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Comparison between Prediction of Liquid Fraction versus Temperature and Experimental Results from DSC and SPSC

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Abstract. The processing window is important for the semisolid processability of alloys. This study focusses on the kinetics of diffusion. It compares prediction of fraction liquid versus temperature taking into account both thermodynamic and kinetics, with experimental results from Differential Scanning Calorimetry (DSC) and Single Pan Scanning Calorimetry (SPSC). SPSC is a novel technique with an order of magnitude higher accuracy than DSC. A range of Al-Si binary alloys has been investigated. The studies reveal that the simulation results predicted by DICTRA (DIffusion-Controlled TRAnsformations) show the same pattern with experimental results in the relationship of fraction liquid-temperature. However, the SPSC results are closer to the prediction results than DSC curves even with the relatively large sample size associated with SPSC. This is potentially a significant result as conventionally one of the difficulties is predicting the liquid fraction versus temperature for the heating of a billet for semi-solid processing. DSC results are known to be unrepresentative because the heating rates which can be achieved in DSC are much lower than those in induction heating. In addition, the DSC results are dependent on sample size and heating rate. The long term aim is to gain confidence in prediction with software packages which will reduce trial and error.

Introduction

Atkinson et al. [1] reviewed aluminum alloy compositions, especially with high performance, that have been thixoformed and proposed that the critical parameters for thixoforming must be as follows: appropriate solidus-liquidus interval; suitable slope of the fraction liquid versus temperature in the region of 30-50% liquid; reheatability of feedstock material (e.g. in the case of vertical heating of alloy slugs, the ability of a billet to support itself in the semi-solid state, and the conduction of heat from the outside to the interior); optimum morphology of structure and rheological properties in the semi-solid state. Kazakov [2] published the first examination of the issues from a thermodynamic prediction and DSC view point. More recently, Liu et al. [3] using the MTDATA thermodynamic package predicted the liquid fraction versus temperature relationship with Al–Si–Cu and Al–Si–Cu–Mg systems. However, the MTDATA modeling does not including the kinetic factors which are very important during melting or solidification. As Curle et al. [4, 5] recently demonstrated, both pure Al and binary Al-Si eutectic alloy can be rheo- or semi-solid processed because of the solidification kinetics during the thermo-arrest. The processing window between 30% liquid and 50% liquid is an important consideration in semi-solid processing.

The aim of this work is to use the simulation package called DICTRA [6], which allows diffusion kinetics to be taken into account alongside thermodynamic prediction. This is the prime novelty of the work presented here. It should be noted that the DICTRA simulation is for solidification rather than melting (and it is melting that would be most relevant to the Thixo-processing simulation). Simulation of melting will be a further step in the development of the DICTRA simulation for this application. The prediction will be compared with experimental results from DSC and also from SPSC (Fig.1). SPSC is a novel calorimetry technique developed by Dong and Hunt [7] to solve the smearing effect in a conventional DSC. The advantages of the new calorimeter are that the sample is

in a uniform temperature enclosure and that it has a large thermal resistance between the sample and its surroundings. According to Dong et al. [8], 95% of the latent heat for pure Al appears over only 0.04 K for a 3g sample; the accuracy and reproducibility are better than 1% for SPSC and this compares with over 5% for a conventional two-pan DSC. In this work, a range of selected Al-Si binary alloys were investigated.

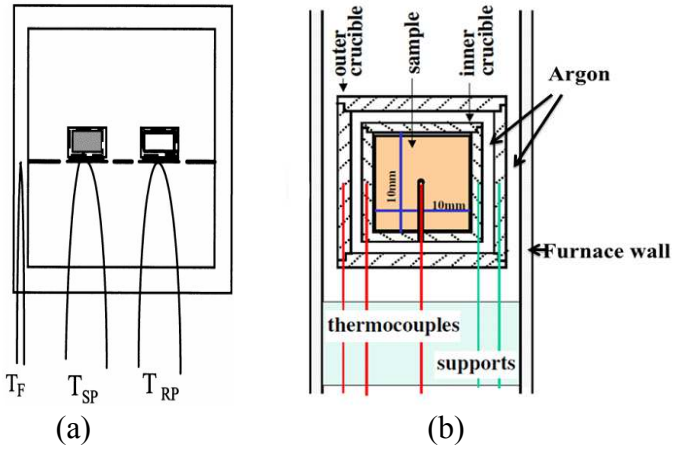

Fig. 1: A schematic diagram of two-pan DSC (a) and the new SPSC calorimeter cell (b) (T_F is the furnace temperature, T_{SP} is the sample pan temperature, T_{RP} is the reference pan temperature)

Experimental Procedure

In this project, a range of Al-Si binary alloys have been studied as shown in Table 1. These are representative of Si contents in commercial alloys used for semi-solid processing.

