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The usage of computer-aided cooling curve thermal analysis to optimise eutectic refiner and modifier in Al–Si alloys

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Abstract Bismuth, antimony and strontium concentrations were optimised to alter the eutectic Al–Si phase in a commercial Al–Si–Cu–Mg alloy by way of computer-aided cooling curve thermal analysis. The results show that the eutectic growth temperature shifted to lower temperatures for all three inoculants. However, addition of Sr resulted in more depression of growth temperature compared with Bi and Sb. No further significant changes were observed with increasing the concentrations to more than 1, 0.5 and 0.04 wt% of Bi, Sb and Sr, respectively. The recalescence of these concentrations, meanwhile, showed a significant increase of magnitude. A good correlation was found between the results of thermal and microstructural analysis. For Bi and Sb, the eutectic depression temperature can be used as an individual criterion to gauge optimal levels of content in the refinement of Si, whereas for Sr, both depression temperature and recalescence magnitude must be considered. Based on the observed depression in eutectic growth temperature and recalescence, it can be concluded that the optimal concentrations to refine the eutectic Al–Si phase with Bi and Sb and to modify it with Sr at the given solidification conditions were 1, 0.5 and 0.04 wt%, respectively.

Keywords Thermal analysis · Refiner · Modifier · Al–Si alloy · Solidification

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Introduction

Al–Si–Cu and Al–Si–Cu–Mg systems are commercially popular alloys that are used extensively in the automotive industry. These alloys have a broad range of applications that include critical automotive components, such as engine blocks and cylinder heads.

Chemical modification of Al–Si cast alloys, by way of adding Na and Sr, is a well-known melt treatment that alters its eutectic silicon morphology. In addition, Sb and Bi, which are in the same group in the periodic table, can refine its eutectic structure. This change in its silicon morphology enhances the mechanical properties of these Al–Si alloys, especially the ductility of casting parts.

It has been reported that the addition of modifier reagents over a certain amount to these Al–Si alloys has some drawbacks, such as increasing its porosity and hydrogen content [1], hot tearing and poor surface finish [2]. On the other hand, some researchers reported that the addition of modifying elements, such as greater than the optimal level of Na, causes over-modification and a detrimental effect on its properties [3–5]. Therefore, proper levels of refining and modifying agents are crucial in controlling the casting microstructure and obtaining the desired mechanical characteristics.

Metallographic techniques to control the quality of melt treatment and determine the optimal concentration of additional elements are time-consuming, and results are related to area sample selection and preparation conditions. Thus, a rapid monitoring technique could be developed to replace it as the primary control tool [6]. Spectro-chemical analysis is an alternative option, but it also requires specimen preparation, and is time-consuming as well. Thermal analysis has been gaining increasing acceptance in many aluminium foundries as a faster, online process control,

non-destructive and quantitative technique [7] that can be used before casting [8].

Computer-aided cooling curve analysis (CA-CCA) is the most popular thermal analysis technique because of its ease of use and low cost. Compared with other techniques, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermo-gravimetry analysis (TGA), CA-CCA is simple, inexpensive and most importantly, suitable for commercial applications [7]. Furthermore, the aforementioned methods often prove to be inadequate for investigating the non-equilibrium solidification of industrial alloys. However, industrial alloys behave far from ideality and equilibrium [9].

Generally, applications of CA-CCA include determining critical characteristic temperatures, forecasting the formation temperature of any phases, the level of grain refinement [10–12], the extent of modification [10–12], the level of impurity [13] and the interaction between grain refiner and modifier [14]. However, researchers are currently attempting to reveal additional abilities of this technique in aluminium foundries. The aim of this study is to optimise Bi, Sb and Sr content in Al–11%Si–Cu–Mg by using CA-CCA.

