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Crystallization Process of Ultra-Light Mg–Li Alloys

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Metallic materials play an essential role in materials commonly used in many developmental industries. A characteristic feature of their crystalline structure is the ordered arrangement of the constituent physical elements in space according to the defined laws of thermodynamics and chemical reactions. Therefore, conscious control of technology to obtain the optimal structure of these materials is based, among other things, on the control of the applied methods of crystallization, modification and optimization of the smelting, casting parameters as well as possible heat treatment procedures, which guarantee the appropriate quality. The presented work discusses the crystallization process of the modified ultra-light Mg–Li cast alloys based on the thermal-derivative analysis, which visually uses the effects of phase transformations occurring in metal alloys in a liquid state, accompanied by a change in energy and the release of the latent heat of crystallization.

topics: latent heat, crystallization, thermal-derivative analysis, magnesium alloys

1. Introduction

Magnesium alloys are used in lightweight structures, especially in the aerospace industry. Weight reduction in means of transport brings savings in operating costs (mainly lower fuel consumption). Magnesium alloys have a low density of about $\rho = 1.8$ g/cm^3 (depending on the alloy grade), high specific strength, and low generation. In addition, an essential feature of magnesium and its alloys is good electromagnetic shielding and a low coefficient of friction ($\mu = 0.1$). The high vibration damping ability and low inertia of the magnesium alloy components enable the use of the magnesium alloys for fast-moving details in areas where the rapid velocity changes occur. The interest in magnesium alloys for aerospace structural components dates back to the 1940s. During World War II, when magnesium and its alloys were used mainly for military purposes, world magnesium production increased nine-fold. Magnesium alloys are also used in other branches of industry. Excellent examples are, e.g. "laptops", cell phones, small household appliances, office machines and car interior elements [1–7].

The alloys of the Mg–Li group are attractive due to the low density of lithium. The density of this group's alloys at a concentration of 14–16% Li reaches 1.35–1.45 g/cm^3. The Mg–Li alloys are interesting structural materials because they have a low density while maintaining high strength. The latest group, often discussed separately, are magnesium alloys produced by unconventional technologies with the so-called rapid solidification (solidification at high speeds). The rapid solidification (RS) method is used to modify the microstructure of alloys. The process is mainly intended for cast magnesium alloys. The effectiveness of the method depends on the rate of heat release of the phase transition during the change of the aggregation state, which in turn is related to the control of heat removal or very fast cooling [8–14]. Furthermore, complementary knowledge of the crystallization process will allow to predict the mechanical properties of the alloy and its structure [15–18].

Moreover, the solidification process of the alloys mainly consists of nucleation, growth processes and the release of latent heat during the crystallization process. The generated latent heat sometimes comes from phase precipitation. The knowledge of the crystallization process and the evolved latent heat is crucial for the proper heat treatment of alloys [19–22].

This paper presents and discusses the crystallization process and thermal behaviour of the ultralight Mg–4.5Li–1.5Al cast alloy modified with TiB and Sr based on the thermal-derivative analysis. This method visually uses the effects of phase transformations occurring in metal alloys in a liquid state, which are accompanied by a change in energy and the release of the latent heat of crystallization.

TABLE I

Chemical composition of analysed alloys [wt%].

Analysed alloy	Li	Al	Si	B	Ti	Sr
Mg–4.5Li–1.5Al	4.64	1.86	–	–	–	–
Mg–4.5Li–1.5Al+0.2TiB	4.66	1.80	0.052	0.0019	0.0069	–
Mg–4.5Li–1.5Al+0.2Sr	4.63	1.80	0.030	–	–	0.019
Mg–4.5Li–1.5Al+0.2 TiB+0.2Sr	4.63	1.85	0.041	0.0012	0.0042	0.021

2. Research methodology

The as-cast magnesium–lithium–aluminium alloy Mg–4.5Li–1.5Al were used in this study. As grain modifiers, TiB and Sr were used. To achieve alloys, high purity Mg ingots (with technical grade — min 99.5% Mg) were melted in a steel crucible under argon gas atmosphere in the temperature range of 700–720°C at a pressure of 650 Tr. The elements Li (99.9% Li) and Al (3N8 — 99.98% Al) in the form of pure metals were added to the melt. The alloys were cast by gravity into the cold mould of graphite to give rod-shaped ingots with dimensions $\text{ø}20 \times 100$ mm^2.