All these alloys were supplied by GRINM (General Research Institute for Nonferrous Metals, Beijing) and the chemical compositions were tested by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at GRINM. The positions of these alloys have been labelled in the respective Al-Si binary phase diagrams in Fig. 2.

Table 1: Chemical compositions of Al-Si binary alloys (Al: Bal.)

Binary Alloys	Chemical compositions [wt.%]		
	Si	Fe	Ca
Al-1Si	1.01	0.0074	0.0024
Al-5Si	5.08	0.023	0.0028
Al-12Si	11.68	0.042	<0.002
Al-18Si	17.54	0.082	0.012

Simulations. In this work, two different methods of computational thermodynamics are applied to predict the relationship of fraction liquid-temperature. Thermo-Calc (Version: TCW5) software was used to predict the phases in both equilibrium and non-equilibrium (Scheil) solidification. Fraction liquid is a critical parameter both for fundamental work and for the control of the semi-solid processing. The effect of added silicon on the fraction liquid was determined. The phase equilibria were calculated using thermodynamic database TTAL7 in Thermo-Calc [9]. DICTRA simulations were carried out under the model of 'solidification path' [10] as follows (Fig. 3). According to the phase diagram in Fig.2, in the semi-solid state, three phases are present for Al-Si binary alloys at equilibriums: liquid, α-Al (FCC) and Si.

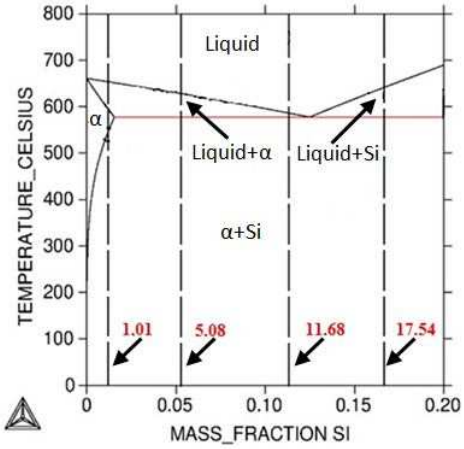

Fig. 2: Table 1 alloys in the Al-Si binary phase diagram. (The phase diagram was calculated with Thermo-Calc [9] with database TTAL7)

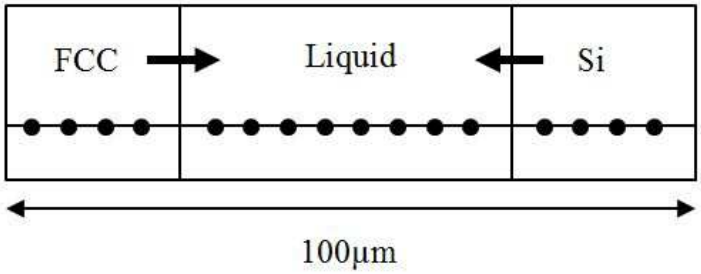

Fig. 3: DICTRA cell model for simulation of solidification

The cooling rate was set as 3K/min and 10K/min from 700°C to 400°C for all binary alloys to cover the whole temperature interval between liquidus and solidus. To be able to simulate solidification, FCC and Si phases are assumed to form at the solid-liquid interface. The starting profile for the simulation was a homogeneous distribution of the alloying element in the liquid phase with 60 grid points (Fig.3) along the cell. Then the liquid fraction/temperature relationship was calculated and plotted.

