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Quantification of the SiC_p content in molten Al–Si/SiC_p composites by computer aided thermal analysis

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Abstract

The aim of this work is to explore the feasibility of the computer aided thermal analysis as a tool for SiC_p content quantification in molten Al–Si/SiC_p composites. This technique was applied to three cases of interest: (1) the metal matrix alloy A356, without SiC_p particle reinforcement, (2) A356/8% SiC_p MMC and (3) A356/18% SiC_p MMC. Tests were performed in order to identify, within the commonly used thermal analysis parameters, the parameters that could be used for SiC_p content quantification. In this regard, the parameters: eutectic temperature, T_{EG}, and local solidification time, t_S, show clear trends and low dispersion in their changes as functions of SiC_p content. It is found that an increase in SiC_p content produces a statistically significant increase of T_{EG} and a decrease of t_S. The behavior of t_S may be explained as a result of the decrease of the latent heat released during solidification as the SiC_p content is increased, such as was indicated by the latent heat data obtained from Newton thermal analysis (NTA) applied to the experimental cooling curves. A simplified analysis of the experimental results indicates that, for the experimental conditions used in this work, the best resolution that could be expected from this method is ±1.3 vol.% of SiC_p content, if the local solidification time is the parameter used to quantify the particle content.

Keywords: Composites; Characterization; Solidification; Cooling curve analysis

1. Introduction

One of the more critical aspects that must be controlled during cast composite production is the volume fraction of SiC_p present in the composite melt prior to pouring. Foundries, which are casting SiC_p-reinforced aluminum composites, must be able to quickly check the volume fraction of SiC_p suspended in the melt before pouring, in order to verify that settling of the SiC_p has not been taken place.

The principal methods for the determination of ceramic particle content in metal matrix composites are gravimetry, metallographic image analysis and direct optical emission spectroscopy (OES). For research purposes, others methods have been developed such as the electrical resistance probe technique [1], which has been used to measure the in situ volume fraction of ceramic particles in molten metals.

Due to its accuracy and precision [2], gravimetry is the reference method for ceramic particle content determination; nevertheless, because it is necessary to digest the sample, gravimetric analysis requires usually several hours. Metallographic image analysis also shows the disadvantage of the time requirement, because of the sample preparation and the number of fields that need to be examined to get a reliable measurement.

Today the only "on line" tool in foundries for the SiC_p content quantification in base aluminum metal matrix composites is the determination of carbon content, principally achieved by direct OES analysis, where the amount of SiC_p is determined by monitoring the carbon signal from the spectrometer output. The contribution of silicon from SiC_p is then subtracted from the total silicon reading to obtain the matrix silicon content. Employing this technique, the amount of SiC_p can be readily determined in few minutes. Obviously, this technique can be applied only in foundries where there is a calibrated spectrometer with a vacuum optical chamber to address the carbon determination.

From this, it is interesting to explore new ways to determine SiC_p content, which could be implemented in the foundry floor by using the existing facilities. In this regard, the thermal analysis technique has become a common tool [3] to control the grain size and the eutectic modifications during processing of the conventional Al–Si-based cast alloys. The technique involves the monitoring of the temperature changes in a sample as it cools through phase transformation intervals, being usually represented by a temperature–time cooling curve and its derivative. During

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solidification, the latent heat released causes changes in the cooling curve, including thermal arrest points, which are characteristic of transformations and reactions occurring during solidification [4].

The correlation among these cooling curve characteristics and arrest points, considered as thermal analysis parameters, and the observed microstructure by statistically based models [5], has allowed the foundryman to monitor the melt quality before pouring.

It has been found [6], that the presence of SiC_p reinforcement in Al–Si-based alloys produces a marked difference in the observed thermal analysis parameters between the reinforced and the unreinforced materials. However, the analysis of the reported trends shown by these parameters as a function of SiC_p content indicates that these changes cannot be taken as a reference for SiC_p content determination. Further analysis of these results has shown [7] that the solidification time decreases as the particle volume fraction increases. It has been suggested that the observed changes in the cooling curve characteristics are the result of the decrease of the amount of heat liberated during solidification, associated to the reduction in liquid alloy volume due to the presence of particles. This aspect has not been supported by experimental determination of latent heat as a function of SiC_p in A356/SiC_p composites.

