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The Boron Solubility in Al-Mg-B Alloys

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Abstract

This study deals with the effect of magnesium content in Al-Mg-B alloy (with a boron content of about 5 wt. %) on the formation of intermetallic phases and elimination of inclusions in the form of boron powder particles in the final structure. At first look, the high melting temperature difference between pure aluminium (660 °C) and boron (2 076 °C) appears to be a potential problem. Moreover, boron has a minimal solubility in aluminium (0.055 wt.%) and the liquidus temperature increases very rapidly with increasing boron content (liquidus temperature approx. 1 160 °C at 5 wt.% for Al-B binary alloy). Alloying with magnesium results in the transformation of the intermetallic phases AlB₁₂ and AlB₂ to the (Al, Mg)B₂ phase and has a significant beneficial effect on the formation of intermetallic boron phases in the aluminium alloy without residual boron powder particles.

Keywords: Casting, Aluminium, Magnesium, Boron, Boron powder

1. Introduction

In almost all industries, including the nuclear power industry, there is a constant drive to reduce the weight of a wide range of products. Materials in the nuclear power industry have specific requirements for mechanical properties, neutron absorption and the ability to resist degradation by radiation. Today, among other things, boron steels are widely used for the storage and transport of nuclear fissile material and products in the energy industry because of their good neutron properties. The drive to reduce the weight of products and components in use today is often made possible by a change in the materials used towards lighter non-ferrous alloys (aluminium, titanium, etc.). Boron enriched aluminium alloys appear to be promising in this context. Boron is widely used in small amounts (hundredths to low tenths of a percent) as an alloying agent for grain refinement and grain boundary strengthening not only in aluminium alloys. Boron is a semi-metal, has a low density (2.3 g/cm³ at room temperature) and a very high neutron absorption cross-section (3 840 Barns for thermal neutrons), so aluminium alloys and composites with

boron contents in the order of units (up to tens) of percent are worth considering. [1], [2], [3]

Figure 1 shows the binary phase diagram of Al-B. At first look, the high melting temperature difference between pure aluminium (660 °C) and boron (2 076 °C) appears to be a potential problem. Moreover, boron has a minimal solubility in aluminium (0.055 wt.%) and the liquidus temperature increases very rapidly with increasing boron content. The diagram also suggests the presence of the intermetallic phases AlB₂ and AlB₁₂ in addition to the solid solution. [1], [2], [4]

Depending on the nature of production and the temperatures achieved during production, Al-B alloys can be divided into powder metallurgy composites (temperatures generally below the solidus limit), foundry composites (liquid matrix) and foundry alloys (temperatures near or above the liquidus temperature). Al-B foundry alloys can be defined as a material that is formed according to the phase diagram from a homogeneous melt well above the solvent temperature and where boron is excluded in the structure in the form of intermetallic phases AlB₂ and AlB₁₂. [1], [5], [6], [7], [8], [9], [10].



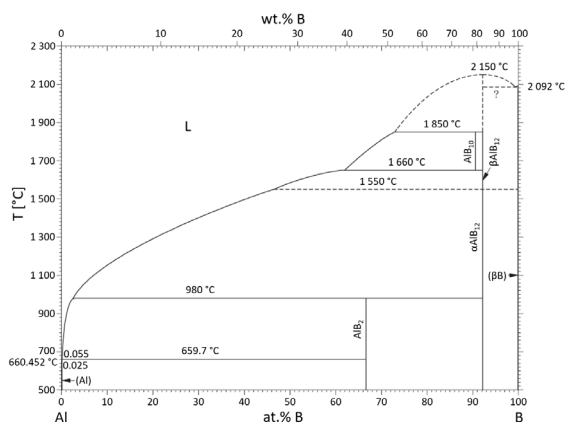


Fig. 1. Al-B binary phase diagram [1]

Cho and Kim in [9] discussed the use of ternary Al-Mg-B alloys. The addition of magnesium to the Al-B alloy results in the transformation of the intermetallic phases AlB_{12} and AlB_2 to the $(\text{Al, Mg})\text{B}_2$ phase and the formation of an Al-Mg eutectic. These structural changes lead to a significant increase in the strength characteristics and improved casting properties of the alloy up to about 6 wt.%. The Al-B alloy with boron content of about 5 wt. % and the Al-Mg-B alloy with boron and magnesium content of about 5 wt. % will continue to be considered as part of this work. [9]