Thermal Analysis by DSC. Differential scanning calorimetry was performed on a NETZSCH 404 DSC in an argon-controlled environment. The high-purity Al_2O_3 pan was used as reference material. Binary alloys were processed into two sizes: 4.5mm in diameter and 3mm in height, ~110mg on average; a small piece around 20mg. The standard heating rates in the DSC are 3K/min and 10K/min. The samples were heated to 700℃ at 3K/min (or 10K/min) and then cooled to 30℃ at the same rate. All samples were put in an Al_2O_3 pan with an Al_2O_3 lid. Argon was fed through the system at a flow rate of 35ml/min to minimize oxidation of the samples. Three repetitions were carried out for each sample (two samples) under each condition. A high reproducibility was obtained. The evaluation of the liquid phase fraction is carried out by the application of peak partial area integration [11].

Thermal Analysis by SPSC. With the SPSC a 10K/min cooling rate cannot be achieved. The calorimetrical measurements were carried out using a constant heat flux mode by controlling the temperature difference between the inner and outer crucible at 18 °C on heating and 6 °C on cooling, with a heating and cooling rate of 3.1±0.1 K/min before any melting and solidification occurs. In this work, pure sapphire was used for calibration of latent heat and pure Al was used for the calibration of temperature. The enthalpy data obtained were used to calculate the evolution of liquid fraction f_L [12]. Eq.1 will be used to determine the liquid fraction evolution as a function of temperature.

$$f_L = \left[\frac{(H-H_{solidus})-C_P\cdot(T-T_{solidus})}{(H_{liquidus}-H_{solidus})-C_P\cdot(T_{liquidus}-T_{solidus})}\right] \quad (1)$$

where H is enthalpy, C_p is the heat capacity, T is the temperature.

Results and Discussion

Back Diffusion in DICTRA. Taking alloy Al-5.08Si for example, Fig. 4 shows the Si composition profiles at 620 °C and 580°C at different cooling rates using the DICTRA solidification path mode. In the solid phase, back diffusion takes place when the interface is moving. In the liquid phase, as the diffusion is much faster than in the solid phase, the Si composition profiles are more uniform. The vertical interfaces for 3K/min lie to the right hand side of those with 10K/min cooling rate and in the solid, phases are below those for 10K/min indicating that the alloy with the higher cooling rate will have a higher liquid fraction at the same temperature.

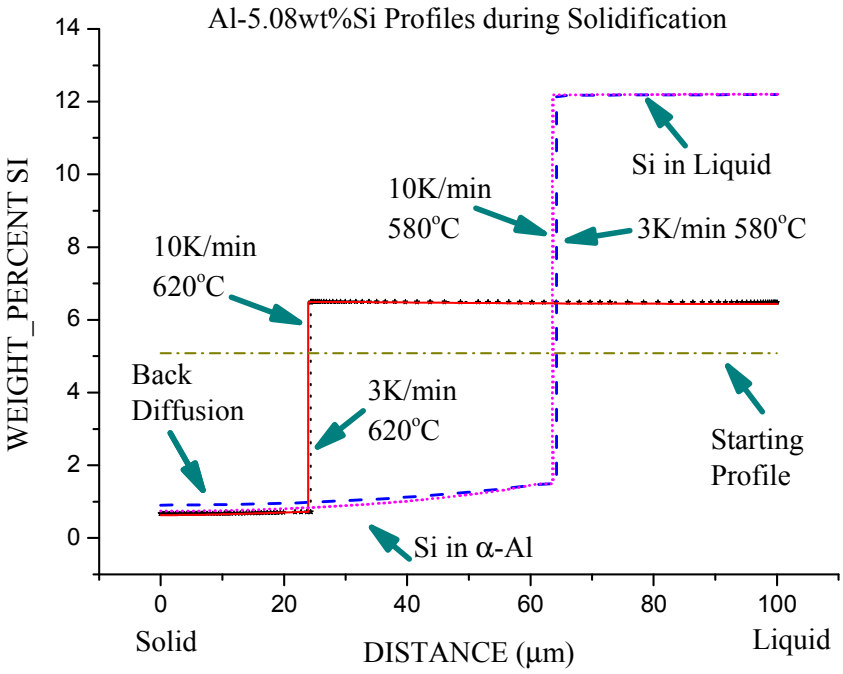

Fig. 4: Solidification simulation of Al-5.08wt%Si using DICTRA: Si composition profiles at 620 °C and 580 °C under different cooling rates (3K/min, 10K/min), cell size: 100 μm