Recently, it has been shown that the numerical processing of cooling curves through the so called computer aided cooling curve analysis (CACCA) [8], can be used to generate information on the latent heat released during solidification. The main features, including the implementation and the limitations of this method, have been discussed elsewhere [3,9].

The purpose of this work is to: (i) identify the cooling curve parameters that may be used for SiC_p content quantification and (ii) analyze the obtained results in order to explore the feasibility of the CACCA as a tool for SiC_p content quantification of Al–Si/SiC_p composites.

2. Experimental

The silicon carbide particle reinforced aluminum alloys were prepared by the melt stirring technique in a clay silicon carbide crucible with an inner diameter of 0.125 m placed inside a resistance furnace. The SiC_p were mixed into the melt using a pitched-blade turbine impeller driven by a variable speed engine. The metal matrix used in this study was a commercial foundry alloy A356 with the chemical composition shown in Table 1. A Sr master alloy was added in order to achieve a Sr content of 0.015 wt.% in the modified A356 metallic matrix alloy.

Three cases of interest were studied in this work: (1) metal matrix alloy A356, without SiC_p particle reinforcement, (2) A356/8% SiC_p MMC, and (3) A356/18% SiCp MMC. Approximately, 2 kg of the matrix alloy was heated to 760 °C in a silicon carbide crucible located inside an electric furnace under an argon atmosphere. Then the desired amount of SiC_p, preheated to 300 °C, was added to the Sr-modified A356 melt and mixed at 1000 rpm for up to 25 min. The silicon carbide particles used in the experiments had a mean size of 15 μm.

Table 1
Chemical composition of the A356 alloy (wt.%)

Si	6.56
Fe	0.51
Cu	0.12
Mn	0.23
Mg	0.10
Zn	0.06
Al	Balance

The pouring temperature was maintained during the study at 720 ± 10 °C. Predetermined quantities of molten composite were poured directly into a cylindrical sand mold with minimum turbulence. A silicate/CO_2 bonded sand mold, with a 3 cm inner diameter, 10 cm in height and 0.75 cm wall thickness was used in all the cases. A type K thermocouple was always positioned at the same distance of 30 mm from the bottom of the mold center, to ensure reproducibility of the analysis. The thermocouple tip was in direct contact with the melts under study.

The cooling curves were obtained by recording the temperature variation as a function of time by using a data acquisition system. All the cooling curves were obtained under the same experimental conditions. A calibration procedure [10] was performed with 99.9% aluminum after each experiment.

The solidified rods were cut into halves, the surfaces were metallographically prepared and the experimental SiC_p content was measured using image analysis. At least 30 fields were analyzed to establish the particle content of each composite probe.

The experimental design has included nine elemental experiments, randomly performed, which includes three replicas for each SiC_p content under study. In these experiments, the independent variable was the SiC_p content, and was analyzed the effect of the change in SiC_p content on the characteristic cooling curve parameter. The replicated results were used to establish a first approximation for the confidence intervals of the observed changes on the cooling curves under the experimental conditions used in this work.

The cooling curve parameters considered in this work, depicted schematically in Fig. 1 were the liquidus parameters T_L, ΔT_L and t_L (the liquidus temperature, the liquidus undercooling and the liquidus undercooling time, respectively); the eutectic parameters T_{EG}, ΔT_E and t_E (the temperature of eutectic growth, the eutectic undercooling and the eutectic undercooling time).

These parameters were determined from direct readings on the experimental cooling curves, as described in the insets included in Fig. 1. Additionally, the cooling rate (dT/dt) and

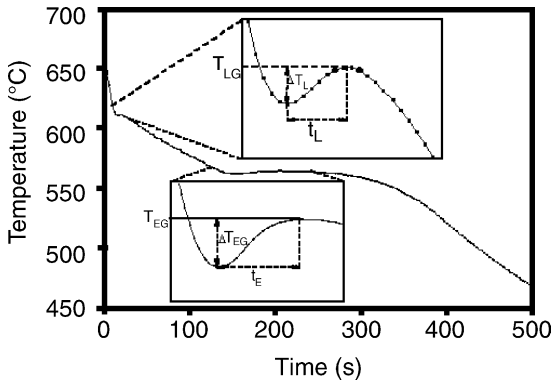


Fig. 1. Representation of the liquidus and eutectic cooling curve parameters analyzed in this study.

