

# Thermodynamic Prediction of Thixoformability in Alloys Based on the Al-Si-Cu and Al-Si-Cu-Mg Systems

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## Abstract

Most commercial semi-solid processing (of which thixoforming is one type) utilises the conventional casting alloys A356 and A357. There is, however, a demand to widen the range of alloys, including those with higher performance which tend to show poor characteristics for thixoforming. Thermodynamic calculation packages, such as MTDATA, provide a tool for predicting thixoformability. Here, the effects of compositional variations, in particular the effect of added copper on the thixoformability of alloy A356 and the effect of added silicon on the thixoformability of alloy 2014, have been investigated using MTDATA thermodynamic and phase equilibrium software combined with the MTAL database. Criteria for thixoformability are identified and a range of alloy compositions based on Al-Si-Cu and Al-Si-Cu-Mg evaluated in relation to these criteria. Compositions which satisfy these criteria include:- 308 (Al-5.5Si-4.5Cu); 319 (Al-6Si-3.5Cu); 238 (Al-10Cu-4Si-0.3Mg); 355 (Al-5Si-1.3Cu-0.5Mg); 2014 based alloys Al-4.4Cu-0.5Mg-(4~6)Si; and a range of alloys ( $7.5 \leq \text{Si} + \text{Cu} \leq 9$  and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$ ) and alloys ( $9 < \text{Si} + \text{Cu} \leq 10$  and  $\text{Si}/\text{Cu} = 1.5$ ) based on the Al-Si-Cu-Mg system.

Keywords: MTDATA, thixoformability, semi-solid processing, Al-Si-Cu and Al-Si-Cu-Mg alloys.

## 1. Introduction

Thixoforming is one branch of semi-solid metal processing, which is the forming of alloys in the semi-solid state to near net shaped products. It relies on the thixotropic behaviour of alloys which have a spheroidal rather than a dendritic microstructure in the semisolid state. The spheroidal microstructure is typically obtained by stirring during casting (for example using Magneto Hydrodynamic stirring in the MHD technique) or by reheating material which has been worked by rolling or extrusion in the strain induced melt activated (SIMA) and recrystallisation and partial melting (RAP) routes. When sheared, semisolid alloys with spheroidal microstructure flow with the viscosity of heavy machine oil and thus can fill a die in a smooth, laminar way, minimising defects normally associated with, for example, die casting. Thixoforming is normally carried out with between 30% and 50% liquid. As it involves a solid billet being reheated into the semisolid state, liquid fractions beyond 50% tend to lead to slumping and collapse of the billet. Reviews include those by Flemings [1], Kirkwood [2], Fan [3], de Figueredo [4] and Atkinson [5].

Almost all commercial thixoforming is carried out with the conventional casting alloys, A356 and A357. There is a demand to widen the range of alloys, including those with higher performance which are conventionally wrought. However, practical experience has highlighted a number of difficulties including: the steep slope of the fraction liquid versus temperature curve for alloys such as 6061 [6,7], hot tearing for

alloys such as 2014 [8-10] and high hot cracking susceptibility for 6082 and 7075 [11]. Considerable effort is therefore being directed to understanding what influences thixoformability (i.e. formability in the semi-solid state) [11-19].

Camacho et al. [19] investigated quantitatively the potential of thermodynamic predictions for identifying thixoformable compositions in the wrought aluminium 7xxx series and the effect of the alloying elements on fraction liquid during solidification and on the phases in equilibrium and non-equilibrium in the Al-Zn-Mg-Cu system by using MTDATA, along with the NPL alloy solution database and SGTE (Scientific Group Thermodata Europe) database. Note that in this work ‘Scheil type’ conditions were assumed on the grounds that ‘during thixoforming, reheating into the semi-solid state takes place rapidly (e.g. ~2 min overall in the Sheffield rig) by induction heating. There is, therefore, insufficient time for equilibrium to be established.’ In the current work, we have given further consideration to the matter of under what circumstances Scheil conditions might be applicable and this is discussed in Section 2.

In this paper, we focus on thixoformability criteria which can be investigated with thermodynamic prediction. The criteria we have selected are:

1. **The highest ‘knee’ on the fraction liquid versus temperature curve should occur between 30 and 50% liquid (see schematic in Figure 1);** this is the binary eutectic temperature i.e. the temperature at which  $\alpha$  - solid solution starts melting. The amount of liquid at the ‘knee’ is the amount of eutectic in the structure. We would argue that, if this occurs between 30 and 50% liquid, liquid formation tends to be controllable because, kinetically, the rate of liquid

formation with time (i.e. the rate of melting of  $\alpha$  solid solution spheroids) above the knee tends to be slower than that below. Evidence for this will be given in the experimental results with DSC for A356.

2. **Fraction liquid sensitivity at 0.4 fraction liquid,  $(df_L / dT)_{f_L=0.4}$ , should be**

**as small as possible, let us say less than  $0.03 \text{ K}^{-1}$** , on the following basis. Experience in thixoforming suggests that the minimum ‘working window’ between the temperature at which the fraction liquid is 0.3,  $T_{0.3}$ , and that at which it is 0.5,  $T_{0.5}$ , is about 6K. This arises because, in induction heating, the ‘skin’ is heated first and the heat must then be conducted into the interior. This takes a finite period of time and during this period the outer skin temperature is still rising. If the fraction liquid in the outer skin exceeds 0.5 then it is likely that liquid will start to drip off the outside. Meanwhile, the temperature at the centre may not have reached a level such that there is sufficient liquid present for forming (i.e.  $> 0.3$  fraction liquid). Assuming, for the sake of explanation, that the fraction liquid versus temperature curve is a straight line between 0.3 fraction liquid and 0.5 (i.e. in the thixoformable regime),