The chemical elements in the studied alloys were analysed by applying an inductively coupled optical emission spectrometer, including inductively coupled plasma (ICP OES) OPTIMA 5300V made by PerkinElmer. The chemical composition of prepared and analysed composites is presented in Table I.

The thermal-derivative analysis (TDA) was done on the cylindrical samples in the shape of 18 mm in diameter and 20 mm in height. Thermal analysis on the samples was performed using K-type thermocouples and connected to a Universal Metallurgical Simulator and Analyse (UMSA), according to the methodology described in [23, 24]. The samples were melted at 700°C in an argon atmosphere. After isothermal holding for 90 s, all the melts were solidified and cooled to room temperature in the crucibles. The Savitzky–Golay filter was used to filter the signal, and the Fityk software was used to determine the baseline. The latent heat of crystallization of the alloys was determined using [23]

$$Q = mc_p \int_{t_N}^{t_{\text{sol}}} \mathrm{d}t \left[\frac{\mathrm{d}T}{\mathrm{d}t} - \left(\frac{\mathrm{d}T}{\mathrm{d}t} \right)_{\text{c}} \right], \tag{1}$$

where m is sample mass, c_p is heat capacity, t_N is time at nucleation temperature, t_{sol} is time at solidus temperature and $(\mathrm{d}T/\mathrm{d}t)_c$ is calorimetric curve (i.e., base line).

3. Results

The phase transitions appearing during crystallisation (i.e., the change of a substance from a liquid to a solid state) are accompanied by the release of heat into the environment, and thus by a decrease in the internal energy of the thermodynamic system. Therefore, enthalpy is a physical quantity representing the amount of heat released. The thermal behaviour of analysed alloys has been presented in Table II. The study revealed that the total enthalpy of dendrite formation α(Mg) upon cooling for the Mg–4.5Li–1.5Al alloy was 139 J/g. Based on the analysis, the highest enthalpy value was reached by the alloy modified with 0.2 wt% TiB and Sr, and it was 188 J/g. The addition of 0.2 wt% of TiB causes an increase in the total enthalpy value of α(Mg) dendrite formation upon cooling to 185 J/g. The addition of a modifier in the form of 0.2 wt% Sr also causes an increase in the total heat of the enthalpy to about 179 J/g.

Figure 1 presents the cooling (crystallization) process of the grain modified Mg–4.5Li–1.5Al alloy, registered with the use of the UMSA device.

The TDA crystallization curve of the Mg–4.5Li–1.5Al alloy (cooled at an average cooling rate of about 0.6 C/s) shows that the nucleation and growth of the primary dendrites at the temperature T_L are nucleation and growth of the α(Mg) phase derived from a liquid state. This process continues up to the temperature T_s, where the crystallization of the melt ends, and the solid phase contribution reaches 100%. The results from the thermal analysis present that the addition of 0.2 wt% TiB and Sr causes changes in the liquidus temperature from 605.0 to 616°C.

The study shows that the addition of modifiers TiB or Sr makes them responsible for the additional exothermic reaction T_η caused by nucleation and crystallization of the intermetallic phase η(LiAl). The process can be described as follows: in the first stage, the hcc of α(Mg) starts solidifying until the liquid composition achieves the maximum growth temperature; after passing that temperature, a transformation in a solid state

TABLE II

Thermal characteristics of analysed alloys. Heat capacity in the liquid state and the solid state are $c_{p_L} = 1.364$ J/(g °C) and $c_{p_s} = 1.137$ J/(g °C), respectively.