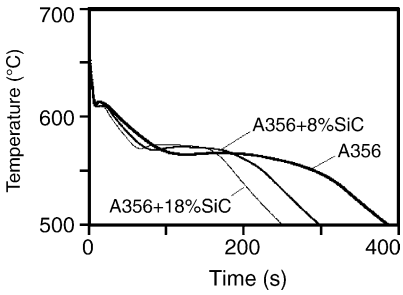


Fig. 3. Typical changes observed in the cooling curves as a result of increasing SiC_p content.

the local solidification time (t_S) were determined using the procedures outlined in Refs. [6,8].

The NTA method [8] was applied to the cooling curves associated to each SiC_p content in order to obtain a quantitative estimation of the effect of particle content on the latent heat released during solidification. It must be mentioned that to take into account the presence of the reinforcement particles on the numerical processing of the cooling curves associated to the experimental composites, the volumetric heat capacity shown in eq. (3) of Ref. [9] was replaced with the effective volumetric heat capacity. This was achieved by using the effective density and heat capacity as described in Ref. [7]. The thermophysical properties used during calculations are shown in Appendix A.

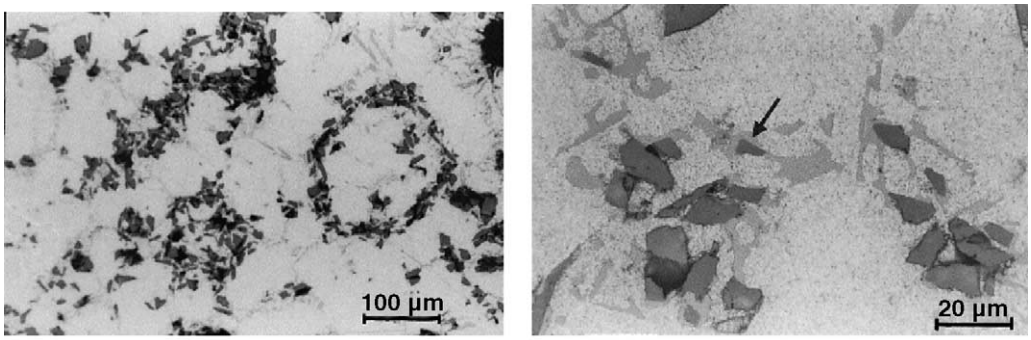
3. Results and discussion

Fig. 2(a) shows a typical microstructure associated to the A356/18% SiC_p composite. It can be observed that the particles were pushed to the interdendritic and intergranular regions. This behavior was observed in all the experimental probes containing SiC_p. There are two main reasons that have been proposed [11] to explain the segregation of reinforcements in the last-freezing zone: (i) the absence of nucleation of the primary phase on the particles and (ii) the rejection of the particles by the solidifying interfaces (particle pushing phenomena).

Fig. 2(b) shows another feature commonly observed on the experimental composites studied in this work, the nucleation of eutectic silicon on the SiC particles. The image analysis of the experimental probes containing particles indicated SiC_p contents of 7.8 ± 1.2 and 18.3 ± 1.4 vol.% for the two levels of particle content in the composites included in this work.

Fig. 3 shows the typical cooling curves associated to the three cases of interest. Here, it can be seen that, as a result of the presence of the SiC_p in the metal matrix A356 alloy, there is a shortening of the cooling curves, as can be noted from the shorter time required to achieve the end of the eutectic plateau. Another feature that can be readily seen in this figure is the increase of the eutectic growth temperature as a result of the increase in SiC_p content. The determination of the thermal analysis parameters considered in this study was carried out in order to know with more detail the effect of increasing SiC_p contents on the characteristics of the cooling curves.