$$\left( \frac{df_L}{dT} \right)_{0.4} \sim \frac{0.5 - 0.3}{T_{0.5} - T_{0.3}} = \frac{0.2}{6} = 0.03 \text{ K}^{-1}. \text{ Note that this figure is specific to}$$

thixoforming where the heating is taking place by, for example, induction heating, and time is required for conduction of heat inwards through the billet. The figure is a representative one for a slug size which would be typical of processing to produce automotive components of approximately 0.5 kg. For alloy systems other than aluminium, a different figure would be required to allow for a different conductivity. Other workers (viz. [18]) have proposed a figure of  $0.015 \text{ K}^{-1}$  more generally for semisolid processes, includes routes such as rheoforming, based on temperature control to within  $\pm 3 \text{ K}$  during processing. Large  $(df_L / dT)_{f_L=0.4}$  will result in substantial variation of the fraction liquid with a small change in temperature. (We have chosen 0.4  $f_L$  as the measuring point because this is mid-way through the working range of 30-50% liquid).

- 3. The solidification interval, the temperature interval between the liquidus and solidus, should not be too wide, let us say less than 130 K.** This criterion originates from the finding that 2014, with a solidification interval of 131K [8], is on the limit of thixoformability [9] because of susceptibility to hot tearing. A356, which is a typical casting alloy, has a solidification interval of 71K [20].

In addition, precipitates formed during ageing after solution treatment and water quenching should give rise to age-hardening to improve the mechanical properties. This is not considered further here.

Alloy compositions targeted for thixoforming need to give mechanical properties which are close to those of wrought aluminium alloys. In this work, the effect on thixoformability of adding copper to A356 to improve mechanical properties and adding silicon to 2014 to reduce the hot tearing tendency have been investigated. In addition, a range of alloy compositions based on Al-Si-Cu and Al-Si-Cu-Mg have been evaluated. The alloy composition space explored is wider than that examined by Kazakov [13].

## 2. Prediction method

Thermodynamic modelling using Thermo-Calc, ChemSage or MTDATA can supplement/complement experimental work and can be used as a guide to alloy development for thixoforming. Here, MTDATA (version 4.73), a thermodynamic prediction software package, developed by the National Physical Laboratory (NPL),

was used to predict the phases in equilibrium and non-equilibrium (viz. Scheil) conditions. Data was drawn from the Al database MTAL (version 5.01 also supplied by NPL). The built-in procedure TSCHEIL was available with MTDATA to predict the phases and fraction liquid versus temperature curve in Scheil solidification (i.e. where there is no diffusion in the solid). Both MTDATA equilibrium and non-equilibrium predictions start with the elements distributed homogeneously. The thermodynamic package cannot be used to distinguish between solidification from the liquid and reheating from the solid. Under Scheil conditions, the first solid to form on solidification has the composition at the intersection of the tie line, at that temperature,  $T_1$ , with the solidus. As the temperature decreases to  $T_2$ , the next solid to form has the composition of the intersection of the tie line for  $T_2$  with the solidus and so on. With Scheil conditions, there is no diffusion in the solid and therefore the structure which arises is a cored structure. If we were considering a casting process, this would apply if the cooling is relatively fast. The final structure for a eutectic aluminium alloy system will consist of cored  $\alpha$ -aluminium with solidified liquid of the eutectic composition. Conversely, if cooling is slow, equilibrium will be established with diffusion in the solid state throughout cooling and the final structure will consist of solid of composition of the end of the eutectic temperature tie line and liquid of eutectic composition. On reheating, for both Scheil and equilibrium, the process is reversed i.e. there is no difference between the predictions for heating and for cooling.

If we now consider reheating in thixoforming, the Scheil calculation is most likely to apply when the starting material has the cored structure described above, which would be expected if the material has been prepared by the MHD route where the cooling

should be relatively fast. With the SIMA and RAP routes, the initial elemental distribution is expected to be relatively uniform apart from where particles/precipitates are present. For the SIMA route this is because the working (e.g. by extrusion) is carried out hot. For the RAP route, it is warm but then further diffusion to achieve homogenisation will occur during reheating for thixoforming. These starting materials may be better represented by equilibrium calculations. In this paper, we are seeking to draw the boundaries of thixoformability in relation to alloy composition, alongside identifying what may be optimum compositions. The state of the starting material is not defined and therefore, for the purposes of comparison we have focussed on Scheil calculations. Results are presented which compare the Scheil and equilibrium calculations with the Differential Scanning Calorimetry results for both a cast alloy composition (A356) and a wrought alloy composition (2014). The focus on Scheil predictions is then discussed.

Fraction liquid is a critical parameter both for fundamental work and for control of the thixoforming process. Prediction of the fraction liquid/temperature relationship is thus useful for identification of alloy compositions suitable for thixoforming. It is necessary that the fraction liquid does not change too rapidly with temperature in the working window and 0.3-0.5 volume fraction liquid is thought to be desirable for thixoformability. The results here are in weight fraction liquid but it is volume fraction liquid which is directly relevant to thixoforming. It is not possible to make a conversion from weight fraction liquid to volume fraction liquid because the data for the exact compositions and temperatures we need it for is not available in the literature. However, the conversion is likely to be such that the shapes of the curves (and hence slopes) are similar to those predicted. The likely difference in absolute

values is probably around 2%, which is confirmed by the conversion in alloy Al-5.9wt%Si based on the density data from reference [21].