Experimental Results. Figs. 5 to 8 show the liquid fraction-temperature relationships from DSC and SPSC data for Al-Si series binary alloys together with the prediction curves for Equilibrium and Scheil condition and DICTRA simulations. The liquid fraction has been estimated from both heating and cooling curves. With DICTRA prediction, at a given temperature, higher cooling rate gives just slightly higher liquid fraction than with a lower cooling rate. The lowest liquid fraction is obtained under equilibrium conditions in the 30-50% liquid range. The inset in Fig. 5 shows the difference between equilibrium and SPSC Cool to be ~0.04, which could be significant in processing terms. Fig. 5 shows that the SPSC heating and cooling curves are very close together and, although the SPSC cannot achieve 10K/min cooling, the curves for 10K/min are expected to be very close to these because SPSC operates via the constant heat flux mode.

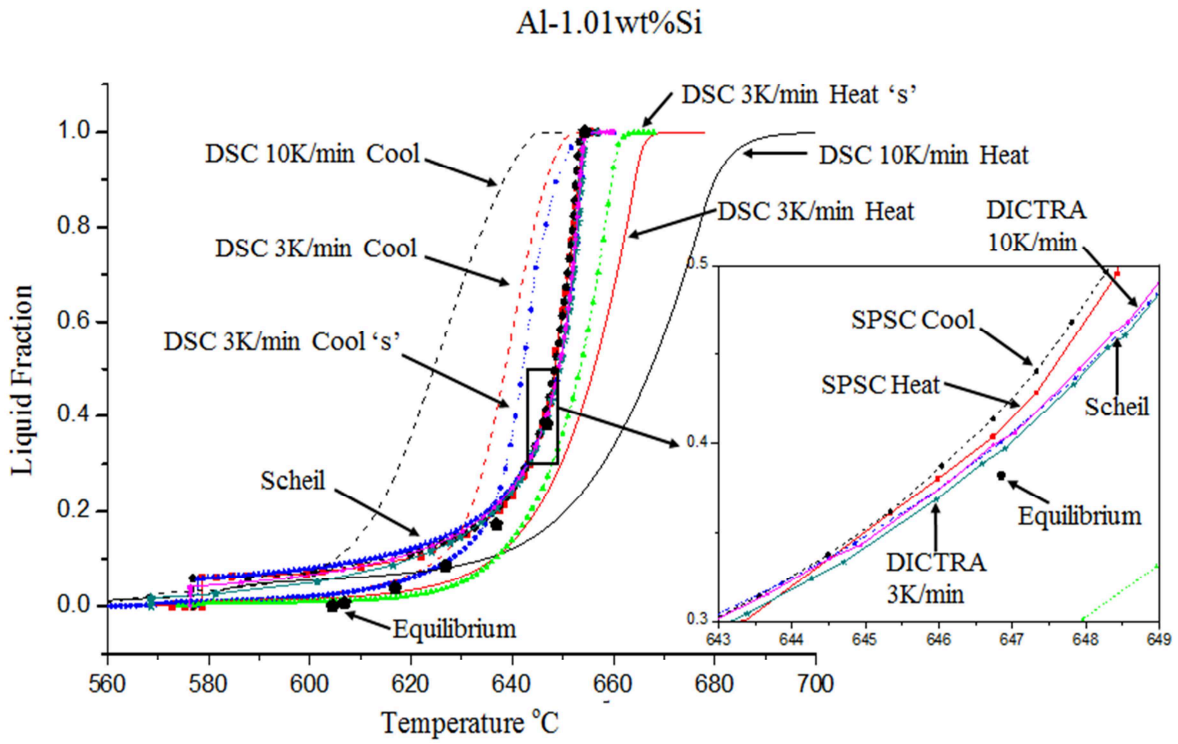

Fig. 5: Liquid fraction as a function of temperature from SPSC & DSC for Al-1.01wt%Si alloy, together with prediction curves. ('s' means small samples for DSC, i.e. the 20mg sample)

