

Eutectic modification of A356 alloy with Li addition through DSC and Miedema model

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Abstract: Eutectic modification of A356 alloy with Li addition was investigated with scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). SEM micrograph results indicate that the transition of eutectic morphology, which is changed from flake-like to fibrous, is dramatically induced with the addition of 0.3% (mass fraction) Li. The larger microhardness corresponds to the modification morphology of the eutectic phase for A356 alloy with 0.3% Li addition. The modification effect is increased with increasing the cooling rate and degraded with prolonging the holding time of temperature. DSC results show that the eutectic solidification temperature of A356 alloy with Li addition is decreased and the eutectic temperature depression with 0.3% Li addition is decreased by 2.9 °C in cast-iron mold. The mixing enthalpies of Li with Si and Al in A356 alloy, which were calculated by the Miedema model, were used to study the mechanism of modification and ascertained its restricted growth theory.

Key words: A356 alloy; eutectic modification; lithium; DSC; mixing enthalpy

1 Introduction

Recent increasing applications of the hypoeutectic cast Al–Si alloy are particularly driven by the need for lightweight components in the automobile and aviation industries because of its excellent mechanical and casting properties [1–4]. But the coarse and acicular eutectic phases in cast Al–Si alloy are the threshold of fracture in the tension environment, and are considered a disadvantage for mechanical properties [5]. To improve mechanical properties, in particular to increase the tensile elongation, the modification of the coarse eutectic phase can be achieved in various ways, such as adding certain elements (chemical modification), a rapid cooling rate (quench modification), semi-solid processing and electromagnetic stirring [2–7]. It is found that adding element is the most popular and effective. The eutectic silicon phase is usually modified from coarse and plate-like to fine and fibrous morphology by adding the elements such as strontium, sodium, antimony and rare earth elements to the melt [6, 7].

Several researches on eutectic modification with elements were conducted for the hypoeutectic Al–Si alloys. KNUUTINEN et al [5] and McDonald et al [8]

studied the eutectic modification in hypoeutectic Al–Si alloys with the addition of Sr or rare earth elements. GENG et al [9] and NOGITA et al [10–12] studied the B addition and the P addition on the hypoeutectic Al–Si alloys and three eutectic solidification modes for Al–Si alloys were put forward [13]. However, few studies focused on the eutectic nucleation and modification with lithium addition in Al–7Si alloy. In this work, the effect of Li addition on eutectic modification in hypoeutectic A356 alloy is investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and the mixing enthalpy is calculated by the Miedema model. Special attention is paid to the effect of Li addition on the modification of eutectic phase of hypoeutectic A356 alloy.

2 Experimental

Table 1 shows the composition of A356 alloy ingot used in the experiment.

Table 1 Composition of A356 alloy (mass fraction, %)

Si	Mg	Fe	B	Sn	Ti	Al
7.39	0.356	0.116	0.0011	0.0027	0.115	Balance

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The as-received commercial A356 ingots were melted in SiC crucible by an 12 kW electrical resistance furnace. The SiC crucible was preheated to 400 °C before charging the commercial A356 ingots. The alloy melt was heated up to 750 °C and carefully skimmed to remove dross and other impurities. Two of the alloy melts were treated with Li addition at the levels of 0.1% and 0.3% in the form of pure Li which was wrapped in aluminum foil, to adjust the chemical composition. Table 2 shows the composition and designation of alloys in this study. The alloy melts were cast into cast-iron mold and sand mold, respectively, where the alloy melts were solidified at different cooling rates.

Table 2 Designation of alloys in this study

Sample No.	w(Li)/%	Mold	t_h /min
A ₀	—	Cast-iron	—
A ₁	—	Sand	—
B ₀	0.1	Cast-iron	—
B ₁	0.1	Cast-iron	30
B ₂	0.1	Sand	—
B ₃	0.1	Sand	30
C ₀	0.3	Cast-iron	—
C ₁	0.3	Cast-iron	30
C ₂	0.3	Sand	—
C ₃	0.3	Sand	30

t_h is holding time of temperature.