### 3. Experimental work

In order to compare the fraction liquid versus temperature curve predicted by MTDATA with experimental data, Differential Scanning Calorimetry (DSC), which can measure directly the evolution of the heat of melting during the solid-liquid phase transformation, was performed to determine the fraction liquid vs. temperature for as-cast alloy A356 (Al-6.82Si-0.32Mg-0.022Cu-0.005Zn-0.112Fe-0.1Ti-0.013Pb-0.042Sn-0.006Ni-0.005Cr, wt%), and as-extruded 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%), using a Dupont 910 Differential Scanning Calorimeter system. Samples 3 mm in diameter and about 15 mg in weight were cut, weighed and put into a carbon pan with a carbon lid, leaving the reference carbon pan empty in an argon atmosphere. Argon was fed through the system at a flow rate of 80 ml/min to minimize oxidation of the samples. The samples were heated to 680°C at 10 K/min and then cooled to room temperature at the same rate. The heat flow and temperature were monitored by thermocouples to obtain heating and cooling curves. The fraction liquid versus temperature relationship was obtained by integration of partial areas under the heating or cooling curves.

### 4. Results

#### 4.1 Comparison between MTDATA predictions and DSC curves

Figure 2 shows fraction liquid vs. temperature measured by Differential Scanning Calorimetry (DSC) during heating and cooling at 10 K/min and the solidification curves estimated by MTDATA in equilibrium and non-equilibrium (Scheil). The compositions are: A356 (Al-6.82Si-0.32Mg-0.022Cu-0.005Zn-0.112Fe-0.1Ti-0.013Pb-0.042Sn-0.006Ni-0.005Cr, wt%) for DSC; 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%) for DSC and MTDATA; and simplified A356 (Al-6.82Si-0.32Mg, wt%) for MTDATA. The full composition for A356 cannot be treated with MTDATA as some of the elements are not included in the MTAL database. For A356, the DSC heating curve lies between the Scheil and equilibrium predictions initially. There is a 'knee' in the Scheil prediction curve at about 5% liquid but not in the equilibrium curve. Then between about 20% liquid and 50% liquid, the Scheil and equilibrium curves are coincident but the DSC curve lags slightly in terms of the amount of liquid for a given temperature. The highest 'knee' then occurs less distinctly in the DSC curve than in the predictions and is at about 60% liquid rather than 50%. It also occurs at a few degrees higher temperature than in the predictions. Above the knee, the fraction liquid is a few percent higher in the DSC curve, for a particular temperature, than in the predictions (which are almost coincident).

For 2014, the DSC heating curve is again initially between the equilibrium and Scheil predictions. The Scheil curve again has a 'knee' (in this case at about 10% liquid) where the equilibrium curve does not. For every point above about 50% amount of liquid present for a particular temperature is below that predicted by either Scheil or equilibrium calculations. The Scheil and equilibrium curves are coincident above about 50% liquid. The DSC cooling curve starts solidification at a lower temperature than the calculations predict. Below about 30% liquid it lies between the

Scheil and equilibrium curves and displays a knee mimicking that in the Scheil curve but occurring at a slightly higher temperature and lower fraction liquid.

#### 4.2 Thixoformability estimation for alloy A356 and A356 modified with added copper

Alloy A356 has been widely used as a thixoformable alloy. Figure 3 and Table 1 show the effect of copper on the MTDATA/Scheil curves of fraction liquid vs. temperature for alloy A356 (Al-7Si-0.3Mg, wt%) and A356 modified with added copper. The slope of the curve at 0.4 fraction liquid is very steep ( $0.133 \text{ K}^{-1}$  by MTDATA/Scheil in this work for A356,  $0.067 \text{ K}^{-1}$  by DSC from Tzimas and Zavaliangos [12]) for alloy A356, i.e. the liquid fraction sensitivity is relatively higher than for A356 modified with added copper. The slopes of the curves at 0.4 fraction liquid,  $(df_L / dT)_{f_L=0.4}$ , become less steep and the fraction liquid sensitivity is reduced from  $0.133 \text{ K}^{-1}$  to  $0.007 \text{ K}^{-1}$ , and the working window between 0.3 and 0.5 fraction liquid ( $\Delta T^{0.3/0.5}$ ) is enlarged from 1 to 32 K, when 10 wt% Cu is added. It should be noted from Table 1 and Figure 3 that the solidification interval is significantly enlarged by adding copper to A356 due to the ternary ( $L \rightarrow \alpha\text{Al} + \text{Si} + \text{CuAl}_2$ ) and quaternary ( $L \rightarrow \alpha\text{Al} + \text{Si} + \text{CuAl}_2 + \text{Mg}_2\text{Si}$ ) reactions which then occur.

#### 4.3 Thixoformability estimation for wrought aluminium alloys

Figure 4 shows the curves of fraction liquid vs. temperature estimated by MTDATA/Scheil for A356 (Al-7Si-0.3Mg, wt%), A357 (Al-7Si-0.6Mg, wt%) and wrought aluminium alloys 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%), 6082 (Al-1.03Si-0.69Mg-0.25Fe-0.45Mn, wt%), 7075 (Al-5.53Zn-2.21Mg-1.41Cu-

0.1Si-0.26Fe-0.0Mn, wt%) and 7010 (Al-6.1Zn-2.3Mg-1.63Cu-0.12Si-0.22Fe, wt%), compared with the curves estimated by MTDATA/Equilibrium for alloys A356 and 2014. Figure 4 indicates that the amount of eutectic for wrought alloys is less than 10 wt% but around 50 wt% for A356 and A357. The slope at 0.4 fraction liquid is very steep for 6082 and A356/A357, but is relatively flat for 2014, 7075 and 7010, which is expected to give a wide processing window in thixoforming. However, the wide solidification interval for wrought alloys 2014, 7075 and 7010 is thought to be responsible for hot tearing. According to the criteria for thixoformability in section 1, composition adjustment for wrought alloys is needed to increase the amount of eutectic and decrease the solidification interval. Figure 5 shows an example of how the amount of eutectic has been increased and the solidification interval decreased by adding Si to alloy 2014, hence giving alloys which are expected to be more thixoformable than alloy 2014. Alloys Al-3.91Cu-0.47Mg-xSi-0.29Fe-0.55Mn, wt%, with Si=3.83~5.83wt%, are likely to be suitable.