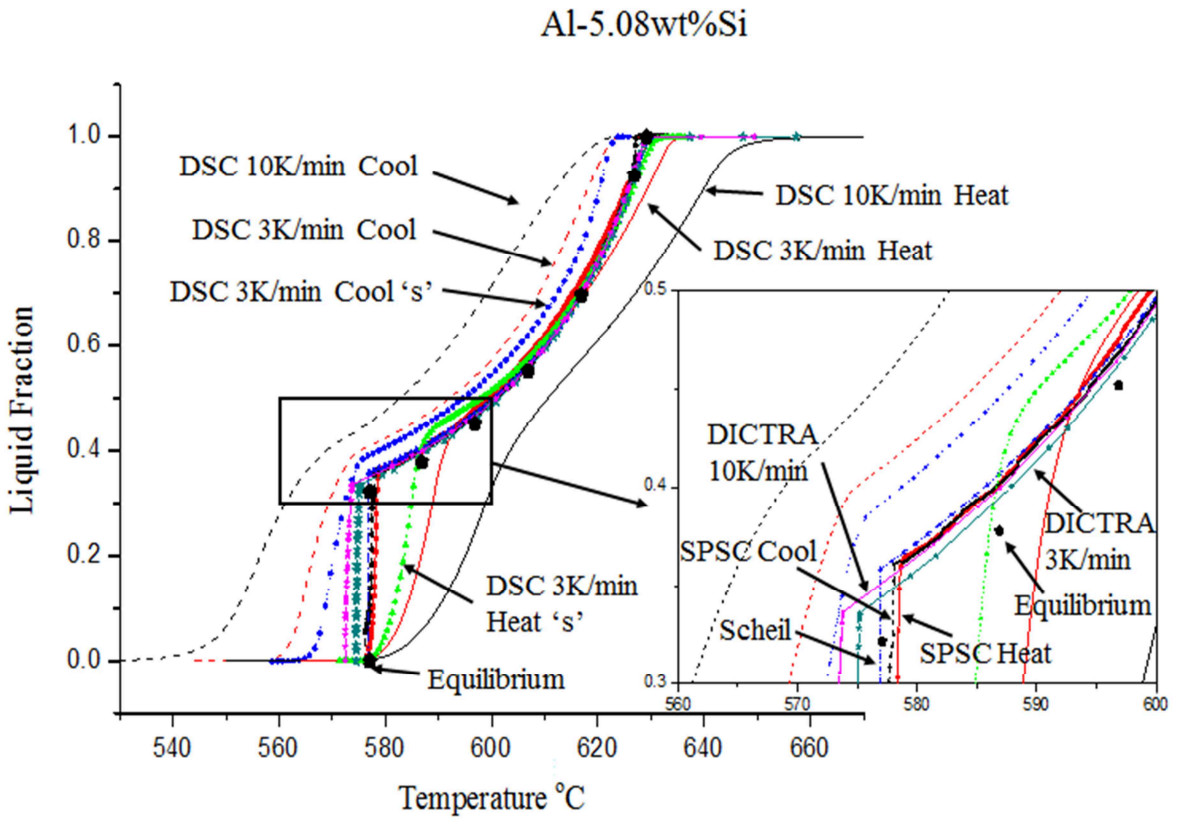

Fig. 6: Liquid fraction as a function of temperature from SPSC & DSC for Al-5.08wt%Si alloy, together with prediction curves. ('s' means small samples for DSC, i.e. the 20mg sample)

