
| 1 | $2Mg + O_2 \rightarrow 2MgO$ | -1029 | -986.9 |
| 2 | $Li + Al + O_2 \rightarrow LiAlO_2$ | -1018.4 | -974.5 |
| 3 | $4Li + O_2 \rightarrow 2Li_2O$ | -988.4 | -930.2 |
| 4 | $Li + 5Al + 4O_2 \rightarrow LiAl_5O_8$ | -962.0 | - |
| 5 | $4LiH + O_2 \rightarrow 2Li_2O + 2H_2$ | -879.5 | -880.2 |
| 6 | $Li + Al + CO_2 \rightarrow LiAlO_2 + C$ | -622.8 | -578.6 |
| 7 | $4Li + CO_2 \rightarrow 2Li_2O + C$ | -592.8 | -534.3 |
| 8 | $4Li + Li_2CO_3 \rightarrow 3Li_2O + C$ | -494.4 | -466.8 |
| 9 | $2,5Li + 0,5Al + H_2O \rightarrow 0,5Li_2Al_2O_3 + 2LiH$ | -360.2 | -318.3 |
| 10 | $4Li + H_2O \rightarrow Li_2O + H_2$ | -345.2 | -279.5 |
| 11 | $0,5Li + 0,5Al + H_2O \rightarrow 0,5LiAlO_2 + H_2$ | -305.7 | -294.6 |
| 12 | $2Li + H_2O \rightarrow Li_2O + H_2$ | -290.7 | -273.7 |
| 13 | $2LiH + H_2O \rightarrow Li_2O + 2H_2$ | -290.7 | -249.9 |
| 14 | $1,32Li + CO_2 \rightarrow 0,66Li_2CO_3 + 0,33C$ | -263.2 | -225.8 |
| 15 | $2Li + H_2O \rightarrow LiOH + LiH$ | -185.1 | -155.7 |
| 16 | $Li_2O + CO_2 \rightarrow Li_2CO_3$ | -98.4 | -71.9 |
| 17 | $Li_2O + H_2O \rightarrow 2LiOH$ | -25.1 | -13.8 |

It has been reported that the only moulding materials suitable for casting Al-Li alloys are iron and sand mixes, using resin as a binder. They also have a negative effect

on the permeability of sand.^{1,2,5} The use of a sand mix using CO₂ and sodium aluminate as binders can lead to porosity in the casting due to reactions between the melt and the mould. A graphite coating has been shown to be very effective in preventing these reactions.¹ Al-Li Alloys could be successfully cast in metal and graphite moulds or in no-bake sand moulds when organic binders are used. Most casting problems are due to the high reactivity of lithium with air, oxygen, water vapour, etc.^{1,3-5,11,12} The use of different moulding materials in combination with different mould coatings is presented in the paper. The influence of melt preparation and Al-Li melt/mould reaction products on the casting quality is highlighted.

2 EXPERIMENTAL PART

The melting process and alloy production path were studied by melting a 931-g charge of an AlSi7Mg base alloy in an induction furnace using a graphite crucible. When the base alloy was melted and heated to 740 °C, 9.40 g of lithium (99.9 w% Li) was added to the melt using a bell. Melting was carried out in an inert Ar atmosphere, which was introduced through the lid (3 L/min) to prevent oxidation of the melt, as shown in Figure 1a to 1c. The chemical composition of the base alloy and the Li-modified alloy, analysed by inductively coupled

