Journal of Alloys and Compounds 486 (2009) 173–177

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Solid fraction analysis with DSC in semi-solid metal processing

Yucel Birol*

Materials Institute, Marmara Research Center, TUBITAK, Gebze, 41470 Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 26 June 2009
Accepted 27 June 2009
Available online 4 July 2009

Keywords:
Semi-solid processing
Aluminium alloys
Differential scanning calorimetry

ABSTRACT

Solid fraction at the forming temperature is a key parameter in semi-solid processing as it affects the slurry viscosity and the subsequent mould filling at the forming stage. The type as well as the rate of scanning in the DSC experiment impacts the solid fraction analysis. Hence, the DSC experiment for solid fraction analysis must be designed carefully to avoid over- or underestimation of the forming temperatures. Thixoforming involves heating into the semi-solid temperature range followed invariably by an isothermal step and uses a melting scan while the rheo route employs controlled cooling from the liquid state and must rely on a solidification scan. Isothermal as well as conventional scanning DSC experiments were performed in order to better approximate the heating and cooling routines employed in industrial scale semi-solid forming operations. Heating below 2.5 K min^{-1} and cooling at 0.5 K min^{-1} produced melting and solidification curves which are in reasonable agreement with the isothermal DSC experiments.

1. Introduction

Semi-solid forming has been established as a high-volume, near-net shape manufacturing process for automotive components [1–3]. Reduced solidification shrinkage, shorter solidification time and laminar die filling offered in semi-solid metal casting, thanks to an already partially solid feedstock, give high integrity, heat treatable castings at die casting cycle times [4,5]. Semi-solid processing is performed in two major routes: thixoforming and rheoforming. Thixoforming involves reheating of non-dendritic slugs to semi-solid temperature range where they are formed into parts. This process suffers from high cost of special non-dendritic feedstock and the inability to recycle its scrap and has thus been applied to niche applications where quality comes before cost. Molten alloy is transformed into a slurry directly before casting in the rheoforming route [6], which thus tackles the cost issue and has become the choice of aluminium foundries who rely on semi-solid forming for high integrity structural parts [7,8].

Whether via the thixo or the rheo route, a key parameter in semi-solid processing is the fraction of solid at the forming temperature. A high solid fraction means higher viscosities while a low solid fraction increases the risk of turbulent die filling [9,10]. Solid fraction analysis may involve direct as well as indirect methods [11]. The former include metallography, thermal analysis, and thermodynamic models [11–22] while indirect methods rely on measuring a property of the alloy such as density [23], electrical resistivity [24] and response to a magnetic field [25] which is then correlated to the solid fraction. The DSC method was employed in the present work to obtain solidification and melting curves of a popular semi-solid alloy, 357. The effect of the type and the rate of DSC scans (heating vs. cooling) on the evolution of solid fraction with temperature, as they relate to thixo and rheoforming practices, were identified.

2. Experimental

The alloy used in this study was a commercial 357 alloy (Table 1). The as-received ingot was homogenized at 500 °C for 8 h and was checked for chemical homogeneity with an optical emission spectrometer. The DSC experiments were performed with 4 mm discs weighting approximately 50 mg, and with an empty reference pan, both as heating (melting) and cooling (solidification) scans in a dynamic argon atmosphere (1 l h^{-1}). The cell was heated to 450 °C at 10 K min^{-1} and then equilibrated at 450 °C for 10 min before the final heating ramp until 700 °C at several rates between 0.5 and 40 K min^{-1}. The solidification scans involved heating the cell to 700 °C at 10 K min^{-1} and then temperature equilibration at 700 °C for 10 min before cooling the cell to 450 °C at 0.5–40 K min^{-1}.

A separate set of DSC experiments was performed to better represent the heating and cooling cycles employed in thixo and rheoforming processes, respectively. The former almost always uses an isothermal holding step in the semi-solid temperature range to improve the globularization of the solid fraction while the latter uses a controlled cooling step across the liquidus line for the same reason [26,27]. Hence, 4 mm disc samples were heated at the maximum rate available with the DSC unit and then held isothermally at various temperatures in the semi-solid temperature range for the thixo route. The samples were heated until after melting and were cooled at 40 K min^{-1} to various temperatures in the semi-solid range where they were held isothermally for the estimation of solid fraction in the rheo practice. These routines were repeated with high purity aluminium samples of equal mass. The heat flow vs. temperature curves obtained in the latter were subtracted from the DSC runs of the 357 samples to isolate the heat exchange linked with the solidification and melting reaction.

One would have to run hundreds of isothermal DSC experiments to produce solid fraction vs. temperature plots from isothermal test data in a manner similar to the continuous DSC scans. This is certainly not practical. Hence, only those temperatures which are relevant for reheating in commercial practice are employed in

* Tel.: +90 262 6773084; fax: +90 262 6412309.
E-mail address: yucel.birol@mam.gov.tr.

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.06.165

Table 1
The analysis of the 357 alloy used in the present investigation (wt%).

Si	Fe	Cu	Mn	Mg	Sr	Ti
6.87	0.181	0.0049	<0.01	0.577	0.0114	0.141

the present work for the isothermal DSC experiments in an effort to illustrate how much continuous and isothermal DSC data agree or disagree.

3. Results and discussion

The DSC thermograms obtained during melting and solidification of 357 alloy at different scan rates are shown in Fig. 1. The melting spectrum of the present alloy is characterized by sequential melting of the ternary Al–Si–AlFeSi eutectic, the binary Al–Si eutectic and the primary α-Al solid solution phase as confirmed by three neighbouring endothermic signals (Fig. 1a) [28,29]. The same reaction sequence takes place in reverse order when the DSC experiment involves cooling from the liquid state. The melting and solidification thermograms are nearly symmetrical with respect to $h = 0$ at a scan rate of 0.5 K min^{-1}. This symmetry is largely retained at 2.5 K min^{-1} (Fig. 1b) but is gradually impaired with further increase in the scan rate (Fig. 1c and d). The individual peaks start to overlap while the signals associated with the melting and solidification of the ternary Al–Si–AlFeSi eutectic disappear due to the expansion of the neighbouring peaks at scan rates higher than 10 K min^{-1}.

