Proceedings of "Applications of Physics in Mechanical and Material Engineering" (APMME 2023)

Calorimetric Analysis of Grain Modified Mg–Li Alloy

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Nowadays calorimetric analysis is a widely used method to study phase transformations occurring in the liquid or solid state in metals and alloys. Information on enthalpy, kinetics and transition characteristics can be obtained with the appropriate configuration of analytical apparatus and establishment of test procedures. In this work, an analysis of the transitions taking place in the grain-modified dual phase α(Mg) + β(Li) Mg–9Li–1.5Al alloy was carried out on the samples taken from casts. The latent heat of the analysed alloys was captured using the UMSA device. The solidification process has been analysed using cooling curve analysis. The latent heat at a natural cooling rate 0.5°C/s was calculated based on the first derivative of the cooling curve. The released latent heat during crystallisation was estimated by applying the Newtonian technique of baseline. The results confirmed that calorimetric analysis can be successfully applied to study phase transitions in this type of magnesium alloy. The work uses thermal derivative analysis to present the possibility of specifying the latent heat of modified ultralight Mg–Li cast alloys.

topics: latent heat, thermal derivative analysis (TDA), grain modification, Mg–Li alloy

1. Introduction

Thermal analysis (TA) of magnesium alloys is a field of materials science that focuses on studying the thermal behavior and properties of magnesium-based materials. It focuses on the application of various techniques to analyze how magnesium alloys respond to changes in temperature, including their phase transformations, thermal stability, and thermal expansion characteristics. Thermal analysis techniques commonly used for studying magnesium alloys include [1–7]:

- **Differential scanning calorimetry (DSC)** DSC measures the heat flow into or out of a sample as a function of temperature. It can detect phase transitions such as melting, solidification, and precipitation reactions, providing information about the alloy's thermal behavior and energy changes.
- **Thermogravimetric analysis (TGA)** TGA measures the change of sample weight as a function of temperature. It can be used to study processes like oxidation, desorption of gases, and decomposition reactions in magnesium alloys.
- **Differential thermal analysis (DTA)** DTA measures the temperature difference between a sample and a reference material as they are subjected to a controlled temperature program. It can identify phase transitions, crystallization and other thermal events.
- **Thermo-mechanical analysis (TMA)** TMA measures the dimensional changes of a sample as a function of temperature. It provides information about the coefficient of thermal expansion (CTE) and thermal deformation behavior of magnesium alloys.

By examining the derivative of a property, thermal derivative analysis (TDA) provides information about thermal events occurring in a material, such as phase transitions, crystallization, decomposition, and other thermal effects. It can help identify characteristic temperatures associated with these events, including onset temperatures, peak temperatures, and completion temperatures [8–15].

This data is useful for understanding the characteristics and behavior of materials in various fields, including materials science, chemistry, and engineering. TDA is commonly employed in research, quality control and product development processes [16, 17].

These thermal analysis techniques allow researchers to characterize the thermal properties of magnesium alloys, understand their phase transformations, evaluate their thermal stability, and optimize their processing conditions. This information is crucial for designing and engineering magnesium alloys for various applications, including automotive, aerospace and consumer electronics, where thermal performance and reliability are important factors [18, 19].

TABLE I

Chemical composition [wt%] of analysed alloys.

Alloy	Li	Al	Si	B	Ti	Sr
Mg–9Li–1.5Al	8.99	1.72	–	–	–	–
Mg–9Li–1.5Al + 0.2TiB	8.93	2.1	0.031	0.0012	0.0067	–
Mg–9Li–1.5Al + 0.2Sr	8.37	1.83	0.065	–	–	0.026
Mg–9Li–1.5Al + 0.2TiB + 0.2Sr	8.72	1.78	0.051	0.0020	0.011	0.025

2. Research methodology

In the preparation of Mg–Li alloys, the following steps were taken:

1. selecting high-purity magnesium (Mg) and lithium (Li) metals with minimal impurities to ensure the desired alloy properties,
2. melting at 720°C in a furnace capable of withstanding the high temperatures required to melt magnesium,
3. preheating the crucible to minimize oxidation,
4. adding measured quantities of Mg and Li into the crucible and heating up till the metals melt,
5. stirring the molten mixture to ensure proper mixing and homogenization,
6. pouring the molten alloy into suitable molds.