The effect of Li addition on the microstructures was studied by means of SEM (ZEISS SUPRA55), and DSC (NETZSCH STA 409 CD) was used to investigate the eutectic temperature depression. The microhardness values of alloy samples were measured by Struers Duramin-A300 and the applied load was 0.98 N.

3 Results and discussion

3.1 Microstructures

The typical SEM micrographs of the cast A356 alloys with Li addition are illustrated in Fig. 1 (cast-iron mold) and Fig. 2 (sand mold). It can be seen from Fig. 1(a) and Fig. 2(a) that coarse structures of flake-like, and long needle-like stick eutectic phase are formed in α (Al) phase. However, with Li addition to the alloys, it is found that there are many short, spherical and fibrous structures of eutectic phase (see Figs. 1(b), 1(c) and Figs. 2(b), 2(c)). Furthermore, the morphology of eutectic phase with 0.3% Li addition is fine fibrous-like (Fig. 1(c) and Fig. 2(c)). From Fig. 1 and Fig. 2, it can be seen that, with a certain Li addition, the morphology of eutectic phase of the alloy sample cast in cast-iron mold is finer than that cast in sand mold. Therefore, the cooling rate is an important factor to control the

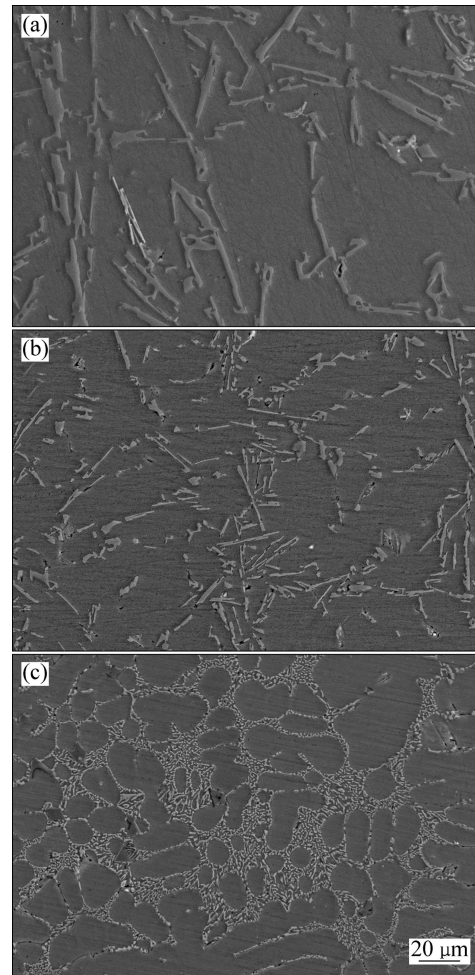


Fig. 1 SEM images of cast A356 alloy with Li addition in cast-iron mold: (a) Li-free; (b) 0.1% Li; (c) 0.3% Li

morphology of the eutectic phase, and eutectic modification of A356 alloy with Li addition is more effective with increasing the cooling rate. It can be suggested that Li element is rejected on the solid–liquid interface during solidification at the higher cooling rate. During the subsequent solidification, the liquid in front of the solid–liquid interface becomes enriched in Li, and as a result, effective Li element for modification is increased. However, when the cooling rate is decreased, the amount of Li enriched in front of the solid–liquid interface is lower because the rejected Li has much more time to diffuse into the liquid. Therefore, modification effect of alloy with Li addition is more obvious in cast-iron mold.

Figure 3 shows the microstructures of the alloys modified by 0.3% Li with different holding time. Compared with the results obtained without holding, the morphology of eutectic phase was dramatically changed from fine fibrous into coarse flake after holding for 30 min. The coarse structures of the flake-like, long needle-like stick eutectic phases, which look like that