2. Materials, Methods and Results

In the first experimental part, the behaviour of magnesium in aluminium alloy at elevated temperatures was investigated. Subsequently, in the second experimental part, the effect of magnesium on the formation of boron intermetallic phases in AlMgB alloy was investigated. The charge consisted of pure aluminium Al 99.85, pure magnesium Mg 99.8 and in the second part of the experiments additionally of boron powder ENV Boron 95.

2.1. Behaviour of magnesium in aluminium alloy at elevated temperatures

The boiling point of magnesium (1 107 °C) is lower than the temperature of the melt and therefore its behaviour in an "overheated" melt is a possible problem. Secondly, the very high affinity of Mg for oxygen in air is problematic.

Liu et al. in [11] investigated the effect of alloying elements on the boiling point of magnesium alloys. They found that the addition of aluminium increases the boiling point of magnesium. Since the boiling point of the metal is affected by interatomic forces in the melt, it can be assumed that no distillation will occur at the boiling point of pure magnesium. Figure 2 shows a plot of the predicted boiling point of the Mg-Al system. It can be assumed that the boiling point for a Mg content of about 5 wt. % is likely to rise above that of pure aluminium. [11]

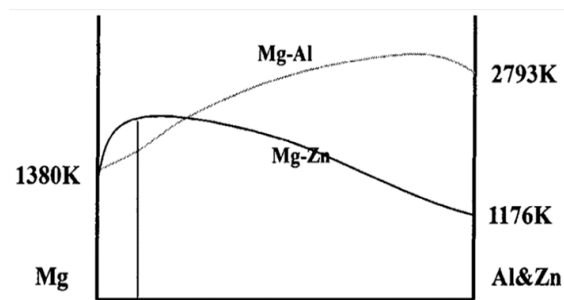
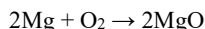


Fig. 2. Theoretical dependence of melt boiling point on chemical composition [11]

Thus, the surface oxidation of the melt appears to be the biggest problem. According to [12], the oxidation of Mg from the melt occurs in air according to the reaction:



Magnesium has a higher affinity for oxygen than aluminium and MgO is therefore preferentially produced from the melt. With decreasing Mg content in the melt, secondary oxidation of MgO occurs according to the reaction [12], [13]:

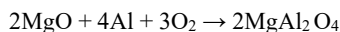


Figure 3 shows the time course of oxidation of AlMg10 alloy at temperatures of 1023 K and 1073 K. The oxidation of Mg from the melt occurs until its complete exhaustion. Therefore, the oxidation of Mg from the melt should be limited or accounted for (add excess Mg or recharge Mg to the melt). [12], [13]

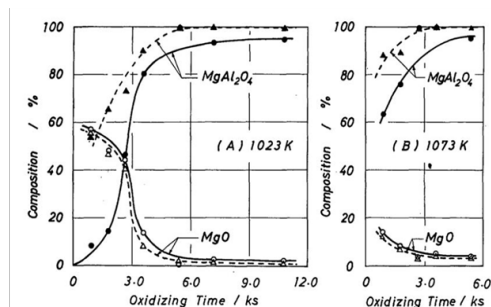


Fig. 3. Oxidation of AlMg10 alloy as a function of time [12]

To confirm the theoretical findings, an experiment was carried out to determine the behaviour of magnesium in high temperature aluminium melt. The experiment was carried out in an electric induction furnace (with graphite crucible) in the presence of a protective atmosphere (Ar) to avoid intense oxidation of the melt. The experiment was carried out with AlMg10 alloy (approx. 1 kg). The samples were cast in a steel mould and were 35 mm in diameter and 30 mm high. A reference sample was taken for spectral analysis of the chemical composition after the steady state at 700°C. The melt temperature was gradually increased in steps of 150 °C up to 1 600 °C and after each step a new sample was taken for spectral analysis of the chemical composition by optical emission spectroscopy (the measurement was performed at

3 points on each sample.). Experiment was repeated twice. From the results, the temperature dependence of the magnesium loss in the melt is further interpreted.