Analysed alloy	Latent heat of sample Q [J]	Latent heat per gram [J/g]
Mg–4.5Li–1.5Al	1075	139
Mg–4.5Li–1.5Al+0.2 TiB	1467	185
Mg–4.5Li–1.5Al+0.2Sr	1495.5	179
Mg–4.5Li–1.5Al+0.2TiB+0.2Sr	1376.0	188

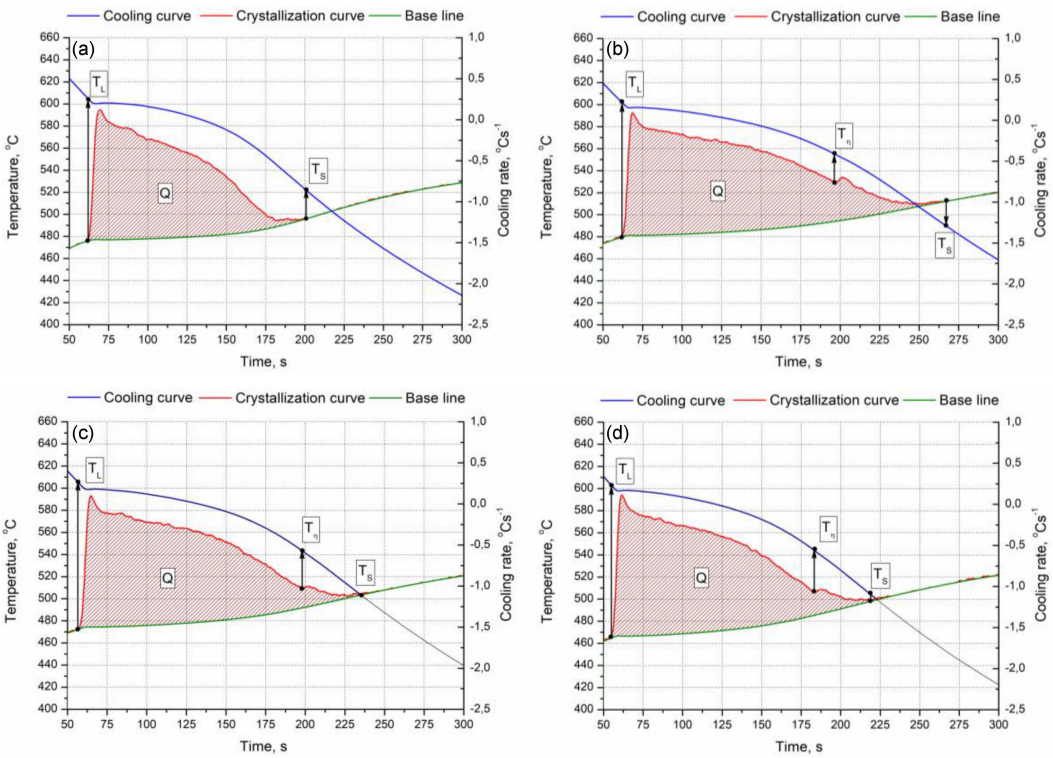

Fig. 1. Thermal-derivative analysis of the alloys (a) Mg–4.5Li–1.5Al, (b) Mg–4.5Li–1.5Al+0.2TiB, (c) Mg–4.5Li–1.5Al+0.2Sr and (d) Mg–4.5Li–1.5Al+0.2TiB+0.2Sr.

occurs (solidus line in Mg–Li binary system), causing the appearance of α(Mg) and η(LiAl) intermetallic compound with B2 structure. The crystallisation process finished at the solidus temperature. This is confirmed by the results of own research [23, 24]. End of crystallization of the whole alloys Mg–4.5Li–1.5Al, Mg–4.5Li–1.5Al+0.2TiB, Mg–4.5Li–1.5Al+0.2Sr and Mg–4.5Li–1.5Al+0.2TiB+0.2Sr occurs at the temperature T_s of 523.6, 492.3, 490.1 and 495.2°C, respectively. Changes in the nucleation temperature of the η(LiAl) phase may be due to crystallization under accelerated cooling conditions. In addition, the formation of a new η(LiAl) phase during the melt crystallization increases the duration of this crystallization process by about 55 s and decreases the solidus temperature by about 40°C.

4. Conclusion

The thermal derivative analysis of the modified Mg–4.5Li–1.5Al alloy with TiB and Sr and the thermal behaviour was investigated. From the presented results, the following conclusions can be drawn:

- TDA analysis provides a quantitative analysis of the kinetics the cooling and solidification process,
- enables the analysis of the crystallization process of the hypoeutectic Mg–4.5Li–1.5Al alloy,
- additions of grain modifiers cause changes in the crystallization process as a result of the nucleation of η(LiAl),
- modification of the alloy increases in latent heat of the analysed alloy about 25%.

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