Experimental procedures

About 3 kg of a commercial Al–11%Si–Cu–Mg alloy was melted in a silicon carbide crucible using a resistance furnace, with a melt temperature of 750 ± 5 °C. Bi, Sb and Sr in the form of metallic shots, metallic granules and an Al-10Sr master alloy, respectively, were added by plunging the alloy wrapped in aluminium foil into the melt. The molten alloy was then poured at a temperature of 730 ± 5 °C into a preheated ceramic mould (Fig. 1) for thermal analysis. The mould can also be dipped into the melt rather than preheated separately. The procedure was run two times for the addition of different content levels of Bi, Sb and Sr. The nominal addition levels were between 0.1 and 2 wt% for Bi, 0.05 and 0.70 wt% for Sb and 0.02 and 0.14 wt% for Sr.

Thermal analysis was carried out by attaching a K-type thermocouple located in the middle of the preheated ceramic mould that solidified in slow conditions to detect characteristic temperatures during solidification. At least two thermal analysis runs were made to ensure the reproducibility of the results and the average data were reported. Before all temperature measurements, the thermocouples were calibrated to ensure accurate and precise reading and recording. The temperature–time data were obtained using the EPAD-TH8-K high-speed data acquisition system linked to a computer with DEWESoft 7 at a dynamic rate of 100 Hz/ch, as shown in Fig. 1.

FlexPro 8 data analysis software was used for smoothing the curves and plotting the cooling curve, as well as the first- and second-derivative curves for extracting characteristic temperatures. The typical cooling, first- and second-derivative curves of the base alloy according to thermal analysis are shown in Fig. 2a. The use of the first-derivative curve enhances the accuracy of determining the characteristic features of the base alloy that cannot be seen on the cooling curve, and the second-derivative curve was used to precisely indicate the nucleation temperature of transformation. The eutectic arrest area and the method to define the three main points of nucleation temperature (T_N), minimum temperature (T_{Min}) and growth temperature (T_G) are shown in Fig. 2b.

Samples for metallography were sectioned horizontally at the tip of the thermocouple, and were mounted and polished. The ground specimens were then subjected to a final polishing with colloidal silica suspension. An optical microscope (Olympus BX60F5) was used to analyse the microstructures. Moreover, chemical compositions of samples were tested by glow discharge spectrometer (GDS).

Results and discussion

Based on thermal analysis data, the cooling rate obtained from the curves, before the nucleation of the primary aluminium phase, was found to be 0.7 °C/s. In other words, the influence of cooling rate is identical in all samples. The