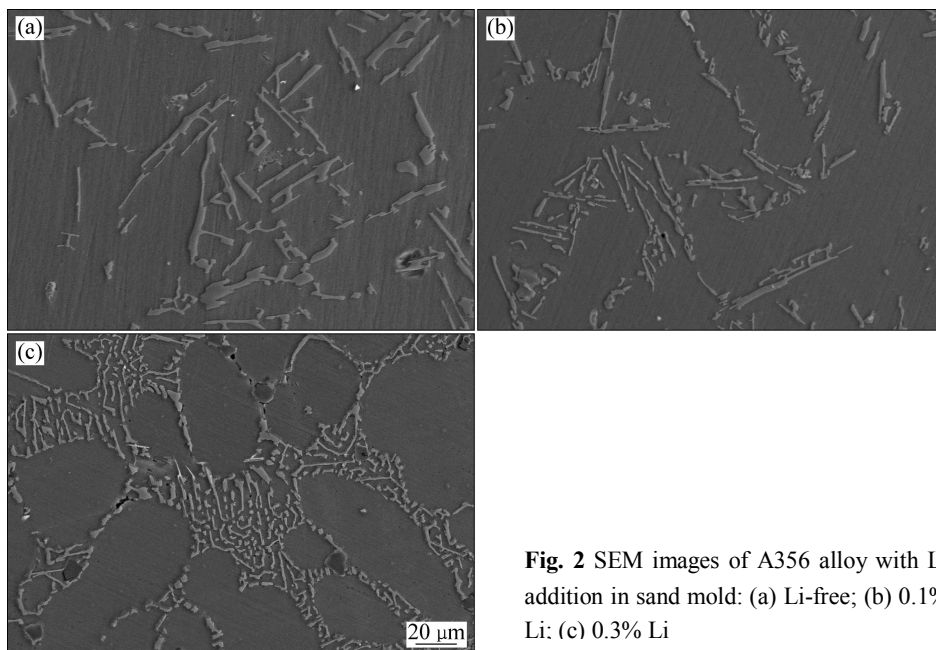


Fig. 2 SEM images of A356 alloy with Li addition in sand mold: (a) Li-free; (b) 0.1% Li; (c) 0.3% Li

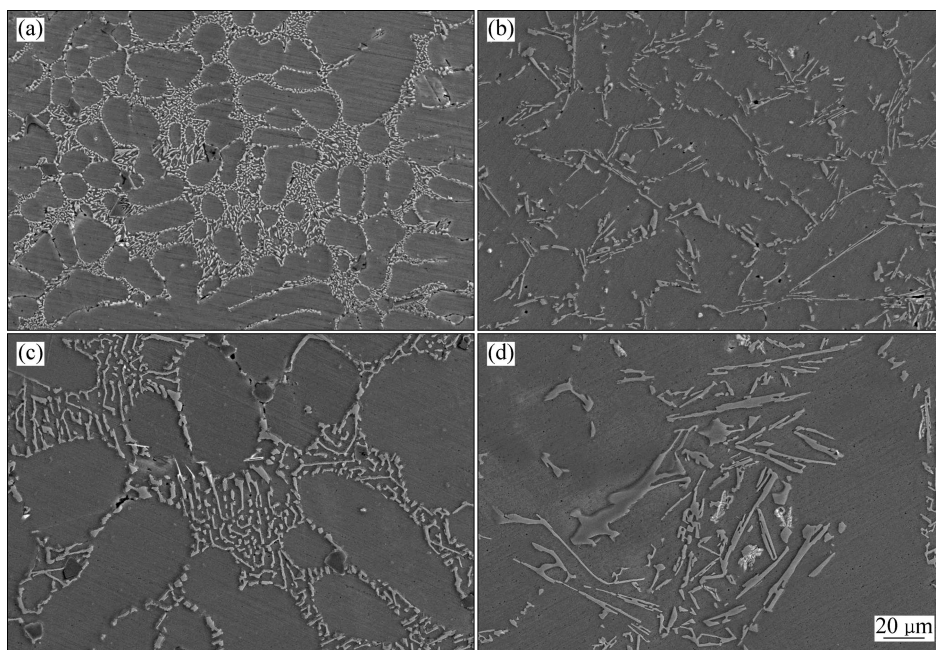


Fig. 3 Microstructures of alloys modified by 0.3% Li with different holding time of temperature: (a) In cast-iron mold without holding; (b) In cast-iron mold with holding time of 30 min; (c) In sand mold without holding; (d) In sand mold with holding time of 30 min

of the un-modification alloy, were observed in the microstructures of alloys with 0.3% Li addition with holding time of 30 min. In addition, there was less eutectic volume fraction in the microstructure of the alloy with holding time of 30 min (shown in Figs. 3(b) and 3(d)). The results indicate that the modification effect with Li addition is degraded with prolonging the holding time. It can be explained that the rejected Li has much more time to diffuse into the liquid and the effective Li is decreased with holding time of 30 min.