The summary of the average values associated to these characteristic parameters as a function of particle content is shown in Table 2. Also the related dispersions in terms of the standard deviations at 95% confidence intervals, are shown. The feasibility of application of cooling curve analysis to the quantification of SiC_p content depends on the existence of one of more cooling curve parameters that changes, showing



(a) (b)

Fig. 2. Microstructural features commonly observed in the experimental composites.

Table 2
Experimental average values and dispersions of the parameters associated to the cases of interest

	SiC_p (vol.%)		
	0	8	18
T_L (°C)	613.4 ± 0.1	609.3 ± 0.2	609.5 ± 0.1
ΔT_L (°C)	1.9 ± 0.1	1 ± 0.3	1.1 ± 0.1
t_L (s)	5.3 ± 0.1	4.8 ± 0.3	4.5 ± 0.7
T_{EG} (°C)	566.4 ± 0.4	570.9 ± 0.1	573.7 ± 0.3
ΔT_E (°C)	1.7 ± 0.2	3.1 ± 0.3	4 ± 0.6
t_E (s)	45.7 ± 5	34.4 ± 0.3	28.9 ± 0.3
dT/dt (°C/s)	−0.57±0.04	−0.79 ± 0.04	−0.9 ± 0.05
t_S (s)	334 ± 2.5	233 ± 6	178 ± 3

clear trends and low confidence intervals, as a function of particle content.

Figs. 4–6 shows the average values of the cooling curve parameters under study plotted for the three SiC_p levels of interest. The observed dispersions are also plotted. Fig. 4 shows that the liquidus parameters do not fulfill the requirements needed to be considered as particle content indicators, at least for the experimental conditions present in this work. Fig. 4(a) and (b) shows that the SiC_p presence produces a decrease of the liquidus temperature and of the liquidus undercooling, but there is not a trend that correlates the change of these parameters as a function of particle content. Fig. 4(c) shows that the observed changes of the liquidus undercooling time as a function of particle content are not significant from the statistical point of view.

On the other hand, Fig. 5(a)–(c) shows clears trends in the eutectic parameters T_{EG}, ΔT_E and t_E changes as a function of particle content, which means that these parameters could be considered as indicators of SiC_p content. However, in the case of ΔT_E, the related confidence intervals shows a limitation for its potential use as a reference in particle content quantification.

With regard to the changes of the cooling rate, dT/dt and local solidification time, t_S, as a function of particle content,

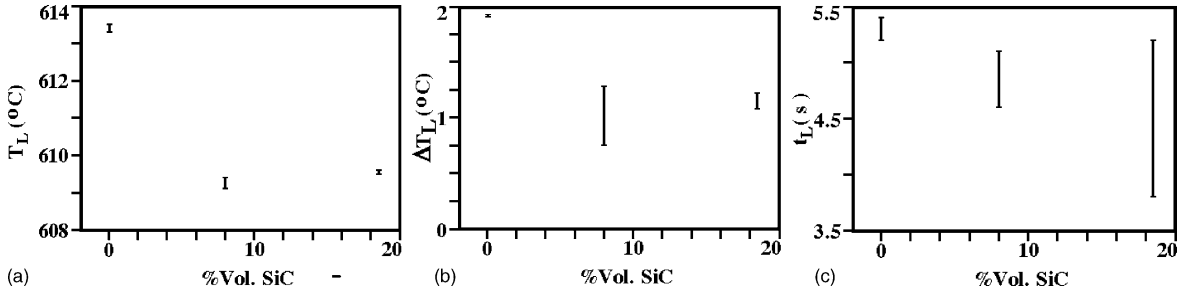


Fig. 4. Contrasting dispersion plots of liquidus parameters as a function of SiC_p content: (a) T_L (°C), (b) ΔT_L (°C) and (c) t_L (s).