#### 4.4 Compositional adjustment for wrought 2014 to aid thixoforming

Alloy 2014 is one of the heat treatable high strength wrought aluminium alloys. Due to its wide solidification interval (131 K by DSC [8]) and the fact that less eutectic liquid is available at the last stages of solidification than for the casting alloy A356, 2014 is considered to be more prone to the formation of porosity. In order to investigate and improve the thixoformability of alloy 2014, a simplified alloy 2014 (Al-4.4Cu-0.5Mg-0.8Si, wt%) was considered. The manganese was taken out of consideration because it has little effect on the fraction liquid vs. temperature curve [8]. A series of curves of fraction liquid vs. temperature for alloys Al-xCu-0.5Mg-

0.8Si and Al-4.4Cu-0.5Mg-xSi (wt%) have been predicted by MTDATA/Scheil and some parameters have been summarized in Figures 6(a) and (b), respectively. Figure 6(a) shows the effect of copper on the solidification interval, amount of eutectic, processing window between 30 and 50% fraction liquid and slope sensitivity at 40% fraction liquid for alloys Al-xCu-0.5Mg-0.8Si (wt%). The ‘amount of eutectic’ represents the position of the highest ‘knee’ i.e. criterion 1. The solidification interval decreases (from 156 to 100 K) and the amount of eutectic increases (from 5.9 to 56.9%) with increase of copper content from 1 to 20 wt%. The slopes of the curves at 0.4 fraction liquid,  $(df_L / dT)_{f_L=0.4}$ , become flatter from 0.02 to 0.003 K<sup>-1</sup> when copper content increases from 1 to 14 wt%, i.e. the sensitivity is reduced. The slope then increases and plateaus (0.029 K<sup>-1</sup>) with the copper content between 15 and 20 wt% because the melting is all of eutectic, with a high slope for  $(df_L / dT)_{f_L=0.4}$ , rather than of  $\alpha$ - solid solution, with a lower slope. (The highest knee is above 40% liquid for the alloys with 15 and 20 wt% copper). The processing window between 0.3 and 0.5 fraction liquid increases from 10 to 57 K with increase in copper content from 1 to 11 wt% and then becomes narrower as copper increases to 20 wt%. It can be seen that alloys Al-(11~17)Cu-0.5Mg-0.8Si (wt%) are most suitable for thixoforming according to criteria 1-3 in Section 1. However, these alloys have limited fluidity [22] due to the high copper content and they are not the first choice for thixoforming.

Figure 6(b) shows the same parameters for alloy Al-4.4Cu-0.5Mg-xSi (wt%). The solidification interval decreases from 147 to 86 K and the amount of eutectic increases from 11.6 to 85.3% with increase in silicon content from 0.8 to 10 wt%. The slope of the curve at 0.4 fraction liquid,  $(df_L / dT)_{f_L=0.4}$ , becomes flatter from 0.01 to 0.004 K<sup>-1</sup> when silicon increases from 0.8 to 4.0 wt%, i.e. the sensitivity is reduced,

then the slope increases to a plateau ( $0.017 \text{ K}^{-1}$ ) for silicon contents between 6 and 15 wt%. It can be seen that alloys Al-4.4Cu-0.5Mg-(4~6)Si (wt%) are most suitable for thixoforming according to the criteria in section 1.

#### 4.5 Thixoformability estimation for the Al-Si-Cu and Al-Si-Cu-Mg alloy systems

Further prediction has been done based on conventional casting alloys. Curves of fraction liquid vs. temperature for Al-Si-Cu and Al-Si-Cu-Mg casting alloys have been predicted by MTDATA/Scheil and some solidification parameters have been summarized in Table 2. Alloys 308 (Al-5.5Si-4.5Cu), 319 (Al-6Si-3.5Cu), 238 (Al-10Cu-4Si-0.3Mg) and alloy 355 (Al-5Si-1.3Cu-0.5Mg) are particularly suitable for thixoforming according to criteria 1-3 in section 1.

Silicon provides good casting characteristics due to the formation of Al-Si eutectic. The addition of copper gives high strength and improved machinability, but with some sacrifice of ductility and resistance to corrosion. Increasing amounts of both copper and silicon in the Al-Si-Cu-Mg system increase the amount of eutectic and decrease the solidification interval. Adding silicon is more effective than copper (see Fig. 6a and b). Magnesium also increases strength but with less contribution to the amount of eutectic, compared with copper and silicon at low magnesium contents. The amount of Cu+Si and the ratio Si/Cu are considered to be important parameters to define the amount of eutectic and identity of solid state precipitates. From consideration of the Al-Cu, Al-Si and Al-Cu-Si phase diagrams and with magnesium fixed at 0.5 wt%, the ranges  $7.5 \leq \text{Cu} + \text{Si} \leq 12.5$  and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$  were chosen for further investigation. The copper content was varied between 2 and 5 wt% to obtain

age hardening and the silicon content was varied between 3 and 10.5 wt% to obtain the Al-Si eutectic. A series of fraction liquid versus temperature curves were calculated by MTDATA/Scheil and are shown in Figure 7. Some parameters are summarized in Table 3. At fixed Si/Cu ratio (for example 1.5), as the Si+Cu content increases, the amount of eutectic increases and solidification interval decreases. At fixed Si+Cu content (for example 9), as the Si/Cu ratio increases, the amount of eutectic increases and the solidification interval decreases. Based on all the calculations, and not just those presented in Table 3, the alloys within the chosen range ( $2 \leq \text{Cu} \leq 5$ ,  $3 \leq \text{Si} \leq 10.5$ ,  $7.5 \leq \text{Si} + \text{Cu} \leq 12.5$  all in wt%, and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$ ) that satisfy the criteria are: Al-Si-Cu-Mg alloys with  $7.5 \leq \text{Si} + \text{Cu} \leq 9$  and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$  and alloys with  $9 < \text{Si} + \text{Cu} \leq 10$  and  $\text{Si}/\text{Cu} = 1.5$ .