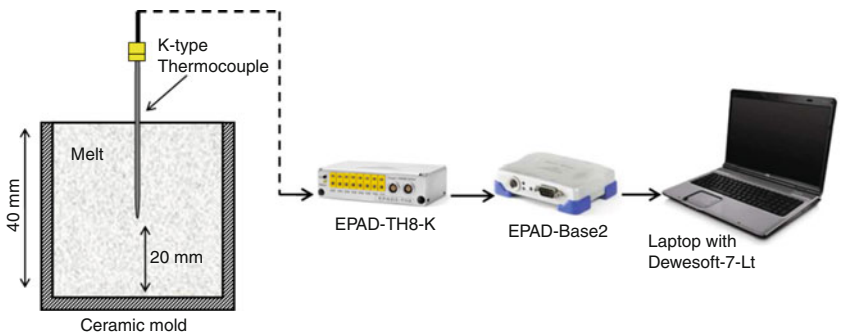

Fig. 1 Thermal analysis set up with ceramic mould and thermocouple

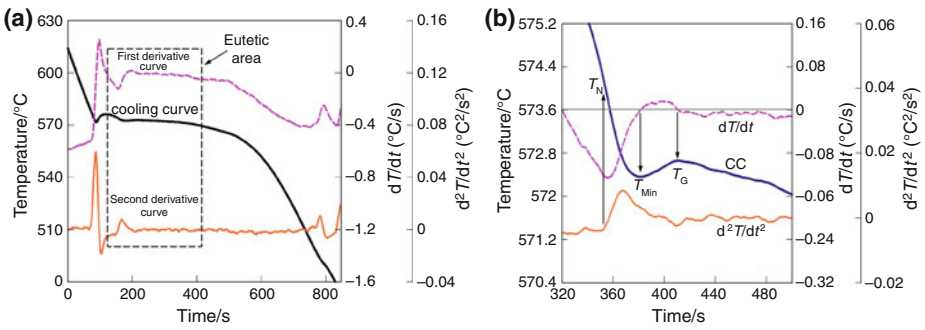

Fig. 2 **a** The cooling curve of the base alloy with its corresponding first- and second-derivative curves; **b** The magnified highlighting of the eutectic arrest area and the main extracted points (T_N, T_{Min} and T_G)

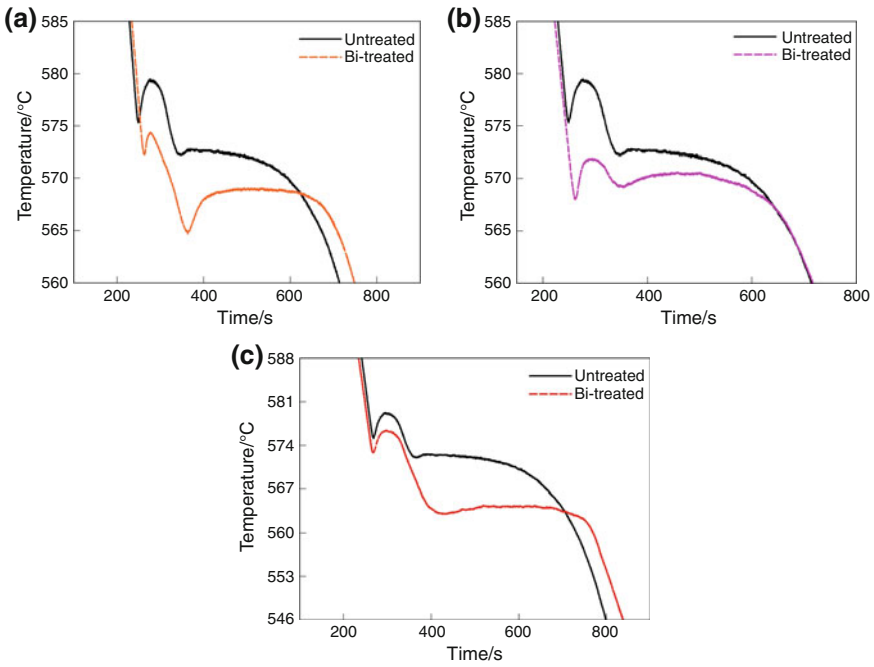

Fig. 3 Typical cooling curves of untreated and treated alloys with **a** 2 wt% Bi, **b** 0.4 wt% Sb and **c** 0.02 wt% Sr

cooling curves were plotted for each alloy condition. Figure 3 shows a comparison between the cooling curves of untreated alloys, Bi-, Sb- and Sr-treated alloys. It can be seen that addition of these elements affects the cooling curve especially in the eutectic region. Therefore, the changes of eutectic area temperature were determined for all samples, to investigate the characteristic temperatures of the alloys after the addition of Bi, Sb and Sr in different concentrations. It must be noted that when a larger number of data point is recorded, the first- and especially second-derivative curves become noisy. Therefore, moving average mode was used to smooth and reduce the noise in derivative curves. To characterise the eutectic region, minimum temperature (T_{Min}) and eutectic growth temperature (T_G) were measured from the cooling curve.

T_{Min} is defined as the minimum reaction temperature during eutectic transformation. Also, T_G is defined as a maximum temperature in the eutectic region, because of the release of latent heat in the eutectic phase formation. When the first-derivative curve (dT/dt) increases and intercepts the zero line, then decreases and then intercepts the zero line again, heat is released at T_{Min} and T_G, as shown in the two cross points on the respective cooling curves.