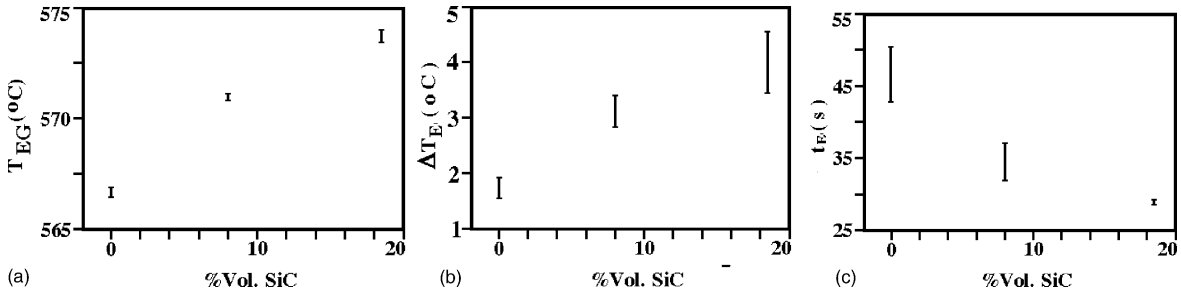


Fig. 5. Contrasting dispersion plots of eutectic parameters as a function of SiC_p content: (a) T_{EG} (°C), (b) ΔT_E (°C) and (c) t_E (s).

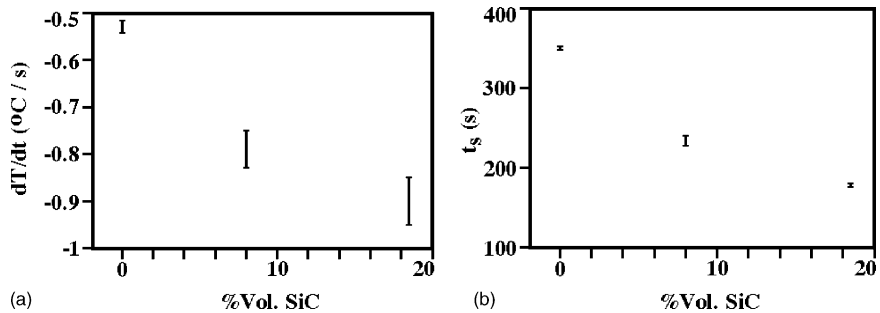


Fig. 6. Contrasting dispersion plots of: (a) dT/dt (°C/s) and (b) t_S (s) as a function of SiC_p content.

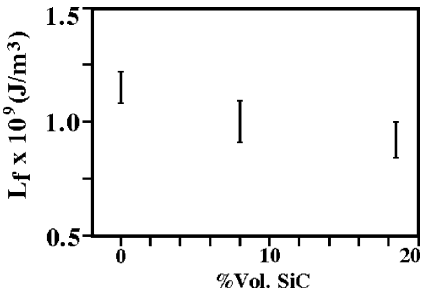


Fig. 7. Contrasting dispersion plot of the latent heat released during solidification as a function of SiC_p content obtained from NTA processing of the experimental cooling curves.

Fig. 6(a) and (b) show that an increase in particle content produces a cooling under more severe conditions and a decrease in t_S. It can be seen in these figures that both parameter changes with clear trends and relatively low confidence intervals as a function of particle content. This result indicates that these parameters could be included in the set of thermal parameters that may be used for SiC_p quantification. In order to generate quantitative data on the latent heat released during solidification of the experimental probes, the NTA method [8] was applied to the experimental cooling curves.

Fig. 7 shows the latent heat released during solidification by unit volume of the cast as a function of SiC_p content, as revealed by NTA analysis. Here it can be observed that one of the main effects of the presence of reinforcement particles in metal matrix composites is the decrease of the latent heat released during solidification. This effect in turn enhances the cooling of the cast under more severe conditions, see Fig. 6(a), promotes the decrease of the time dependent cooling curve parameters t_S, t_L and t_E, and hence the shortening of the cooling curves, see Fig. 3.

However, when the particle content is increased, the associated reduction in latent heat cannot explain the increase in the eutectic growth temperature. This effect may be associated to the changes in solidification kinetics caused by the interaction between the particles and the melt during eutectic solidification, as suggested by the nucleation of eutectic silicon on SiC_p, see Fig. 2(b). Further work on metal matrix solidification kinetics is needed to understand this behavior.