Despite the advantageous effect of Li addition on the modification of the eutectic silicon phase, the forming of Li-containing alloys is prone to casting defects such as porosity (see Fig. 1, Fig. 2 and Fig. 3). However, there is less porosity in the case of sand mold with holding time of 30 min (see Fig. 3(d)). Further study on this result was beyond the range of this paper.

3.2 Microhardness

Table 3 shows the Vickers microhardness of alloy

samples cast in cast-iron mold. The microhardness results indicate that the microhardness of A356 alloy with 0.3% Li addition is higher than that with 0.1% Li addition. This result is in accordance with the modification morphology of the eutectic phase for A356 alloy with 0.3% Li addition.

Table 3 Vickers microhardness of alloy samples cast in cast-iron mold

Alloy	Microhardness, HV
A356	85.0±3.2
A356–0.1%Li	97.5±4.5
A356–0.3%Li	106.2±6.3

3.3 Eutectic temperature depression

To investigate the reason of modification of the eutectic Si crystals with Li addition, the eutectic temperature depression of each modified alloy was measured. Eutectic temperature depression is general phenomenon for the modification of eutectic Si crystals [14, 15]. Figure 4 shows the DSC traces at cooling rate of 10 °C/min for A356 alloys with Li addition cast in cast-iron mold. It can be seen that DSC curve of alloy with Li addition shift left a little compared with that of Li-free alloy, namely, the eutectic temperature is decreased with Li addition. Table 4 shows the peak eutectic temperature depression of each modified alloy. The Li addition can lower the crystallization temperature of the eutectic reaction, and the peak eutectic temperature depression with 0.3%Li addition is higher than 2 °C in cast-iron mold. In other words, the eutectic-phase crystallization takes place under proper undercooling, and the increased undercooling is considered to be the result of modification. This is well consistent with the findings by NOGITA and DAHLE et al [10, 13]. They investigated the solidification mode of the eutectic phase in cast Al–7Si alloys by electron back-scattering diffraction and found that the eutectic

nucleation mode is strongly dependent on the additive elements. It is suggested that the eutectic Si phases are modified as a result of the activation of some other nucleation sites for the eutectic cells under a certain undercooling. So, the eutectic temperature depression for modified alloy is approximately the same as the undercooling levels.

Table 4 Peak eutectic temperature depression of A356 alloys with 0.3% Li addition in cast-iron mold

Alloy	Eutectic peak temperature/°C	Eutectic peak temperature depression/°C
A356	562.9	–
A356–0.1%Li	562.0	0.9
A356–0.3%Li	560.0	2.9

3.4 Thermodynamic analysis

DEROER et al [16] proposed that the Miedema model can be used to calculate the mixing enthalpy of Al–Si alloys. They considered that the boundary condition can cause alloying effect when it transforms from pure metals to alloys. There are two factors which affect the boundary condition: 1) ϕ^* , the parameter of chemical potential for the electronic charge; 2) N_{WS} , the electron density at the boundary of the Wigner–Seitz atomic cell, are different from two elements of alloyage. Considering above, they suggested that the mixing enthalpy $\Delta H_{A \text{ in } B(\text{interface})}$ when A element is dissolved by B element can be expressed as:

$$\Delta H_{A \text{ in } B(\text{interface})} = \frac{2V_A^{2/3}}{(N_{WS}^{-1/3})_{av}} \left[-P(\Delta\phi^*)^2 + Q(\Delta N_{WS}^{1/3})^2 \right] \quad (1)$$

where $\Delta H_{A \text{ in } B(\text{interface})}$ contains the key expression for the sign of the enthalpy of formation of binary alloys; $V_A^{2/3}$ is the molar surface area of element A; $(N_{WS}^{-1/3})_{av}$ is the average of $N_{WS}^{-1/3}$ about A and B; P and Q are the proportionality constants of model and $Q/P=9.4$. There are three situations of value P : when A and B are both transition elements, $P=14.1$; one is but another is not, $P=12.3$; both are not, $P=10.6$.