It can be seen from Fig. 3 that the addition of Bi, Sb and Sr decreases the eutectic growth temperature (T_G). When the Bi level was increased from 0 to 0.75 wt%, the T_G decreased from 572.7 to 571.2 °C, as shown in Fig. 4a. It then remains constant at 569 °C for higher than 1 wt% Bi. It can be seen in Fig. 4b that T_G decreased continuously by increasing Sb content. T_G reached 569.9 °C when the Sb level was increased to 0.5 wt% and remained constant for 0.6 and 0.7 wt% Sb. Figure 4c indicates that T_G decreased sharply to 565.3 °C when 0.02 wt% Sr was added to the base alloy. It must be noted, however, that T_G dropped to 563.9 °C for 0.04 wt% with further increases in concentration not affecting on the growth temperature. Dahle et al. [15] found that introducing barium, calcium and yttrium as well as ytterbium to the melt reduces T_G in A356.0 (Al–

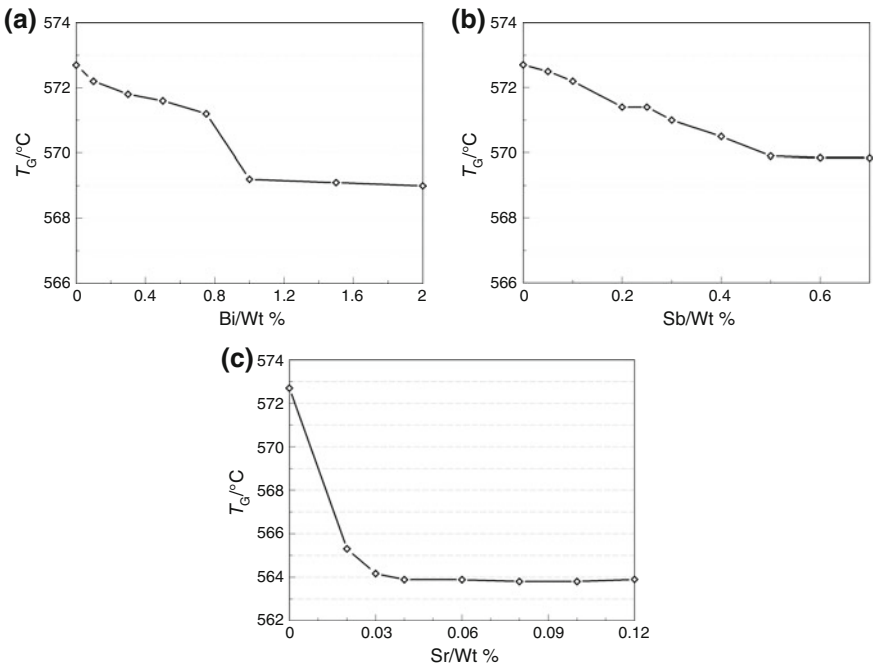

Fig. 4 Changes of eutectic growth temperature (T_G) versus **a** Bi, **b** Sb, and **c** Sr content

7%Si–Mg) alloy. The decrease of T_G was reported in 319 [16, 17] and Al-10%Si alloys [18] because of the addition of strontium to the melt. Moreover, a depression of the growth temperatures was observed with adding lanthanum [19] and scandium [20] in Al–Si–Mg alloy.