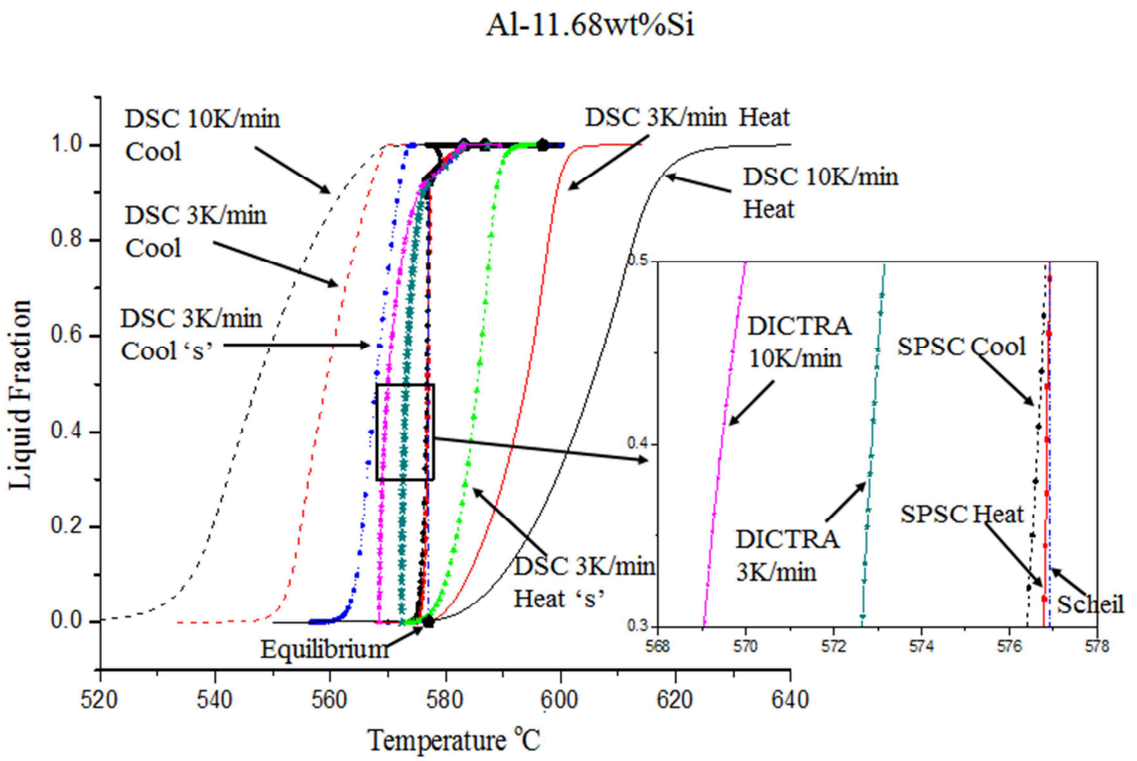

Fig. 7: Liquid fraction as a function of temperature from SPSC & DSC for Al-11.68wt%Si alloy, together with prediction curves. ('s' means small samples for DSC, i.e. the 20mg sample)