The experiment showed that there is a slight decrease in the Mg content of the melt up to a temperature of about 1 300 °C. At 1 300 °C a break occurs and the rate of Mg loss increases significantly. This is due to the rapid evaporation of Mg from the melt and is followed by intense optical emission (see Table 1 and Figure 4).

Table 1.
Temperature dependence of relative Mg cont. in AlMg melt.

Temp. [°C]	Relative Mg cont. [%]	Mg cont. [wt. %]
700	100	10.46 ± 0.66
850	98.09 ± 0.01	10.26 ± 0.65
1 000	95.53 ± 3.77	9.98 ± 0.24
1 150	92.19 ± 3.83	9.63 ± 0.21
1 300	86.75 ± 4.16	9.06 ± 0.14
1 450	56.31 ± 3.05	5.90 ± 0.69
1 600	23.51 ± 12.30	2.50 ± 1.44

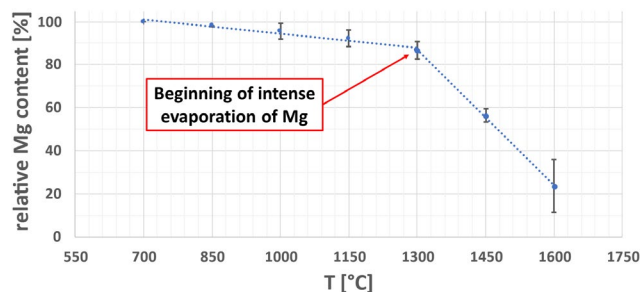


Fig. 4. Temperature dependence of relative Mg content in AlMg melt (under Ar protective atmosphere).



Fig. 5. Intensive evaporation of Mg from the melt

The experiment does not directly contradict the theoretical findings mentioned above. At the boiling point of pure magnesium (1 107 °C), no melt boiling occurs. However, it can be seen that above a temperature of approximately 1 300 °C, the evaporation of magnesium from the aluminium melt is accelerated. It can be assumed that the loss of magnesium from the melt is a function of temperature and time and can be compensated for during the metallurgical process by over-

allying the starting alloy and by further addition of Mg to the melt.

2.2. Effect of magnesium on the formation of boron intermetallic phases in AlMgB alloy

From the results obtained in the previous experiment, the estimate of the Mg loss is approximately 50% and the predicted final composition of the alloy therefore corresponds to AlMg5B5 (initial composition AlMg10B5). The experiment was carried out in an electric induction furnace (with graphite crucible) in the same form as the experiments previously carried out with AlB5 alloy. The aluminium (850 g) was first melted and then alloyed with a magnesium (100 g). A boron powder (50 g) was added to the melt after reaching a temperature of 1 150 °C. After reaching 1 400 °C, the first sample was cast. Subsequently, samples were cast after a residence time of 15 and 30 minutes, in case there would be a gradual (time) transformation of B powder into intermetallic phases. The samples were cast in a steel mould and were 35 mm in diameter and 30 mm high.

Figures 6 and 7 shows the microstructures of AlB and AlMgB samples (magnification 25x). It can be seen that the AlMgB samples have relatively high porosity, which was not present in the AlB samples. The pores reach up to 400 µm in size. The presence of pores can be explained by the intense evaporation of Mg from the alloy at the casting temperature.



Fig. 6. Microstructure of AlB alloy (25x)

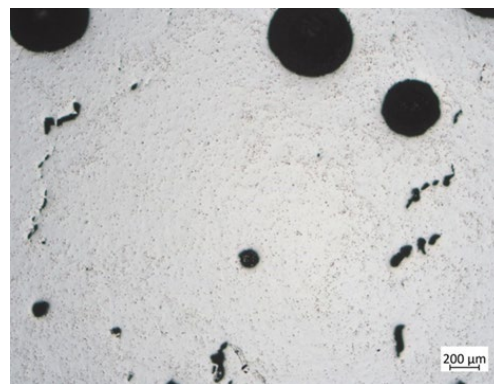


Fig. 7. Microstructure of AlMgB alloy (25x)

Figures 8 and 9 shows the microstructures of AIB and AlMgB samples (magnification 500x). It is evident that the addition of Mg has a positive effect on the microstructure and solubility of the powder in the matrix. The structure of the AlMgB samples, unlike the AIB samples, is essentially free of undissolved B particles. Thus, it can be argued that the Mg additive has a significant beneficial effect on the formation of intermetallic boron phases in the aluminium alloy. The experiment showed that in the case of AlMgB alloy, the residence time has no effect on the transformation of B powder in the intermetallic phases.