## 5. Discussion

### 5.1 Discrepancies between predictions from MTDATA and results from DSC

In Section 2, we discussed the premise that Scheil calculations are most likely to accord with starting material which is 'cored', whereas equilibrium calculations should more closely match material which has a homogeneous distribution of the elements. From Fig. 2, for A356, the DSC curve initially lies between the two, suggesting that, although the starting material was as-cast, the cooling rate was not high and therefore the elemental distribution in the  $\alpha$ -solid solution is relatively homogeneous rather than 'cored'. However, the material is not entirely homogeneous because the material between the  $\alpha$ -spheroids starts to melt at about the same temperature as the Scheil calculations predict. The highest knee in the DSC curve is

then occurring above the knee in the predictions. This is likely to be due to kinetic factors. Above this knee, it is the  $\alpha$ -solid solution spheroids which are melting rather than any eutectic. The lack of a 'sharp' knee suggests that this process is occurring at different stages at various places in the material. It is not clear why the DSC curve then lies above the predictions. To return to the justification for criterion 1 in Section 1, using the DSC curve, the first 50%-60% of the liquid is being formed in a temperature interval of about 10K (and hence a time of about 1 min given the DSC heating rate of 10K/min), but the next 40-50% liquid (obtained by melting  $\alpha$ -solid solution spheroids) is taking about 4 min to form. This is the basis for the argument that the existence of a knee around 50% liquid gives controllability in the thixoforming process.

Examining Fig. 2 for 2014, the DSC heating curve follows the shape of the equilibrium curve more closely than that of the Scheil, supporting our premise that extruded material should give results closer to equilibrium because the elements should be distributed relatively homogeneously. However, at a particular temperature the amount of liquid in the DSC heating curve lags behind that predicted. This must be due to kinetic factors (it takes nearly 9 mins for 10% liquid to form) in that the melting is almost all of  $\alpha$ -solid solution spheroids, there being little, if any eutectic in the structure. On cooling, it is not clear why there is a discrepancy between the DSC and the predicted curves, but the cooling curve then follows the shape of the Scheil curve more closely than that in equilibrium, probably due to the inhomogeneous melt resulting from no soaking time before cooling. Towards the end, elements capable of taking part in a eutectic reaction are co-located, so that a knee is observed.

In this paper, the focus has been on Scheil predictions for the purposes of comparison and for clarity of presentation, although as discussed above there is some evidence from DSC that equilibrium may be more appropriate for alloys in a wrought starting condition. In terms of the thixoformability criteria, the slope of the fraction liquid versus temperature curve at 40% liquid tends to be similar for Scheil and equilibrium predictions, with the equilibrium curve slightly steeper (see Fig. 2). For the solidus-liquidus interval, the equilibrium curve tends to give a narrower interval than the Scheil. More alloys will be excluded as a result of this criterion with Scheil results than with equilibrium. Hence, the Scheil results will tend to be conservative from a practical point of view. This is probably appropriate given the difficulties with hot tearing (the basis for this criterion).

The finding that the fractions liquid calculated by using MTDATA/equilibrium are lower than those calculated by applying MTDATA/Scheil agrees with work in [22,23]. Chen and Huang [24] argue that it is likely that some solid state diffusion does occur during solidification, while concentration gradients still exist, and the real fraction liquid should fall between the predictions from MTDATA/equilibrium and MTDATA/Scheil. They found that ~20 K discrepancy was observed in the DTA (differential thermal analysis) cooling curve for binary alloys Al-10wt%Cu, Al-4.5wt%Cu, Al-6.5wt%Mg and Al-4.25wt%Mg, compared with the solidification curves calculated by the lever model and Scheil model [24]. A similar discrepancy was found between predictions from MTDATA/Scheil with Thermo-Calc software and experimental results via computer-aided cooling slope curve analysis (CA-CCA) by Aliravci et al. [25] for solidification of commercial alloys AA1050, AA5182 and

AA6111. Empirical correction factors were needed to normalize the Scheil fraction solid versus temperature curves at different cooling rates.

There are sources of uncertainty in the MTDATA calculations. These include:

- 1) Uncertainty in specification of the composition. Alloy specifications provide limits for the various amounts of elements. If the slope of the liquidus with respect to the amount of a particular element is large then a different liquidus temperature could be predicted for nominally the same alloy even if the modelling and calculations were perfect.
- 2) Parameters in the database not giving 'true' equilibria. Generally for low order systems, binaries say, the calculated results can be thought of as 'the results that would be obtained from the perfect experiment' as they represent the distillation of many different phase diagram and thermodynamic studies. (The prediction is not simple curve fitting as thermodynamic measurements such as activities/enthalpies of mixing etc. are modelled as well as phase diagram information). If a few elements are added to a well known binary system, such as Al-Si or Al-Cu, to form a multicomponent system then extra uncertainties should be small as the basis binary will not be perturbed much. Uncertainties will be larger if many assessed low order systems are combined to form a multicomponent system with many elements present in large amounts.
- 3) Missing phases. In general, it may be that there is a phase that is important in the multicomponent system of interest but which is not included in the database. This should not be the case here as these are well characterised systems.

- 4) Assumption of ideal interactions between components. For some interactions between elements data is missing and the assumption is made that the interaction is 'ideal'. This is a source of uncertainty but again should be minimal in the calculations here where the elements are common alloy components.
- 5) Bulk material. MTDATA calculates a result for a bulk material. Kinetics may have a part to play in reality and results may be different for systems on a very small scale. This may contribute to the discrepancy between the DSC results (which are for relatively small samples) and the predictions.