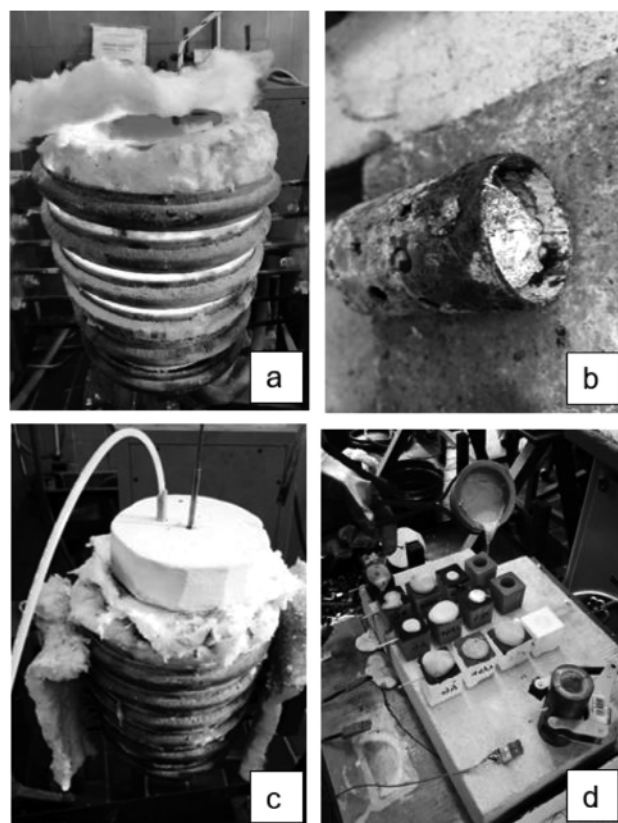


Figure 1: AlSi7MgLi procedure of melting and casting: a) induction furnace, b) steel bell for Li addition c) argon gas flux with the lid and d) pouring into different moulds

plasma mass spectrometry (ICP-MS Agilent 7700x), is given in **Table 2**. The base alloy was analysed directly from the ingot and a sample of the prepared AlSi7MgLi alloy was taken from the melt and cast into the steel mould.

Table 2: Chemical composition of alloys in mass fractions, (w%)

| Alloy | Al | Si | Fe | Cu | Mg | Zn | Ti | Li |
|-----------|------|------|------|------|------|------|------|------|
| AlSi7Mg | Rest | 6.7 | 0.44 | 0.01 | 0.35 | 0.01 | 0.1 | – |
| AlSi7MgLi | Rest | 7.06 | 0.41 | 0.03 | 0.36 | 0.02 | 0.09 | 0.80 |

The AlSi7MgLi alloy was cast into moulds from different materials, graphite mould (G), steel mould with boron nitride coating (S), Croning moulds, CO₂ moulds and calcium silicate moulds. Croning, CO₂ and calcium silicate moulds were un-coated and coated with three different alcohol-based coatings, graphite coating (AG), zirconium graphite coating (AZG) and aluminate graphite filler coating (AAGF). The intention to use different mould materials in combination with different coatings was to study their suitability for casting Li-containing aluminium alloys. **Figure 1d** shows the moulds during casting. All the moulds had the same geometry of (50×50×50) mm with a casting cavity having a truncated cone of 20 mm diameter and 30 mm height. The steel mould had a different geometry with cylindrical casting with three diameters of 10 mm, 20 mm and 30 mm, each with a height of 30 mm. All the described moulds are shown in **Figure 2**.

X-ray diffraction (XRD) was successfully used to analyse the reaction products between different moulds and a molten aluminium alloy. A Philips PW3710 X-ray diffractometer operating at 40 kV and 30 mA, with Cu-K_{α1} (0.154060 nm) and Cu-K_{α2} (0.154443 nm) radiation passed through a nickel filter was used to obtain the diffraction patterns from the powders obtained from the

castings. The scanning speed was 1.2 °min⁻¹ over an incident angle range of 3–70° (2θ). The results were evaluated qualitatively and semi-quantitatively with data from the PAN-ICSD database version 2.3, which is included in the PAN analytical X'Pert HighScore Plus software version 4.8.

3 RESULTS AND DISCUSSION

3.1 Alloy preparation

The melt of AlSi7MgLi was successfully prepared in the induction furnace using a graphite-clay crucible with the insulating lid for argon gas introduced already during the melting process and Li addition. The chemical composition of the newly developed alloy is shown in **Table 2**, from which it can be seen that the yield of Li addition was approximately 80 % and the amount of it in the alloy is therefore 0.8 w%. The 20 % of Li appears to burn out and forms oxide layers on the surface of the melt, which are visible in **Figure 1d**. It can also be seen that the melt glows orange because the casting temperature is relatively high as Li increases the liquidus temperature (T_L).¹²

3.2 Casting results

After melt preparation, it was cast into the measuring cells described above. The focus of the research was on the observation of the casting surface quality and the reaction products formed. **Figure 3** shows four castings made of Croning cells coated with different coatings. The upper surfaces of the castings are covered with a white-to-grey layer of reaction products and the side surfaces are – depending on the coating – blacker. Most likely the black layers are caused by binder resin, coatings, and the lack of oxygen. It appears that the best side surface of the casting is the one from the uncoated