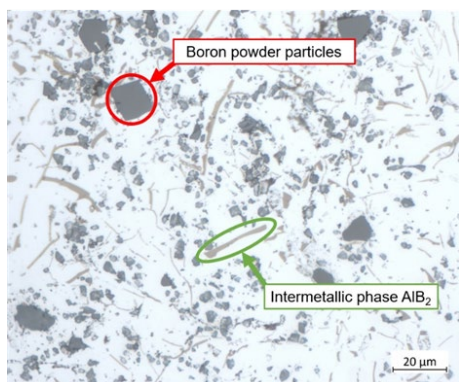


Fig. 8. Microstructure of AIB alloy (500x)

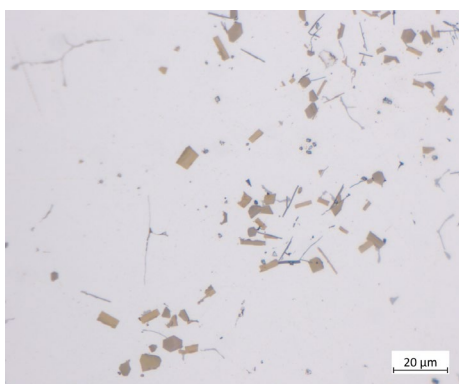


Fig. 8. Microstructure of AlMgB alloy (500x)

The AlMgB alloy is mainly composed of the α -Al solid solution aluminium matrix with a participation of (Al, Mg)B₂ phases with polyhedral morphology. These phases were further specified as most probably Mg_{0.4}Al_{0.6}B₂ by SEM and XRD analysis. Accurate phase composition determination is complicated by the fact that the contained B is a low atomic number element that cannot be analysed by conventional X-ray spectral methods. Boron forms with both aluminium and magnesium a series of equilibrium intermediate phases which could theoretically also be present in the AlMgB alloy, however, these could not be identified. Furthermore, fine silvery FeAl₃ phases with needle/plate morphology were identified in the structure based on SEM and XRD analysis. Figure 9 shows the structure based on SEM and XRD analysis. Figure 9 shows the spot analyses for the individual phases and the measured chemical composition of the 2 selected spots. Figure 10 shows the element distribution maps (SEM).

A considerably high amount of casting defects (microcalcifications, gas porosity) was detected in the α -Al solid

solution matrix. These are mainly caused by the high temperature during melt processing. Casting defects are shown in Figures from 11 to 13.