According to Eq. (1), the value of mixing enthalpy that Li is dissolved by Si is -61.1 kJ/mol, which is more negative than the mixing enthalpy of -35.2 kJ/mol when Li is dissolved by Al.

With regard to the mechanism of eutectic modification, LU and HELLAWEEL [17] proposed an impurity induced twinning theory. They considered that the modified silicon fibers contain more twins than the unmodified silicon. One theory for the effect is that atoms of the modifier are absorbed at the growth step of the silicon solid–liquid interface, which is supported by the observation that modifiers become concentrated in the silicon, not in the aluminum phase. In this work,

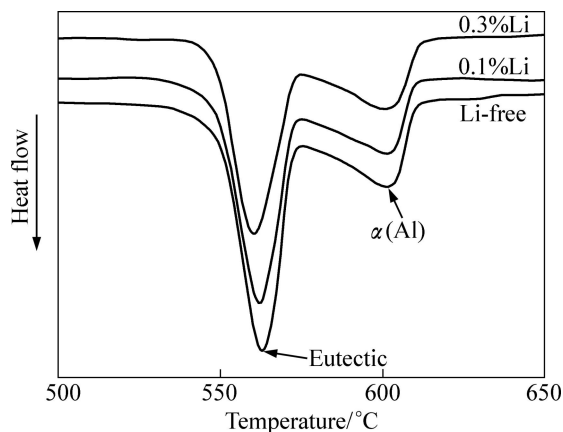


Fig. 4 DSC traces at cooling rate of 10 °C/min for A356 alloys with Li addition in cast-iron mold

thermodynamics was considered. In comparison of $\Delta H_{\text{Li in Al(interface)}}$ and $\Delta H_{\text{Li in Si(interface)}}$, the mixing enthalpy of the modifying agent Li with Si is more negative than that with Al. Therefore, the affinity of Li with Si is larger and Li is easier to coalesce with Si, which is the same as the result of LU and HELLAWELL [17]. Basically, there are two theories about the mechanism of modification, and they are restricted nucleation theory and restricted growth theory [1]. With the results of mixing enthalpy, Li has larger negative mixing enthalpy with Si, so it is easier to coalesce with Si in order to restrict the eutectic Si growing up. Therefore, with the results of DSC and mixing enthalpy, the modification mechanism of Al–7Si alloy with Li addition is based on the restricted growth theory.

4 Conclusions

1) Li is an effective element for modification of eutectic morphology in A356 alloy and the optimum addition is about 0.3%. Li is not the long-term effect modification agent.

2) DSC results show that the eutectic solidification temperature of A356 alloy with Li addition is decreased and the eutectic temperature depression with 0.3% Li addition is 2.9 °C in cast-iron mold.

3) With the results of DSC and mixing enthalpy, the modification mechanism of A356 alloy with Li addition is based on the restricted growth theory.

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利用 DSC 和 Miedema 模型研究锂变质处理 A356 合金的共晶变质

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摘 要: 通过 SEM 和 DSC 研究添加锂对 A356 合金的共晶变质效果的影响。SEM 显微组织观察表明: 当锂的添加量为 0.3%(质量分数)时, A356 合金的共晶组织形貌由条片状转变为纤维状的变质效果很明显, 与之对应的显微硬度也较高; 变质效果会随着冷却速率的加快而增强, 随着保温时间的延长而衰退。DSC 结果表明: 共晶凝固温度随着锂添加量的增加而降低, 并且在铸铁铸型中, 共晶温度降低了 2.9 °C。用 Miedema 模型计算 A356 合金中锂与硅及锂与铝的混合焓, 结果表明锂的变质机制为阻止晶粒长大的变质理论。

关键词: A356 合金; 共晶变质; 锂; DSC; 混合焓

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