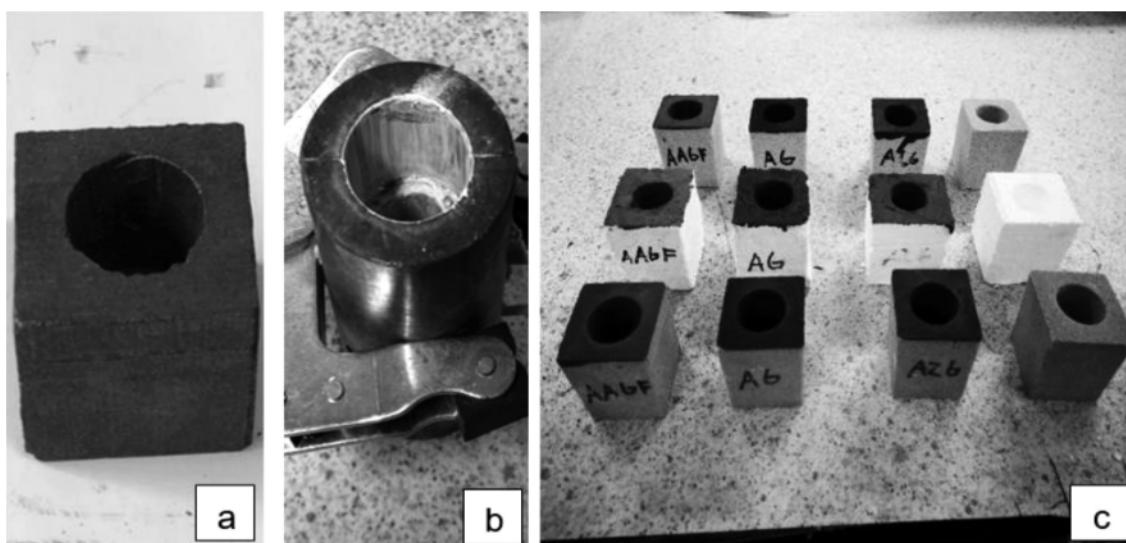


Figure 2: Prepared moulds: a) graphite mould, b) steel mould, and c) first row Croning process moulds with different coatings, second row calcium silicate moulds with different coatings, and third row CO₂ process moulds with different coatings

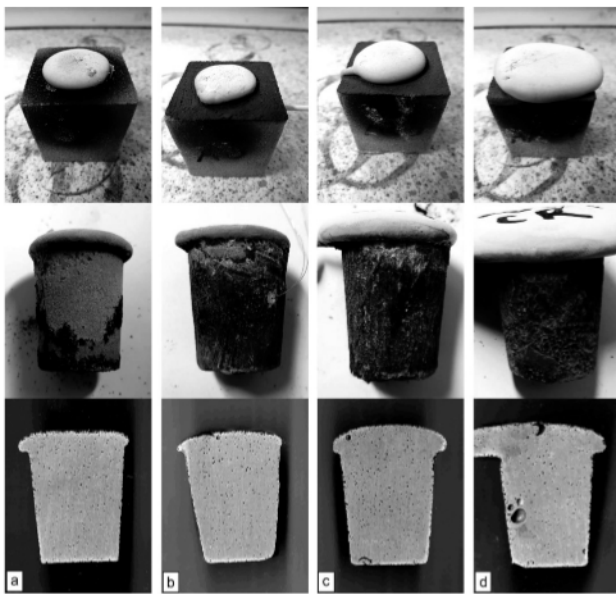


Figure 3: Croning moulds with castings and casting cross-sections: a) without coating, b) AG coating, c) AZG coating and d) AAGF coatingst

mould. The cross-sections of the castings have a large amount of porosity, which is distributed over the entire casting cross-sections and is even more pronounced at the edges of the castings. From the samples observed, it can be concluded that the coatings used to prevent reactions with the mould have not proved to be effective because the castings with different coatings are very similar. From the appearance of the porosity it can be confirmed that the reaction products are gaseous, the most likely being hydrogen, which causes gas porosity in combination with shrinkage porosity. Gas porosity is also a reason for the mushroom-shaped top surface of the castings, as it occurs during solidification and causes the casting to expand, even if the melt shrinks during solidification. The strongest gas porosity is present in the mould with the AAGF coating.