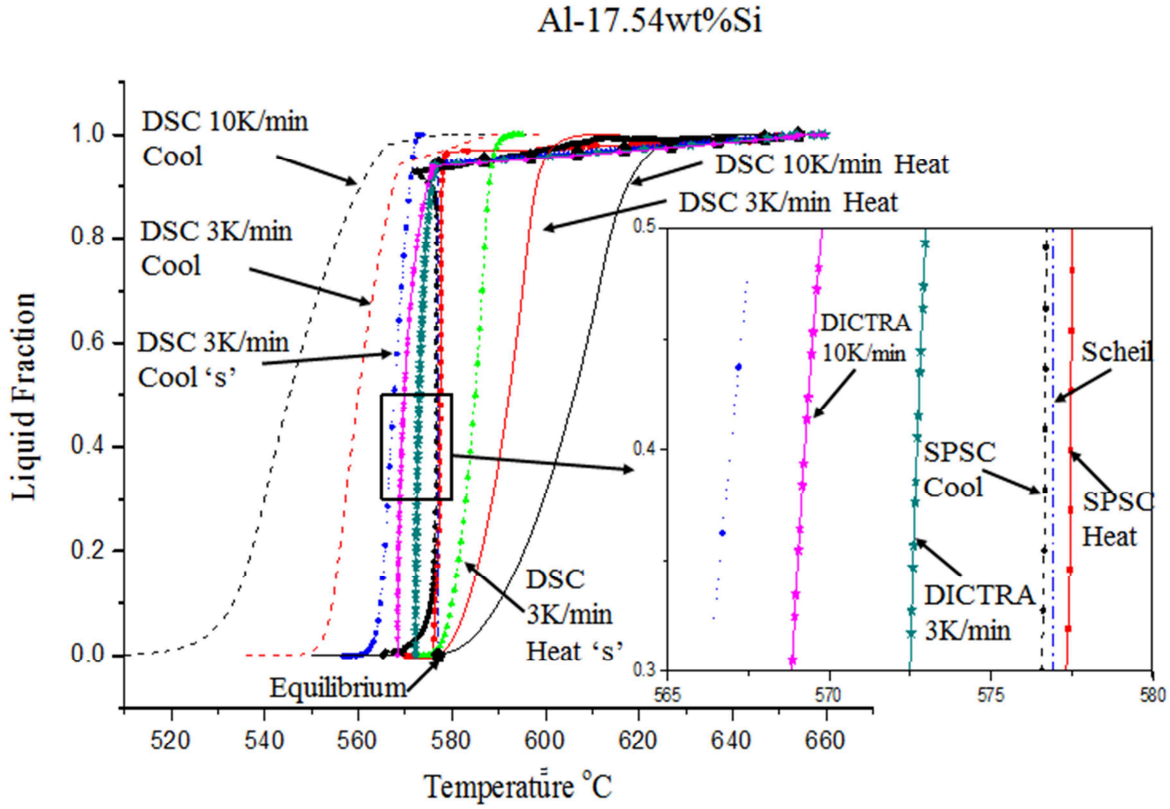

Fig. 8: Liquid fraction as a function of temperature from SPSC & DSC for Al-17.54wt%Si alloy, together with prediction curves. ('s' means small samples for DSC, i.e. the 20mg sample)

The general trend for the experimental curves in the upper part of the graphs is the following order (from left hand side to right hand side): DSC 10K/min cooling→ DSC 3K/min cooling → DSC 3K/min cooling (small sample) → SPSC cooling→SPSC heating → DSC 3K/min heating (small sample) → DSC 3K/min heating → DSC 10K/min heating. The prediction curves are close to the SPSC results.

The influence of heating (cooling) rate on the DSC curves for alloys is shown by the fact that the processing window between the fraction liquid 30% and 50% is wider for 10K/min heating (cooling) rate than for 3K/min (i.e. the slope of the curve is steeper for 3K/min). The solidus temperatures for alloys on the DSC heating curves are the same for every alloy. For the Al-5.08wt%Si alloy, the knee (shown magnified in Fig.6) at the eutectic point is smoother in the DSC 10K/min heating (cooling) rate curve than in the 3K/min. In addition, the knee on the DSC heating curves is associated with more liquid (~44%) than the DSC cooling (~38%), SPSC (~36%) and Scheil (~36%) curves.

The DSC is controlled to a constant heating (cooling) rate. Increasing the heating rate results in a broader peak and a higher onset temperature when the DSC signal is plotted versus temperature [13]. In addition, the liquid fraction was calculated by the integration of the peak area, so, the liquidus-solidus temperature range for the high heating (cooling) rate is wider than for a low rate. As a result, the curve for the 10K/min heating (cooling) rate on DSC is lying on the right (left) hand side of the curve for the 3K/min heating (cooling) rate.

With a higher mass sample, the rate at which a sample can absorb or release heat is slower than for a low mass sample. This leads to a broader peak for the large mass sample when plotting versus temperature but the onset temperature for solidification will not vary provided the cooling rate is the same [13]. This is consistent with the fact that the curve for the DSC 3K/min heating (cooling) rate with small sample mass is lying to the left (right) hand side of the curve for the DSC 3K/min with the large sample.

The DSC is controlled to the ramp rate, while the SPSC is using a constant heat flux mode. The DSC curves change significantly due to the influence of the sample mass and the heating rate, which affects the liquid fraction versus temperature. For the DSC with two pans, to minimize errors, it is generally recognized that small samples and low heating/cooling rates must be used when latent heat is evolved. Even when samples are small the errors have been reduced but not eliminated. For SPSC, when melting or solidification occurs, the measured temperature is exactly the sample's temperature.

With the 10K/min DSC heating rate, a higher temperature is required than for the 3K/min heating rate to form the same fraction of liquid. Moreover, the eutectic knee (for the Al-5.08wt%Si sample) on the liquid fraction-temperature curve occurs at a higher temperature, hence giving a wider temperature range for processing between 30 and 50% liquid. The main reason for this phenomenon is that with a higher heating, the solute cannot be redistributed rapidly over a short time interval to obtain areas with a composition suitable for melting (given an inhomogeneous starting composition across the sample as would usually be found with a semi-solid processing billet). However, the DSC results are significantly different from those in the SPSC and the DICTRA simulation predictions. The next challenge is to investigate how far the DICTRA simulation can be relied on for practical processing.