It is well-established that the modification of the Al–Si eutectic by Na and Sr is accompanied by a depression in the eutectic growth temperature (ΔT_G) [10, 21]. It has been suggested that this depression reveals the modification level automatically without microstructure analysis [15, 17]. The Al–Si eutectic depression temperature is defined as the difference between eutectic growth temperature of untreated and treated alloys based on the following equation:

$$\Delta T_G = T_{G(\text{untreated})} - T_{G(\text{treated})}, \quad (1)$$

where T_G (untreated) and T_G (treated) is the maximum temperature obtained during the recalescence of the melt, without and with addition of modifying/refining agents, respectively [17]. The changes of ΔT_G are plotted in Fig. 5 as a function of Bi, Sb and Sr content, where ΔT_G increased to 3.7 °C when Bi is increased to 1 wt%. In addition, a further increase in concentration only had a minor impact on the depression of eutectic growth temperature as shown in Fig. 5a. ΔT_G increased with Sb addition, reaching 2.8 °C for 0.5 wt% Sb, and then stabilised with further increases in Sb content, as illustrated in Fig. 5b. When Sr is increased to 0.02 wt%, ΔT_G increased remarkably to 7.4 °C and continued to increase to a maximum depression of 8.9 °C for 0.04 wt% Sr. After that point, ΔT_G did not change noticeably.

By using the depression of the Al–Si eutectic growth as a criterion of a proposed quantitative tool [17], the optimum content of Bi, Sb and Sr is 1, 0.5 and 0.04 wt%, respectively.

The effect of optimal content of Bi, Sb and Sr is illustrated in Fig. 6. A coarse plate-like Al–Si eutectic structure was observed in untreated alloy, as shown in Fig. 7a. Figure 6b and c shows that the Al–Si eutectic morphology changes from coarse plates to a lamellar morphology, with the introduction of 1 and 0.5 wt% Bi and Sb, respectively. In fact, the optimal concentration of both Bi and Sb (1 and 0.5 wt%) can refine the Al–Si eutectic structure. Furthermore, the addition of 0.04 wt% Sr (the optimal content) induced a plate-like to fibrous transition, as illustrated in Fig. 6d. This silicon morphology alteration increases the mechanical properties especially ductility and fatigue strength [22, 23].

However, it has been reported that the depression of eutectic growth temperature is accompanied by an increase in the magnitude of recalescence [3, 15]. Therefore, not only the changes in ΔT_G but also the changes of recalescence were considered for all samples. Recalescence temperature is defined as the difference between eutectic growth temperature and minimum temperature based on the following equation:

$$\text{Recalescence} = T_G - T_{\text{Min}}. \quad (2)$$

Nucleation and growth are two important mechanisms for phase formation during solidification. Reduced growth temperature is an indication of growth effects, whereas