The second set of moulds and castings made from the CO₂ mixture is shown in **Figure 4**. The results are even worse than in the case of Croning moulds. The upper side of the castings shows a large amount of grey reaction products in the form of thick layers that are cracked. From the cracked layers it can be concluded that gaseous products are present in the castings, causing their expansion and cracking of the formed layers. The side surfaces of the castings are also covered by a layer of reaction products like the top surfaces. From this point of view, it can be concluded that coatings have not improved the casting quality, on the contrary, the surfaces are even worse when coatings are used.

The cross-sections of castings have a very large amount of porosity, which is a combination of shrinkage and gas porosity. The gas porosity caused mushroom-like top of the castings. The porosity is very severe

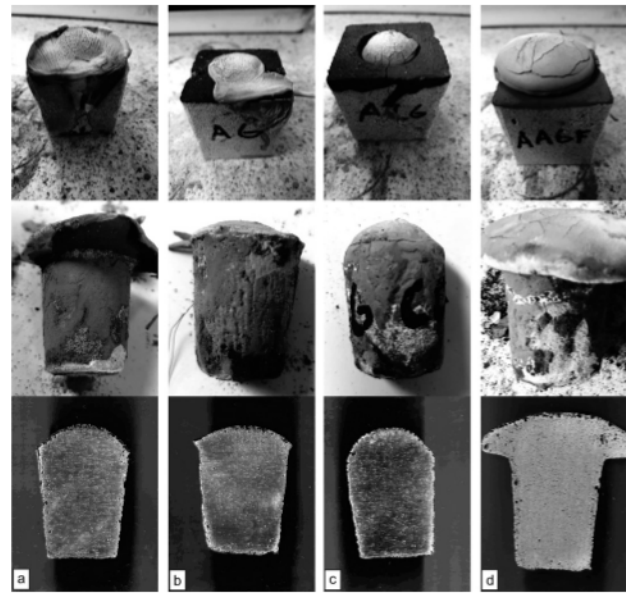


Figure 4: CO₂ moulds with castings and casting cross-sections: a) without coating, b) AG coating, c) AZG coating and d) AAGF coating

at the casting surfaces where the pores are larger, making the caing surface very rough and uneven.

Figure 5 shows the castings from calcium silicate moulds. It is known that calcium silicate brick is an isolative material, which leads to longer solidification times. From this point of view, reactions took place over a longer period of time, which led to the most severe cases of reaction products among all the samples presented. It can be seen that the grey layers of the reaction products on the upper side of the castings are 2–3 mm thick and also became cracked because the gaseous products caused the melt to expand during solidification. The

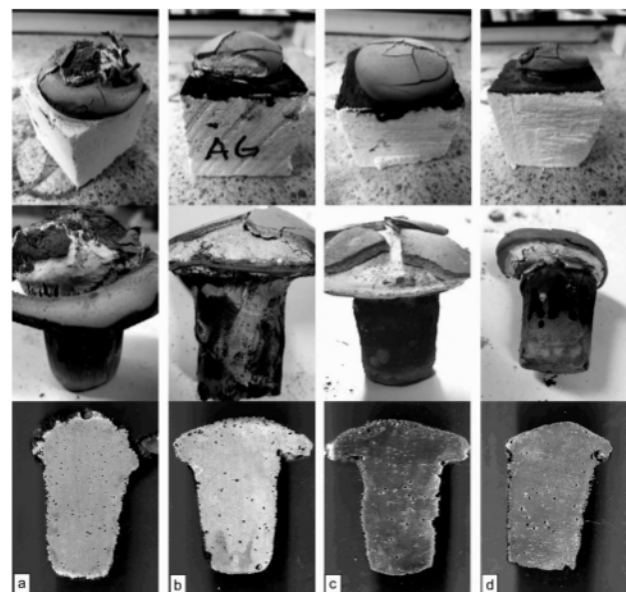


Figure 5: Calcium silicate moulds with castings and casting cross-sections: a) without coating, b) AG coating, c) AZG coating and d) AAGF coating