Start and finish temperatures and the temperature ranges for the melting and solidification reactions at different scan rates are listed in Table 2. The horizontal displacement of the two curves with respect to each other is essentially due to the marked shift in the finish temperatures of the melting and solidification reactions while the start temperatures of both reactions remain relatively unchanged. Melting starts at approximately 555 °C regardless of the heating rate but is completed at two very different temperatures, 621 and 702 °C, at 0.5 and 40 K min^{-1}, respectively. Two orders of magnitude increase in the scan rate apparently produces over a two-fold increase in the melting range. Likewise, solidification which starts at approximately 620 °C at the cooling rates employed in the present work, finishes at 545 and 471 °C, at cooling rates of 0.5 and 40 K min^{-1}, respectively. The melting and solidification ranges at a scan rate of 40 K min^{-1} is apparently very large evidencing the impact scan rate has on solid fraction analysis. The vertical displacement of the two curves with respect to each other, on the other hand, is linked with the slightly different heat capacities of the liquid and solid alloys.

Table 2
Solidification and melting features estimated from heating (melting) and cooling (solidification) scans.

Type of scan	Scan rate (K min^{-1})	Liqidus point (°C)	Solidus point (°C)	Solidif. interval (°C)
Heating	0.5	621.3	555.7	65.6
	2.5	626.9	555.1	71.8
	10	638.6	554.8	83.8
	40	702.0	552.6	149.4
Cooling	0.5	618.3	544.9	73.4
	2.5	617.0	536.4	80.6
	10	618.5	521.7	96.8
	40	620.8	471.1	149.7

The solid fraction (F_s) vs. temperature (T) curves during melting as well as solidification reactions were obtained from the DSC thermograms in Fig. 1. The DSC measures the energy supplied to maintain the sample and the reference cells at the same temperature throughout the experiment. Assuming uniform temperature distribution in both cells and resistance to heat transfer only between the sample holder and the sample container [30], the energy conservation in the sample and reference cells can be expressed as [31–33],

$$C_s\left(\frac{dT_s}{dt}\right) = \left(\frac{dq_s}{dt}\right) + \left(\frac{dh}{dt}\right) \quad (1a)$$

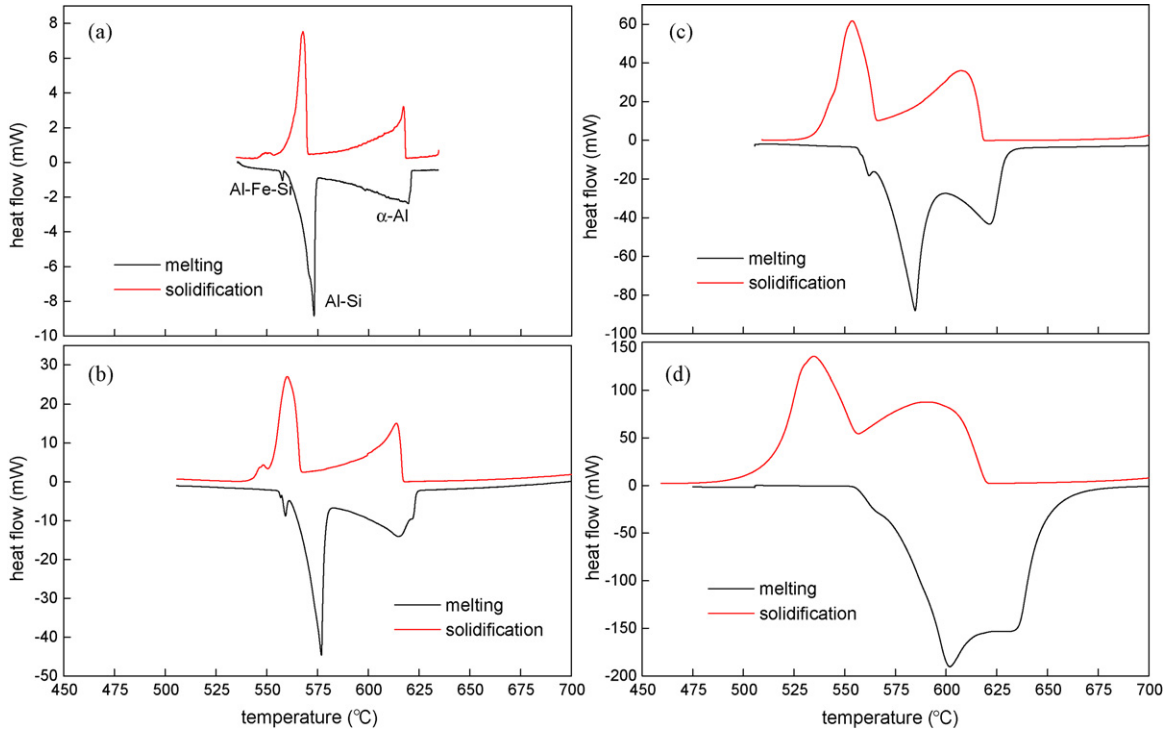

Fig. 1. Heat flow vs. temperature curves of the 357 alloy recorded during heating from the solid and cooling from the molten states at (a) 0.5 K min^{-1}, (b) 2.5 K min^{-1}, (c) 10 K min^{-1}, and (d) 40 K min^{-1}.