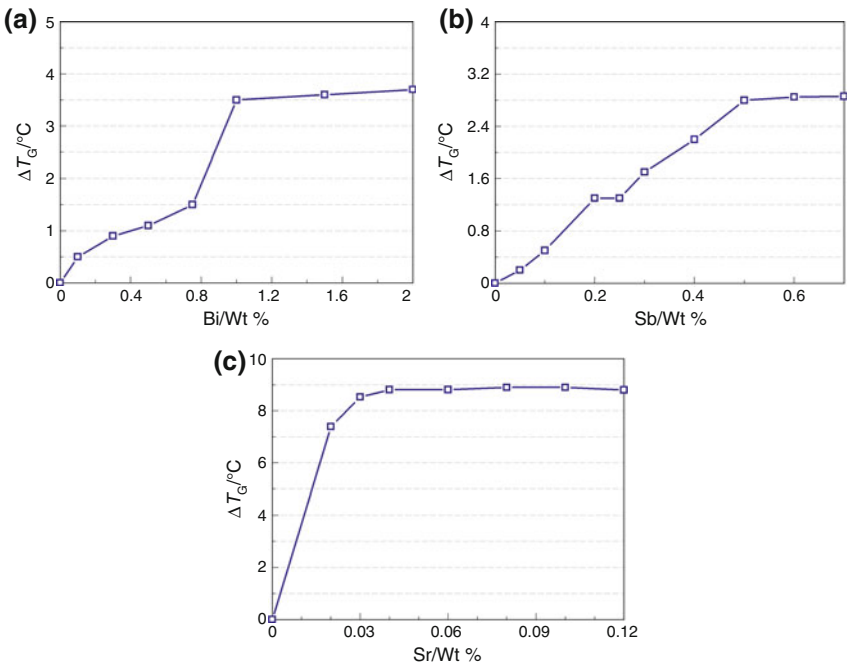

Fig. 5 Changes of ΔT_G as a function of **a** Bi, **b** Sb and **c** Sr content

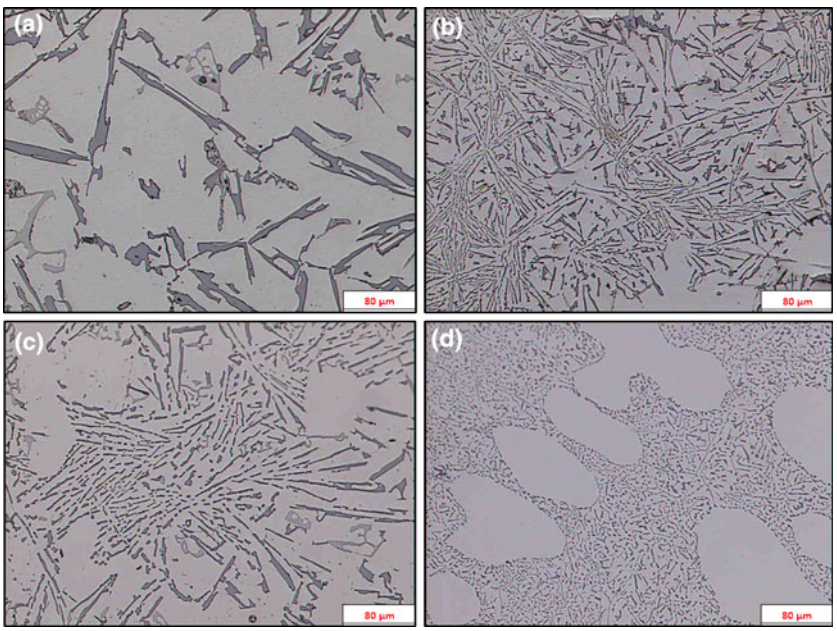

Fig. 6 Optical microstructures of **a** untreated and treated with **b** 1 wt% Bi, **c** 0.5 wt% Sb and **d** 0.06 wt% Sr

recalescence indicates the effect of additional elements on the nucleation of the eutectic Al–Si phase [15].

The changes of recalescence as a function of Bi, Sb and Sr content are plotted in Fig. 7. It must be noted that the untreated alloy shows negligible recalescence around 0.5 °C before eutectic growth. It can also be seen that these additions of elements affect recalescence.

Figure 7a indicates that the addition of Bi between 0 and 0.75 wt% does not significantly affect recalescence, with the alloy still appears as in the untreated condition. Its magnitude, however, increases significantly to 3.7 °C with the increase of Bi content to more than 0.75 wt%. In addition, recalescence does not change remarkably when the content of Bi exceeds 1 wt%. It has been reported that recalescence increased to 3 °C for 0.0036 wt% Ca and became constant for more addition in A356.0 alloy [15]. It is evident from Fig. 7b that Sb has the same effect on undercooling change. In fact, undercooling magnitude increased continuously with an increase in Sb content, and becomes practically constant after an addition of 0.5 wt%. Furthermore, the addition of Sr initially expanded the magnitude of undercooling, but a further increase of Sr