The analysis of the chemical composition of the alloy was performed using ICP-OES Optima 5300 V, made by PerkinElmer. The chemical composition of the analysed composites is presented in Table I.

A test sample had dimensions of 18 mm (diameter) and 20 mm (height). The K-type thermocouple was placed at the center of the sample height and linked to the personal computer with high-speed National Instrument data acquisition system (UMSA) [18–20].

The cooling conditions were kept constant during experiments, i.e., melting temperature 700°C, argon atmosphere, holding time 90 s, cooling rate 0.5°C/s. Every TA trial was repeated three times. To increase the precision of the data without distorting the signal tendency, the achieved cooling curve was smoothed by a Savitzky–Golay digital filter.

The latent heat of crystallization of the alloys was determined from the equation [21–23]

$$Q = m\, c_p \int_{t_N}^{t_{sol}} \mathrm{d}t \left[\frac{\mathrm{d}T}{\mathrm{d}t} - \left(\frac{\mathrm{d}T}{\mathrm{d}t} \right)_c \right]. \tag{1}$$

3. Results

In the presented work, thermal-derivative analysis was applied to register cooling curves and calculate their corresponding first derivatives of the investigated Mg–Li alloys.

TABLE II

Thermal characteristics of the analysed alloys.

Heat capacity	Liquid state		Solid state	
c_{p_l} [J/(g °C)]	1.498		1.248	
Analysed alloy	Mg-9Li-1.5Al	Mg–9Li-1.5Al+0.2 TiB	Mg–9Li–1.5Al+0.2Sr	Mg–9Li–1.5Al+0.2TiB+0.2Sr
Latent heat of sample, Q [J]	860	1082	1477	1247
Latent heat per gram [J/g]	157.5	161	171	159.6

The literature shows that the thermal and thermodynamic data are unavailable for the ultra-light Mg–Li grain modified alloys. Moreover, the presented paper analysed the influence of grain modifiers on the latent heat released during the crystallisation process of the α(Mg) + β(Li) Mg–9Li–1.5Al alloy.

Figure 1 presents the thermal-derivative curves of the grain-modified Mg–9Li–1.5Al alloy with the corresponding crystallisation curves and baselines on which characteristic points can be identified. Those characteristic peaks reflect the observed phase changes corresponding to the transformation of liquid metal during crystallisation.

Peak T_L (see Fig. 1b, c and b) is related to the initial time of the nucleation process and the growth of the α(Mg) + β(Li) phase, which lasts up to temperature T_s, where crystallization of the melt ends and the solid phase volume reaches 100%. Between the liquidus and solidus temperatures, a slightly visible peak T_η can be noted. This event represents the formation of the η phase, which is related to the precipitation of the lithium–aluminium phase (LiAl) [23].

It can be seen that the shape of the cooling curves strongly depends on the grain modifiers used in the investigated magnesium–lithium alloys.