To quantify these uncertainties in detail is the subject of further work.

## 5.2 Anomaly in thermodynamic prediction

Although thermodynamic modelling seems to be a promising approach to identify alloy compositions suitable for thixoforming, there are some anomalies. For example, in the predictions by MTDATA/Scheil, alloys A356 and A357 give very steep slopes in fraction liquid versus temperature curves in the thixoforming regime (30-50% liquid), steeper than those for wrought aluminium alloys such as 2014, 6082, 7075 and 7010. Predicted results (using Thermo-Calc software in combination with the Al-DATA database [17]) suggest that the suitable fraction liquid range for stable processing (i.e. where the slope of fraction liquid versus temperature is gentler) is 50-70% for alloy A356 rather than 30-50% which implies alloy A356 is more suitable for rheocasting than for thixoforming. However, in fact, both alloys A356 and A357 have been used widely in commercial thixoforming. As discussed above in relation to

criterion 1, the origin of this anomaly may lie in the kinetics of melting of  $\alpha$ -solid solution in that, although the slope between 30% liquid and 50% liquid is steep, the existence then of the knee at around 50% liquid allows control of the process; the knee, in effect, acts as a 'brake' on the liquid formation. The fact that this occurs at around 50% liquid (i.e. the percentage of liquid at the limit before slumping) for A356 and A357 is, in essence, the reason why these materials are so suitable for thixoforming. Therefore, we can conclude that, if the curve of fraction liquid versus temperature is steep in the 30-50% liquid regime, then there must be a 'knee' at around 50% liquid or just below for the alloy to be thixoformable. There is, in effect, an interplay between the thermodynamic driving force and the kinetics of melting [26].

In contrast to A356 and A357, 6082 has an equally steep fraction liquid versus temperature curve between 30 and 50% liquid (see Fig. 4), but there is no 'knee' to put a brake on liquid formation, and the alloy is not amenable to thixoforming.

### 5.3 The effect of addition of copper to alloy A356

Alloy A356 has excellent casting characteristics, weldability, pressure tightness, and corrosion resistance. It is heat treatable to provide various combinations of tensile and physical properties that are attractive for many applications, including aircraft and automotive parts [27]. The addition of copper to Al-Si alloys causes precursors to  $\text{CuAl}_2$  phases and other intermetallic compounds to form which increase strength and heat treatability [28]. However, the addition of copper also reduces hot tear resistance and decreases castability [29]. Alloy A356 solidifies over a relatively narrow

temperature range of around 60 K, with the final stages of solidification involving about 50% eutectic liquid. Therefore, the feeding of the last eutectic liquid to solidify is relatively easy and porosity is rare. With the addition of copper to alloy A356, the solidification interval is enlarged significantly with a range of 117 K for the initial addition of 1 wt% Cu. The solidification interval decreases slowly to 91 K as the copper content increases to 10 wt%. Cáceres et al. [30] investigated the effect of copper additions between 0 and 1% on the level of porosity in Al-Si-Mg alloy (A356) and found that a copper content exceeding 0.2% results in a 7-fold increase in dispersed microporosity, which is related to the formation of interdendritic ternary liquid that solidifies at a lower temperature than the Al-Si eutectic and is therefore difficult to feed. However, increasing the levels of copper beyond 1% and up to 4% results in a relatively small increase in porosity [31]. The MTDATA/Scheil prediction also showed that the addition of copper to alloy A356 decreases the fraction liquid sensitivity at 0.4 fraction liquid and enlarges the working window between 0.3 and 0.5 fraction liquid which is of benefit to thixoforming.

#### 5.4 Effect of silicon on alloy 2014

Alloy 2014 is one of the heat treatable high strength wrought aluminium alloys. Due to its wide solidification interval (131K by DSC) and the fact that less eutectic liquid is available in the last stages of solidification than for the casting alloy A356, 2014 is considered to be more prone to the formation of porosity. In order to increase the proportion of the eutectic, i.e. increase the 'highest knee' in the fraction liquid vs. temperature curve, and improve the castability for alloy 2014, silicon was added.

MTDATA/Scheil prediction shows that this increases the amount of eutectic and decreases the solidification interval which should improve the thixofomability.

### 5.5 Effect of silicon and copper on the constitution of Al- Si-Cu-Mg alloys

MTDATA/Scheil predictions show, for alloy Al-4.4Cu-0.5Mg-xSi, when the silicon content is 0.8 wt%, that the primary  $\alpha$ -aluminium dendritic network forms below 642°C, leading to a monotonic increase in the concentration of copper in the remaining liquid. At about 506°C, a eutectic of CuAl<sub>2</sub> with interspersed  $\alpha$ -aluminium forms. When  $2 \leq Si(wt\%) \leq 10$ , a primary  $\alpha$ -aluminium dendritic network forms, then the eutectic solid mixture of silicon and  $\alpha$ -aluminium forms at the Al-Si eutectic temperature (around 560°C), leading to further increase of the copper content in the remaining eutectic liquid. The amount of aluminium-silicon eutectic increases with the increase in silicon content (see Fig. 6b). Thixoforming requires precise control of feedstock reheating to obtain a fraction liquid between 30 and 50%. Heating must accomplish melting of the eutectic without also melting too much of the  $\alpha$ -aluminium phase. A lower amount of liquid phase (less than 30%) could impede the flow of solid phase during thixoforming, however it would become difficult to control the heating temperature and fraction liquid if there was too much liquid (more than 50%), resulting in slumping or tilting known as “elephant footing” because there is a tendency for liquid to migrate to lower billet extremes when the fraction liquid is over 50% [32]. When the silicon content is 15 wt%, the primary phase is not  $\alpha$ -Al but primary silicon crystal and then the eutectic mixture of silicon and  $\alpha$ -aluminium forms. For alloy Al-0.5Mg-0.8Si-xCu (Fig. 6a), the eutectic amounts to less than 8.0% at  $1 \leq Cu(wt\%) \leq 3$ . When the copper content increases to 4.4%, the primary  $\alpha$ -