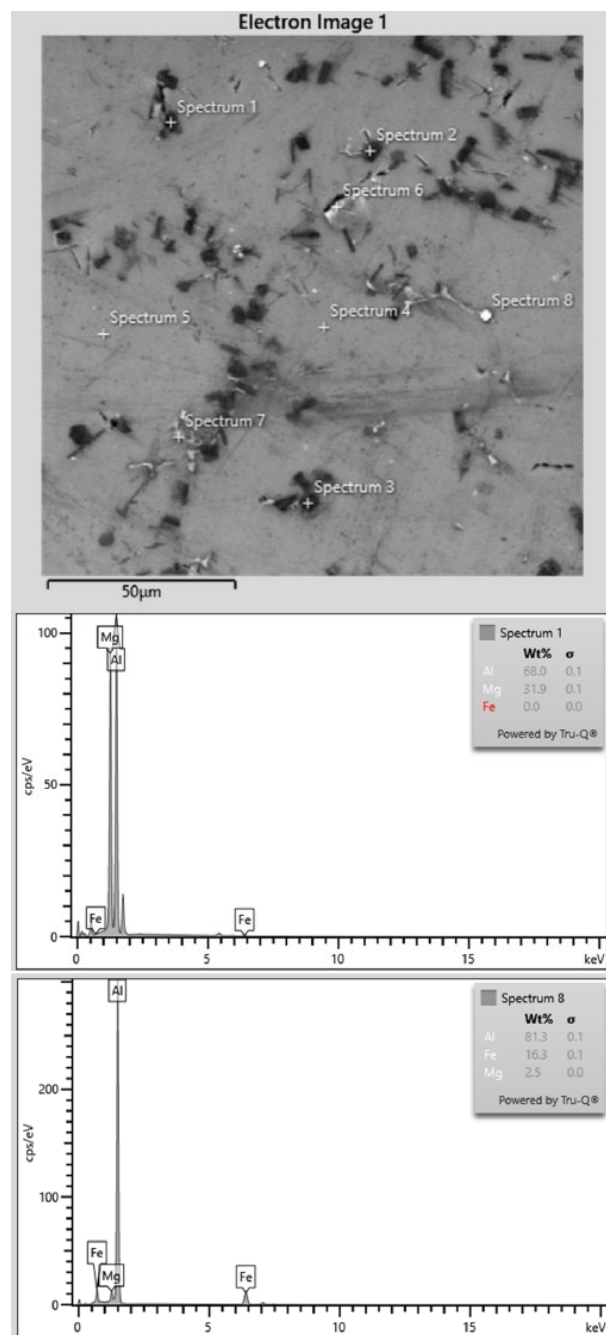


Fig. 9. Spot analyses in selected areas (SEM)

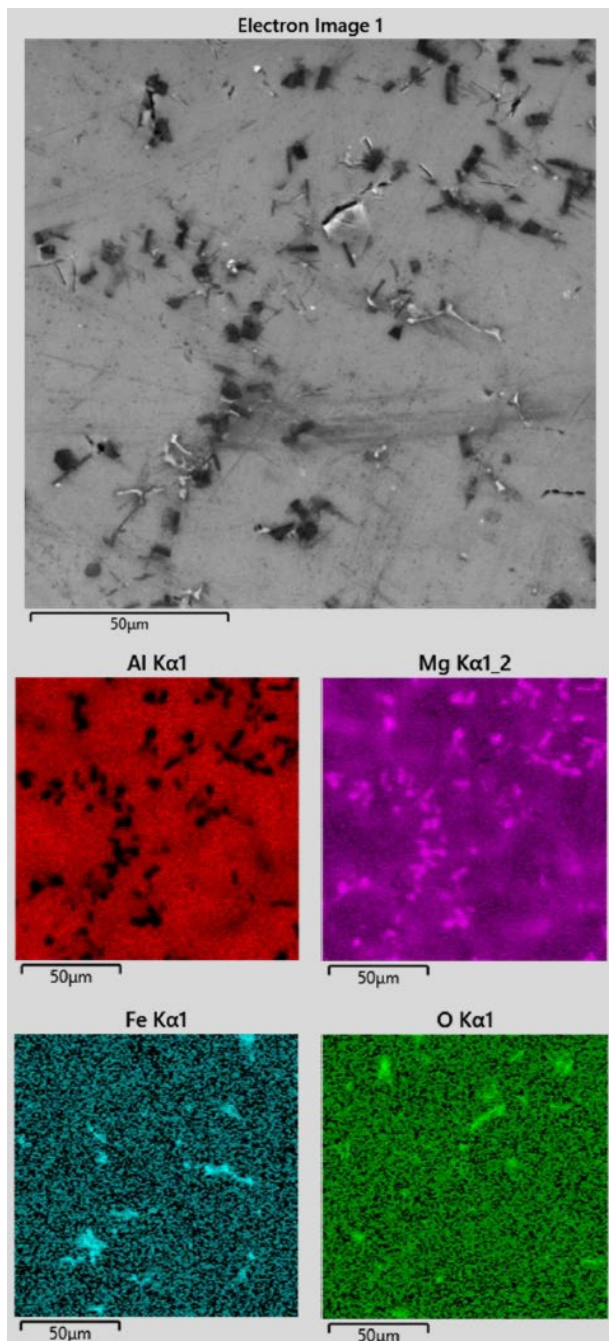


Fig. 10. Element distribution maps (SEM)