In order to have an estimation of the resolution of the method, without further experimental information on the behavior of the parameters T_{EG}, t_E, dT/dt and t_S as a function of SiC_p content, it is interesting to make a rough analysis, based on the available experimental results. This can be achieved by applying a linear regression to the average and dispersion values associated to each parameter as a function of SiC_p content in order to obtain the related slope m_i and the fitting standard error (FSE_i). The relation (FSE_i/m_i) can be taken as a rough estimation of the best resolution that could be expected from the parameters used as SiC_p content indicators. Table 3 shows the linear equations, the FSE and the expected resolutions associated to each parameter.

Table 3
Linear equations, FSEs and expected resolution associated to the use of selected thermal analysis for SiC_p content quantification

Equation	FSE	Resolution (SiC_p, vol.%)
$T_{EG} = 567.1 + 0.4\%\ SiC_p$	0.7	±0.9
$t_E = 47.8–1.1\%\ SiC_p$	4.3	±2
$dT/dt = -0.57–0.02\%\ SiC_p$	0.06	±1.5
$t_S = 333–9\%\ SiC_p$	22.7	±1.3

The results indicated in Table 3 show that the cooling curve parameters best suited for SiC_p quantification are the eutectic growth temperature and the local solidification time. However, regarding the sensibility of T_{EG} measurement to calibration errors, it is thought that the more promising results can be obtained if the local solidification time is selected to quantify the SiC_p content from cooling curve analysis. When this parameter is used for SiC_p quantification, the best resolution that can be expected under the experimental conditions present in this work is approximately ±1.3 vol.% SiC_p.

4. Conclusions

The best suited cooling curve parameters for SiC_p quantification are the eutectic growth temperature, T_{EG} and the local solidification time, t_S. These parameters show clear trends and low dispersion in their changes as a function of SiC_p content. It was found that an increase in SiC_p content produces a statistically significant increase of T_{EG} and a decrease of t_S values. The behavior of t_S may be explained as a result of the decrease of the latent heat released during solidification as the SiC_p content is increased, as was indicated by the latent heat data obtained from NTA applied to the experimental cooling curves. The changes of T_{EG} as a function of particle content could be related to the nucleation of eutectic silicon on SiC_p.

A simplified analysis of the experimental results indicates that, under the experimental conditions presented in this work, the best resolution that could be expected for this method is approximately ±1.3 vol.% of SiC_p content, when the local solidification time is chosen to quantify the particle content of Al–Si/SiC_p composites.

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Appendix A

Thermophysical properties used for NTA calculations

Property	A356 (liquid)	A356 (solid)	SiC_p
Density (kg/m^3)	2430	2430	3200
Heat capacity (J/kg °C)	998	907	840

References

[1] G.S. Hanumanth, G.A. Irons, S. Lafreniere, Met. Trans. B 23 (1992) 753.
[2] T.F. Klimowicz, G. Kepner, in: K.G. Upadhya (Ed.), in: Proceedings of the Conference on Processing, Fabrication and Application of Advanced Composites, USA, 1993.
[3] J.Q. Barlow, D.M. Stefanescu, AFS Trans. 105 (1997) 349.
[4] M. Mahfoud, F. Micciardi, J.E. Gruzleski, AFS Trans. 105 (1997) 473.
[5] O.M. Suárez, C.R. Loper Jr., AFS Trans. 105 (1997) 929.
[6] S. Gowri, F.H. Samuel, Metall. Trans. A 23 (1992) 3369.
[7] L. Kurian, R. Sasikumar, Mater. Sci. Technol. 12 (1996) 1053.
[8] K.G. Upadhya, D.M. Stefanescu, K. Lieu, D.P. Yeager, AFS Trans. 97 (1989) 61.
[9] E. Fras, W. Kapturkiewicz, A. Burbielko, H.F. López, AFS Trans. 101 (1993) 505.
[10] D. Sparkman, A. Kearney, AFS Trans. 102 (1994) 455.
[11] J.K. Kim, P.K. Roahtgi, Metall. Mater. Trans. A 31 (2000) 1295.