Overall, the key finding in this work is that the results from the SPSC are very close to the DICTRA predictions. The DICTRA predictions are based on a solidification route rather than melting (which would be more appropriate for at least some forms of semi-solid processing). In practice in semi-solid processing, the heating route must be analysed to determine the heating rate in the various parts of the billet and hence predict the liquid content variation across the billet at stages in the processing.

Conclusions

A number of Al-Si binary Aluminum alloys have been thermally analysed with a conventional DSC and with the novel SPSC and been simulated by the thermodynamic prediction software Thermo-Calc and DICTRA. The SPSC data are closer to the prediction results than the DSC curves

even with relatively large sample size used in SPSC. The window between 30 % and 50% fraction liquid is enlarged by higher heating/cooling rate or larger sample size in the DSC.

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References

[1] H.V. Atkinson, P. Kapranos, D.H. Kirkwood, Alloy development for thixoforming, in: Proceedings of the 6th International Conference "Semi-solid Processing of Alloys and Composites", Turin, Italy; Sep 27-29, Brescia, Italy: Edimet-Spa; 2000, pp. 443-450.

[2] A. A. Kazakov, Alloy compositions for semisolid forming, Advanced Materials & Processes, 157 (2000) 31-34.

[3] D. Liu, H.V. Atkinson, H. Jones, Thermodynamic prediction of thixoformability in alloys based on the Al–Si–Cu and Al–Si–Cu–Mg systems, Acta Materialia, 53 (2005) 3807-3819.

[4] U. Curle, H. Möller, J. Wilkins, Shape rheocasting of high purity aluminium, Scripta Materialia, 64 (2011) 479-482.

[5] U. Curle, H. Möller, J. Wilkins, Shape rheocasting of unmodified Al–Si binary eutectic, Materials Letters, 65 (2011) 1469-1472.

[6] A. Borgenstam, L. Höglund, J. Ågren, A. Engström, DICTRA, a tool for simulation of diffusional transformations in alloys, Journal of Phase Equilibria, 21 (2000) 269-280.

[7] H.B. Dong, J.D. Hunt, A novel single-pan scanning calorimeter: measurement of thermophysical properties of metallic alloys, Journal of Thermal Analysis and Calorimetry, 64 (2001) 341-350.

[8] H. Dong, M. Shin, E. Kurum, H. Cama, J. Hunt, Determination of liquid fraction during solidification of aluminium alloys using a single-pan scanning calorimeter, Fluid phase equilibria, 212 (2003) 199-208.

[9] Information on http://thermocalc.com.cn/thermo_calc/datebasepdf/TTAL7.pdf

[10] Information on http://www.thermocalc.com/res/pdfDICTRAflyers/DICTRA27_Examples.pdf

[11] D. Larouche, C. Laroche, M. Bouchard, Analysis of differential scanning calorimetric measurements performed on a binary aluminium alloy, Acta Materialia, 51 (2003) 2161-2170

[12] H.B. Dong, R. Brooks, Determination of liquidus temperature in Al–Si and Al–Si–Mg alloys using a single-pan scanning calorimeter, Materials Science and Engineering A 413 (2005) 480-484.

[13] G. Höhne, W.F. Hemminger, H. J. Flammersheim, Differential scanning calorimetry, Springer, 2003.

Semi-Solid Processing of Alloys and Composites XIII
10.4028/www.scientific.net/SSP.217-218

Comparison between Prediction of Liquid Fraction versus Temperature and Experimental Results from DSC and SPSC
10.4028/www.scientific.net/SSP.217-218.442

DOI References
[7] H.B. Dong, J.D. Hunt, A novel single-pan scanning calorimeter: measurement of thermophysical properties of metallic alloys, Journal of Thermal Analysis and Calorimetry, 64 (2001) 341-350. 10.1023/A:1011578205887
[12] H.B. Dong, R. Brooks, Determination of liquidus temperature in Al-Si and Al-Si-Mg alloys using a single-pan scanning calorimeter, Materials Science and Engineering A 413 (2005) 480-484. 10.1016/j.msea.2005.09.016