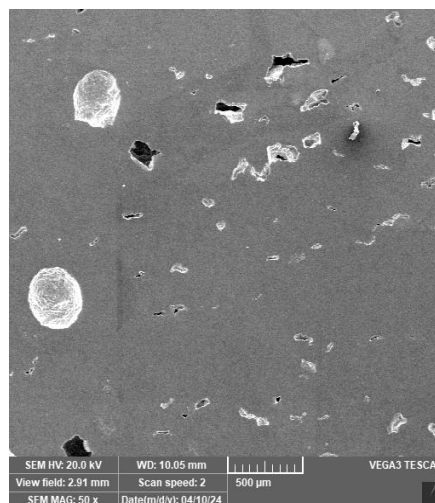


Fig. 11. Casting defects in AlMgB alloy (50x) (SEM)

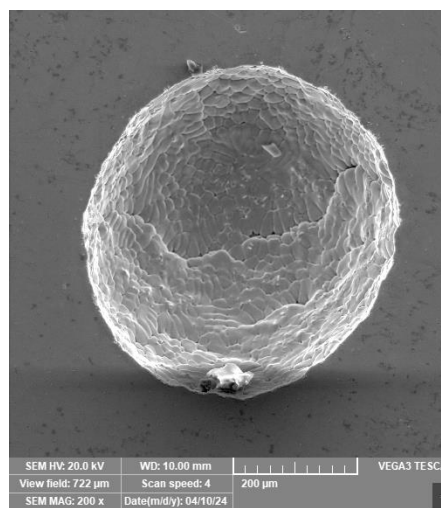


Fig. 12. Gas porosity in AlMgB alloy (200x) (SEM)

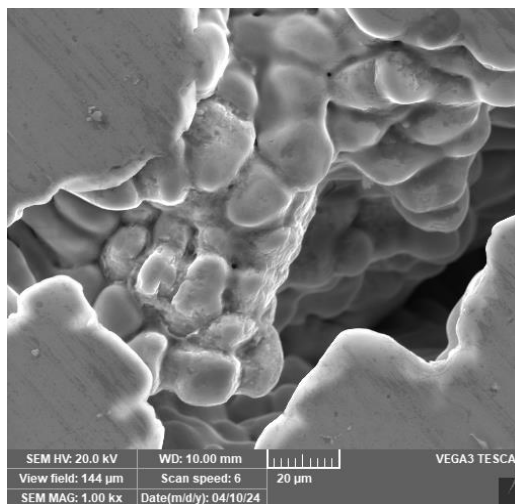


Fig. 13. Shrinkage porosity in AlMgB alloy (1000x) (SEM)

3. Conclusions

Magnesium strongly promotes the formation of intermetallic phases from boron powder particles in aluminium alloy. Alloying with magnesium results in the transformation of the intermetallic phases AlB_{12} and AlB_2 to the $(Al, Mg)B_2$ phase and has a significant beneficial effect on the formation of intermetallic boron phases in the aluminium alloy without residual boron powder particles. The temperature dependence of the magnesium content of the AlMg melt is slowly decreasing up to 1 300 °C and above 1 300 °C there is an intense evaporation of Mg from the melt. As a result of the intense evaporation of magnesium from the melt, a very significant porosity is formed in the form of bubbles (up to several hundred μm in diameter). A significant problem is the measurement of the Boron content. To accurately measure the Boron content, it would be necessary to produce an etalon of accurate chemical composition for calibration of the measuring devices. However, this would be very expensive and is not within our capabilities. However, the goal is to develop an alloy with a Boron content of 5 to 10 weight percent, which we are able to achieve with knowledge of the input raw materials. We assume that magnesium and aluminium "burn out" at temperatures above 1 200 °C even under the protective atmosphere and boron does not. So, if the quantity has been charged at the original weight for a 5% of boron content, then its actual content with respect to the "burn out" will be between 5-10%.

This study is only an introduction to the problem of AlB alloys. In further research, we will look into the formation of intermetallic boron phases in AlMg alloy at lower temperatures in order to avoid the formation of porosity originating from the intense evaporation of magnesium. Further research will focus on the influence of other alloying elements and their possible synergy effect.

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