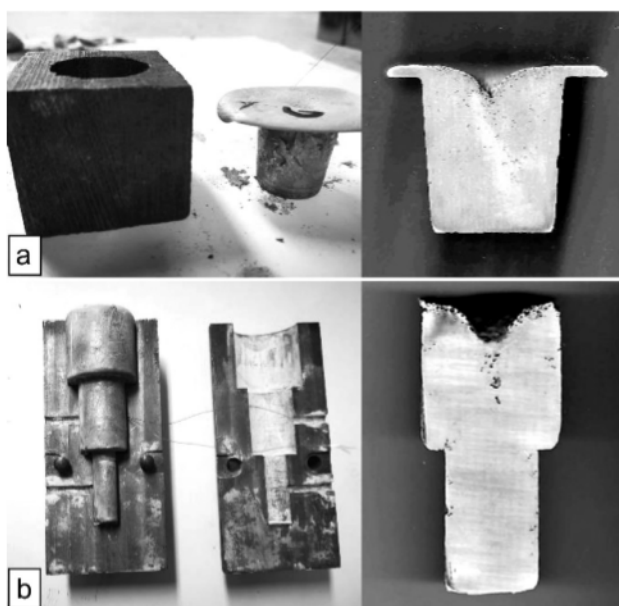


Figure 6: a) Graphite mould with casting and casting cross-section and b) steel mould with casting and casting cross-section

side surfaces of the castings are also covered with black reaction products and are also very thick, which can be seen from the cross-sections of the castings, where they do not have the exact shape they should have. A large amount of gas porosity can also be seen in Figure 5. Solidification took a long time and during solidification an exothermic reaction developed, which caused the castings to glow for some time. During this time, the reactions between the melt, the atmosphere and the moulding material took place. Figure 1d shows the glowing castings from calcium silicate moulds (bottom row) during solidification.

In contrast to the others, the graphite mould and the steel mould produced the best quality of the castings. The amount of reaction products on the top of the castings and on their sides is relatively small, almost negligible (Figure 6). In addition, the mushroom-like top of the castings is not formed but V-shaped shrink hole is present. A very low amount of gas porosity is visible in the graphite mould casting, but in the steel mould casting a small amount of gas porosity is visible on the sides of the casting, which shows that some reactions have taken place there as well. The reason for the small amount of reaction products could be that the graphite and steel do not react with the melt, or the high solidification rate, as the solidification time was only few seconds.

3.3 XRD results

In three cases, XRD samples were taken from uncoated moulds made of Croning moulding material, CO₂ sand mixture and calcium silicate brick. The results are shown as XRD patterns in Figures 7a to 7c. Figure 7a shows the XRD pattern from Croning mould and indicates that metallic Al is present. The origin of Al could

be from the casting surface or it could be detected from the sample holder during analysis. SiO₂ is present in the powder of the reaction product and may have its origin in the quartz sand as the base material for the Croning sand mixture. Another reaction product is the Al₂O₅Si com-