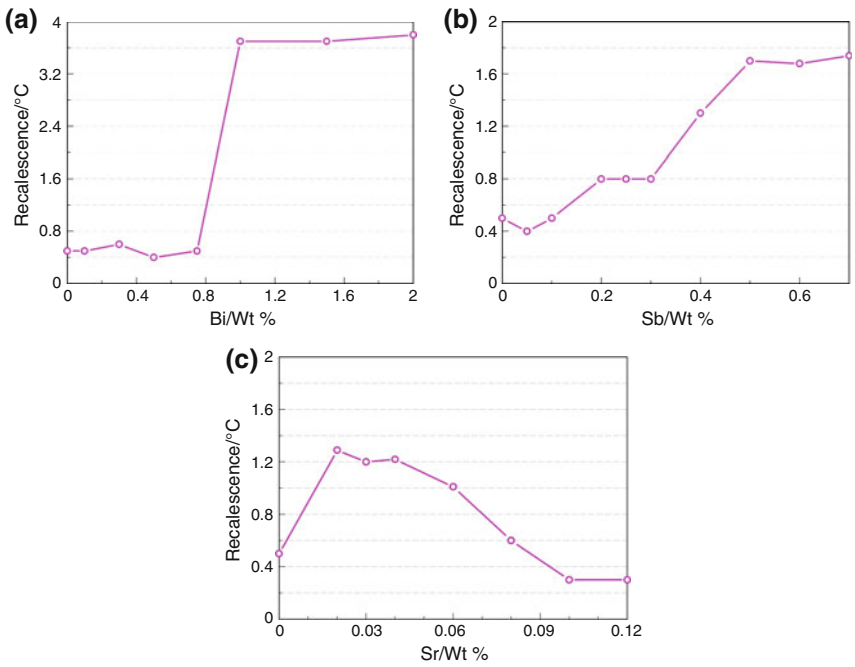

Fig. 7 Changes of recalescence as a function of **a** Bi, **b** Sb and **c** Sr content

caused a fall off in the undercooling to 0.3 °C as shown in Fig. 7c. It has been reported that recalescence increased to 1.9 °C with addition of 0.012 wt% strontium and decreased gradually to 1.2 °C for 0.04 wt% Sr because of the impingement and coalescence of Sr particles [16].

With the addition of a Sr modifier, the eutectic growth depression (ΔT_G) changes more than when Bi and Sb silicon refiners are added. The same results have been reported where antimony additions resulted in a depression of the growth temperatures and an increase in the amount of recalescence before growth, whereas larger effects were observed with strontium additions in Al-10%Si alloy [9].

On the other hand, with regard to Fig. 6 for Bi and Sb, the eutectic depression temperature in the production of a lamellar structure can be used as an individual criterion to gauge optimal levels of content in the refinement of Si, whereas for Sr, in the introduction of fibrous morphology, both depression temperature and recalescence magnitudes must be considered.

With regard to the increase of eutectic depression temperature to a higher magnitude and the requisite recalescence, the optimal content of Bi and Sb to refine the eutectic Al–Si is 1 and 0.5 wt%, respectively, whereas the optimal concentration of Sr to modify the eutectic phase is 0.04 wt% for Al–11%Si–Cu–Mg at the given solidification conditions.

The optimal level of additional elements, which was determined by thermal analysis, was reinforced by microstructural observations. These observations show good correlation between thermal analysis parameters and changes in the eutectic structure. These results clearly indicate the ability of CA-CCA to optimise the addition of elements in aluminium foundries.

Conclusions

In this study, CA-CCA was used to optimise the content of Bi, Sb and Sr to alter the eutectic Al–Si phase in a commercial Al–Si–Cu–Mg alloy. The addition of all three elements caused an increase of Al–Si eutectic depression temperature to a higher magnitude, which eventually stabilised when the respective content levels were increased.

With the addition of a Sr modifier, the eutectic growth depression (ΔT_G) changes more than Bi and Sb (refiners). On the other hand, for Bi and Sb, the eutectic depression temperature in the production of a lamellar structure can be used as an individual criterion to gauge optimal levels of content in the refinement of Si, whereas for Sr, in the introduction of fibrous morphology, both depression temperature and recalescence magnitude must be considered. The optimal content for Bi and Sb to refine the eutectic Al–Si is 1 and 0.5 wt%, respectively, whereas the optimal concentration for Sr to modify the eutectic phase is 0.04 wt%.

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