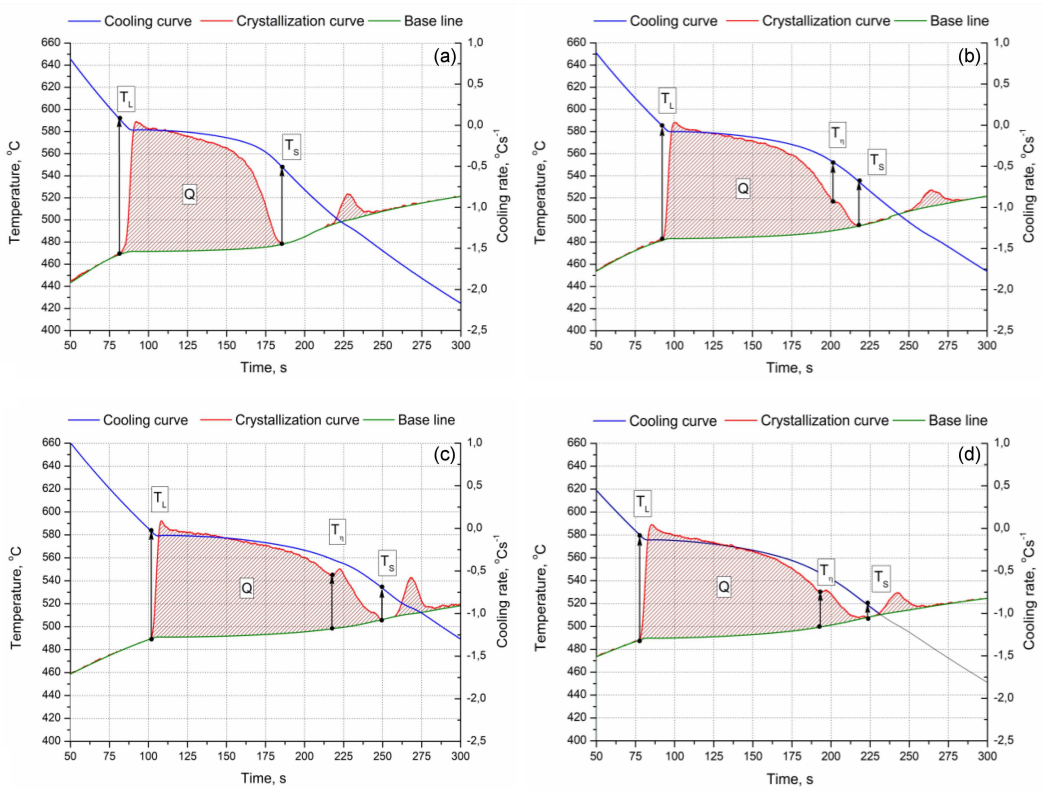

Fig. 1. Thermal analysis of (a) Mg–9Li–1.5Al, (b) Mg–9Li–1.5Al + 0.2TiB, (c) Mg–9Li–1.5Al + 0.2Sr, (d) Mg–9Li–1.5Al + 0.2TiB + 0.2Sr.

The thermal analysis presents that the addition of 0.2 wt% TiB and Sr affects the beginning of the nucleation of $\alpha(\mathrm{Mg}) + \beta(\mathrm{Li})$ from 596 to 579°C and the duration of the crystallisation process from 47 to 59°C of the investigated alloys.

Strontium significantly influences the shape of crystallisation curves. The addition of Sr decreases the nucleation and the solidus temperature from 596 to 587°C and 549 to 536°C, respectively.

The analysis of the obtained results indicates that adding modifiers in the form of TiB or Sr is responsible for the additional exothermic peak T_η generated by the nucleation and crystallization of the intermetallic phase η(LiAl). Nucleation of the intermetallic phase η(LiAl) occurs at 552°C, 559°C, and 546°C for Mg-9Li–1.5Al + 0.2TiB, Mg–9Li–1.5Al + 0.2Sr, and Mg–9Li–1.5Al + 0.2TiB + 0.2Sr alloys, respectively. In the case of nucleation of the η(LiAl) phase, the addition of TiB has the most significant influence.

The calculated latent heat of the investigated grain-modified Mg–9Li–1.5Al alloy has been presented in Table II. The study revealed that the alloy with the addition of Sr has a higher latent heat, and the TiB content has some impact on the amount of released latent heat, but is not as significant as Sr.

The highest latent heat was generated by the alloy Mg–9Li–1.5Al modified with Sr and was equal to 171 J/g. The addition of TiB causes an increase in the total enthalpy to 161 from 157 J/g. The addition of the modifiers TiB and Sr also causes an increase in the total heat of enthalpy to approximately 159 J/g.

The presented results show that the thermal derivative analysis carried out by the UMSA device can be an extremely helpful tool for calculating thermal and thermodynamic data of ultra light Mg–Li grain-modified alloys. Appropriate numerical calculations based on the obtained test results can be successfully used in the application of artificial neural networks to determine individual parameters of the crystallisation process on the course, as well as the proportion of the solid fraction and the volume of the generated latent heat. The results indicate that the use of the UMSA device can decrease the costs of research concerning the crystallisation of metal alloys by eliminating the necessity to use specialised and expensive testing apparatus.

4. Conclusions

The thermal derivative analysis of the grain-modified Mg–9Li–1.5Al alloy with TiB and Sr and the thermal behavior was investigated.

The following conclusions can be drawn:

- TiB and Sr control the solid fraction and temperature of the nucleation of the η(LiAl) phases and the influence the amount of latent heat released.

- Additions of grain modifiers cause changes in the crystallization process, i.e., the beginning of nucleation and the solidus temperatures.
- Application of Sr as a modifier leads to significant increase of the generated latent heat $\approx 10\%$.

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