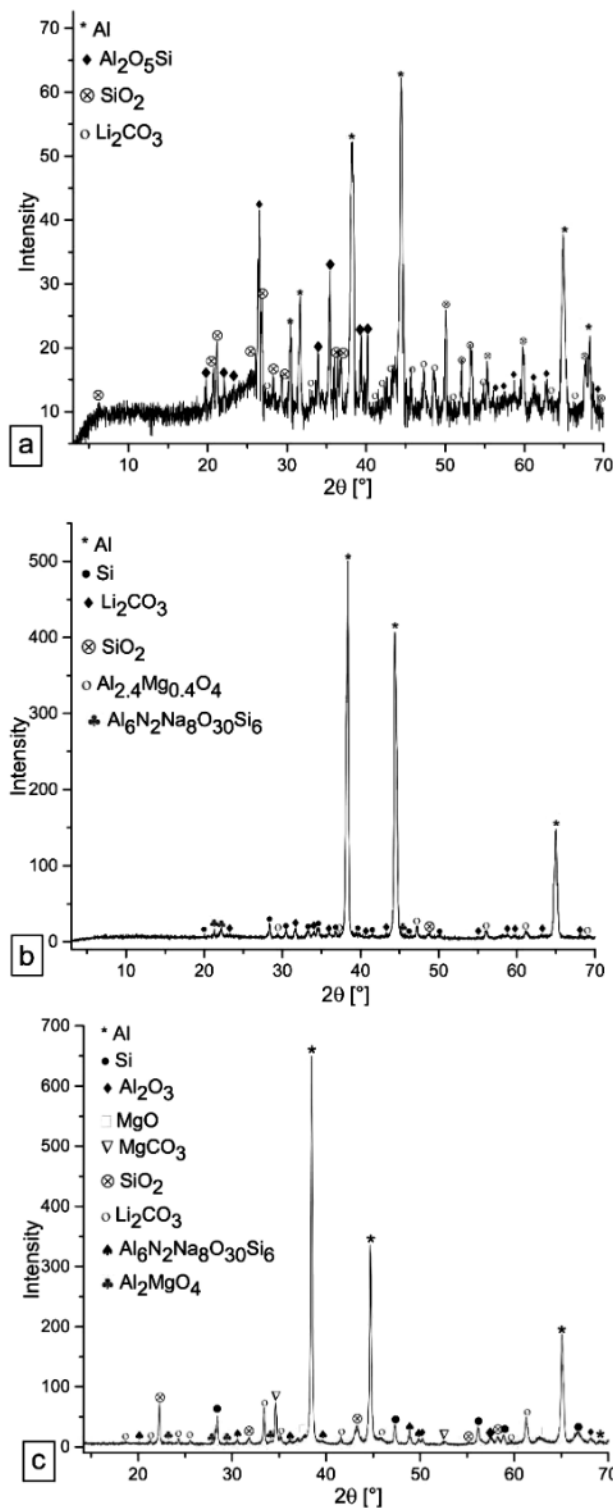


Figure 7: XRD patterns of reaction products from: a) Croning mould, b) CO₂ mould and c) calcium silicate mould

pound or the spinel $\text{Al}_2\text{O}_3 \times \text{SiO}_2$, which can also be formed from the sand mixture and Al melt. As a result of the added Li and its high reactivity, another product is lithium carbonate (Li_2CO_3), which can be formed in the presence of carbon or CO_2 , as described in the Introduction section.

The results from the CO_2 moulds are shown in **Figure 7b**. Corresponding to the larger amount of reaction products as described above, a larger number of reaction products were found. In addition to all the above, the spinel compound $\text{Al}_{2,4}\text{Mg}_{0,4}\text{O}_4$ and $\text{Al}_6\text{N}_2\text{Na}_8\text{O}_{30}\text{Si}_6$ compound (Sodalite) are detected. The first of the two compounds is probably the result of the chemical composition of the alloy and the presence of other reactants such as binder resin from moulding material, which influence the formation of it. The second compound must also be the result of sodium silicate resin from the binder system of the CO_2 sand mixture and the presence of atmosphere.

The calcium silicate mould in combination with AlSi7MgLi alloy produced the highest number of reaction products. Among those listed, elemental Si is also present in small quantities. Most likely it originates from the casting, less likely it is formed from SiO_2 and other elements present in the alloy. Al_2O_3 and MgO are most likely present as an oxidation product of the melt and $\text{Al}_2\text{O}_3 \times \text{MgO}$, which normally forms when both oxides are present at elevated temperatures.¹¹ Additionally, magnesium carbonate (MgCO_3) is formed.

As seen above, an aluminium alloy with the addition of Li is very reactive with various moulding materials. The only compound formed with Li is lithium carbonate, which appears to have the most negative free energy of formation in the system under study. It seems that Li_2O is not formed in this system. The reactions taking place are not yet known, but according to the literature review, numerous reactions must take place before lithium carbonate is formed. In addition to Li-carbonate, other compounds are formed, which are probably a by-product of the reactions and depend on the moulding material used.

4 CONCLUSIONS

Al-Li cast alloy was successfully produced in an induction furnace with a graphite-clay crucible with inert argon atmosphere introduced through the lid. Li was added to the base alloy after melting, and the yield of introduced Li was 80 %.

Croning mould material, CO_2 mould material and calcium silicate mould material proved unsuitable for

casting Al-Li alloys, and neither coating improved the performance of the listed materials. In all cases, the large amount of reaction products appeared on the casting surfaces and all were very porous.

Various reaction products were formed on the casting's surfaces, such as Al, Mg and Si-oxides, some spinels and the $\text{Al}_6\text{N}_2\text{Na}_8\text{O}_{30}\text{Si}_6$ compound. The only Li compound formed in the systems investigated is Li-carbonate, which seems to be the most stable Li compound, even more stable than Li-oxide.

The graphite mould and the steel mould gave better results with a low amount of reaction products and gas porosity. The reason for the best results is still not exactly known, either the high cooling rate, which does not allow reactions to take place, or the low reactivity of the mould materials.

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