aluminium dendritic network forms and this is followed by the formation of  $\alpha$ Al-CuAl<sub>2</sub> eutectic . With the copper content increasing from 4.4 to 20 wt%, the amount of  $\alpha$ Al-CuAl<sub>2</sub> eutectic increases from 11.6 to 56.9%. The increase of eutectic is of benefit to thixoforming due to the associated decrease in hot tearing susceptibility. This is also confirmed by Spittle and Cushway [33] who showed that Al-Cu alloys (normally with a wide solidification interval) containing more than 7 wt% Cu exhibited minimal and zero hot tearing susceptibility because the higher volume fraction of eutectic in the alloys ensures interdendritic feeding and healing of incipient tears.

Compared with copper, the addition of silicon is more effective in increasing the amount of eutectic, i.e. the addition of 1 wt% silicon increases eutectic from 7 to 11% but the addition of 1 wt% copper increases eutectic from 1.4~2.9% (see Fig. 6a and b).

#### 5.6 Promising alloys predicted to be suitable for thixoforming

Alloys A356 and A357 have been used widely in semi-solid metal processing in recent years. Other aluminium alloys that have been developed for semi-solid processing or are in process of development include: AlSi6Cu1Mg (C355) intended for achieving higher strength than alloy 357 while requiring only a T5 temper; AlSi6Cu3Mg (319) intended for achieving high tensile, yield strength and hardness in the T6 condition with some sacrifice in ductility; AlMg5Si2 designed for thin walled parts (with no heat treatment) requiring medium yield strength and high elongation; hyper-eutectic aluminium-silicon alloys intended for wear resistant parts [32] and

alloy AlSi4Cu2.5Mg [34]. In the present work, commercial casting alloys 308 (Al-5.5Si-4.5Cu), 319 (Al-6Si-3.5Cu), 238 (Al-10Cu-4Si-0.3Mg) and 355 (Al-5Si-1.3Cu-0.5Mg) and modified alloys based on 2014, Al-4.4Cu-0.5Mg-(4~6)Si, and a range alloys ( $(7.5 \leq \text{Si} + \text{Cu} \leq 9$  and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$ ) and alloys ( $9 < \text{Si} + \text{Cu} \leq 10$  and  $\text{Si}/\text{Cu} = 1.5$ ) based on Al-Si-Cu-Mg system have been identified to be promising alloys for thixoforming. The predictions in this work include most of the alloys which have been tested in practical thixoforming. However it is difficult to explore the whole alloy space with the thermodynamic prediction method. Hence, for example Al-7Si-3Cu-Mg (A57U3G), has not been included (it does not match the compositions in Table 2 because Mg is not 0.5 wt%), but is thixoformable with high tensile properties (UTS 440 MPa, YS 340 MPa, EL 9~10%) [35]. Also some alloys such as alloys Al-7Si-0.3Mg-(1~4)Cu are possible candidates allowing for discrepancies and anomalies in thermodynamic prediction.

## 6. Conclusions

MTDATA thermodynamic software (supplied by the UK National Physical Laboratory) has been used to investigate the effects of compositional variations, in particular the effect of added copper on the thixoformability of alloy A356 (Al-7Si-0.3Mg, wt%) and the effect of added silicon on the thixoformability of alloy 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%). The slopes of the curves of fraction liquid vs. temperature at 40% fraction liquid become less steep and the working window between 30 and 50% fraction liquid is enlarged by adding up to 10 wt% copper to alloy A356. The addition of silicon increases the amount of eutectic and decreases the solidification interval in alloy 2014. This should benefit

thixoformability and also decrease the tendency for formation of porosity. A range of alloy compositions based on Al-Si-Cu and Al-Si-Cu-Mg have been evaluated according to criteria for thixoformability. Those which are most suitable according to these criteria include alloys 308 (Al-5.5Si-4.5Cu, wt%), 319 (Al-6Si-3.5Cu, wt%), 238 (Al-10Cu-4Si-0.3Mg, wt%), 355 (Al-5Si-1.3Cu-0.5Mg, wt%) and 2014 based alloys Al-4.4Cu-0.5Mg-(4~6)Si. Alloys with  $7.5 \leq \text{Si} + \text{Cu} \leq 9$  and  $1.5 \leq \text{Si}/\text{Cu} \leq 2.33$  and alloys with  $9 < \text{Si} + \text{Cu} \leq 10$  and  $\text{Si}/\text{Cu} = 1.5$  also satisfy the criteria. The 'highest knee' in the fraction liquid vs. temperature curve, i.e. the temperature at which  $\alpha$ -solid solution starts melting, plays a critical role in putting a 'brake' on the liquid formation if the fraction liquid versus temperature curve is steep in the 30 to 50% liquid regime.

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Table 1 Solidification parameters given by MTDATA/Scheil for alloy A356 and alloy A356 modified with added copper (Al-7Si-0.3Mg-xCu, wt%)

Cu (wt%)	$T_s$ (°C)	$T_l$ (°C)	$\Delta T^{\text{solidus/liquidus}}$ (K)	$(df_L / dT)_{f_L=0.4}$ (K <sup>-1</sup> )	$\Delta T^{0.3/0.5}$ (K)
0 *	570	632	62	0.067	4
0	557	616	59	0.133	1
1	496	613	117	0.067	3
2	496	610	114	0.040	5
3	495	607	112	0.029	7
4	495	604	109	0.022	10
10	495	586	91	0.007	32

\*DSC data from Tzimas [12]

Table 2 Solidification parameters given by MTDATA/Scheil for Al-Si-Cu and Al-Si-Cu-Mg casting alloy systems

Alloys	Si	Cu	Mg	Solidification interval (°C)	Amount eutectic (%)	Slope at 0.4 liquid $K^{-1}$	Process window (K)
308	5.5	4.5		107	46.83	0.022	15
319	6	3.5		106	49.40	0.029	9
380	8.5	3.5		89	70.76	0.029	8
383	10.5	2.5		77	86.55	0.04	5
384	11.2	3.8		68	95.65	0.027	8
208	3	4		125	26.23	0.006	38
295	1.1	4.5		135	12.56	0.01	22
296	2.5	4.5		126	22.97	0.006	35
238	4	10	0.3	112	43.14	0.007	46
332	9.5	3	1	92	77.47	0.02	11
354	9	1.8	0.5	101	71.79	0.04	6
355	5	1.3	0.5	129	37.16	0.005	26
390	17	4.5	0.6	157	94.00	0.017	13

Table 3 Effects of Si+Cu and Si/Cu on the fraction liquid curves given by

MTDATA/Scheil for alloys Al-Si-Cu-Mg (wt%) (with Mg 0.5wt%)

Si+Cu (wt%)	Si/Cu	Si (wt%)	Cu (wt%)	$\Delta T^{s/l}$ (K)	Eutectic (%)	$\Delta T^{0.3/0.5}$ (K)	$(df_L / dT)_{f_L=0.4}$ K <sup>-1</sup>
7.5	1.5	4.5	3.0	128	35.8	33	0.004
8	1.5	4.8	3.2	125	38.6	29	0.004
9	1.5	5.4	3.6	120	44.3	20	0.022
10	1.5	6.0	4.0	115	49.7	11	0.020
12	1.5	7.2	4.8	104	61.0	7	0.015
9	1.5	5.4	3.6	120	44.3	20	0.022
9	2	6.0	3.0	118	47.9	12	0.029
9	2.33	6.3	2.7	117	50.1	8	0.025

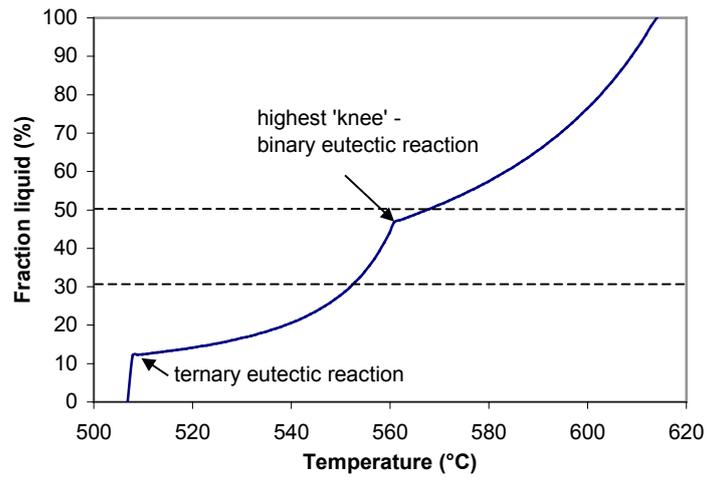


Figure 1. Schematic of a typical fraction liquid versus temperature curve from MTDATA prediction

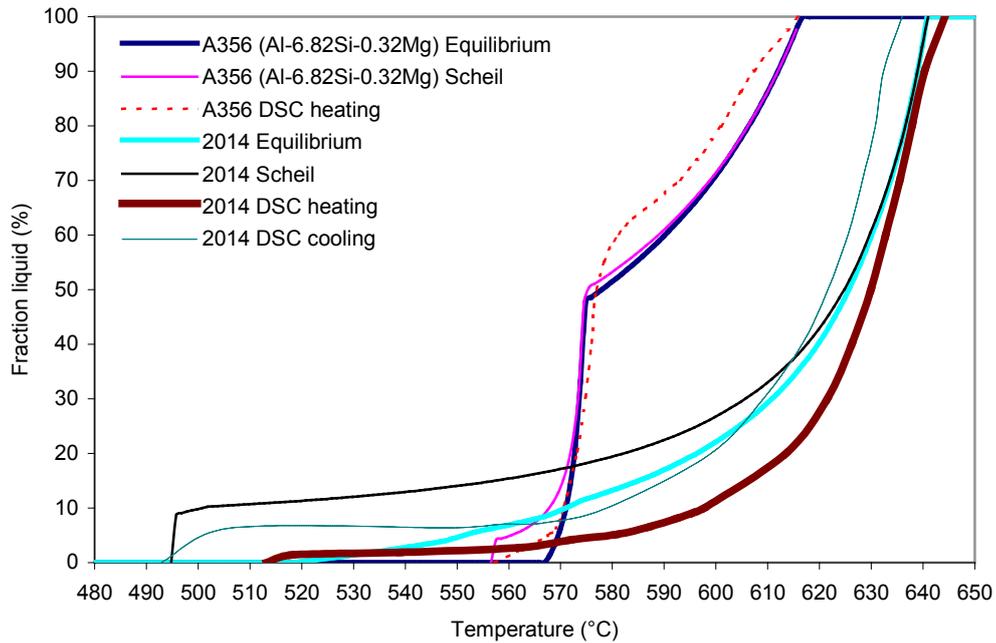


Fig. 2 Fraction liquid vs. temperature from MTDATA and DSC (rate 10K/min) for as-cast alloy A356 (Al-6.82Si-0.32Mg-0.022Cu-0.005Zn-0.112Fe-0.1Ti-0.013Pb-0.042Sn-0.006Ni-0.005Cr, wt%), and as-extruded alloy 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%). The MTDATA calculations for A356 are for a simplified alloy: Al-6.82Si-0.32Mg wt%. For 2014, the composition for the MTDATA calculation is the same as for the DSC sample.

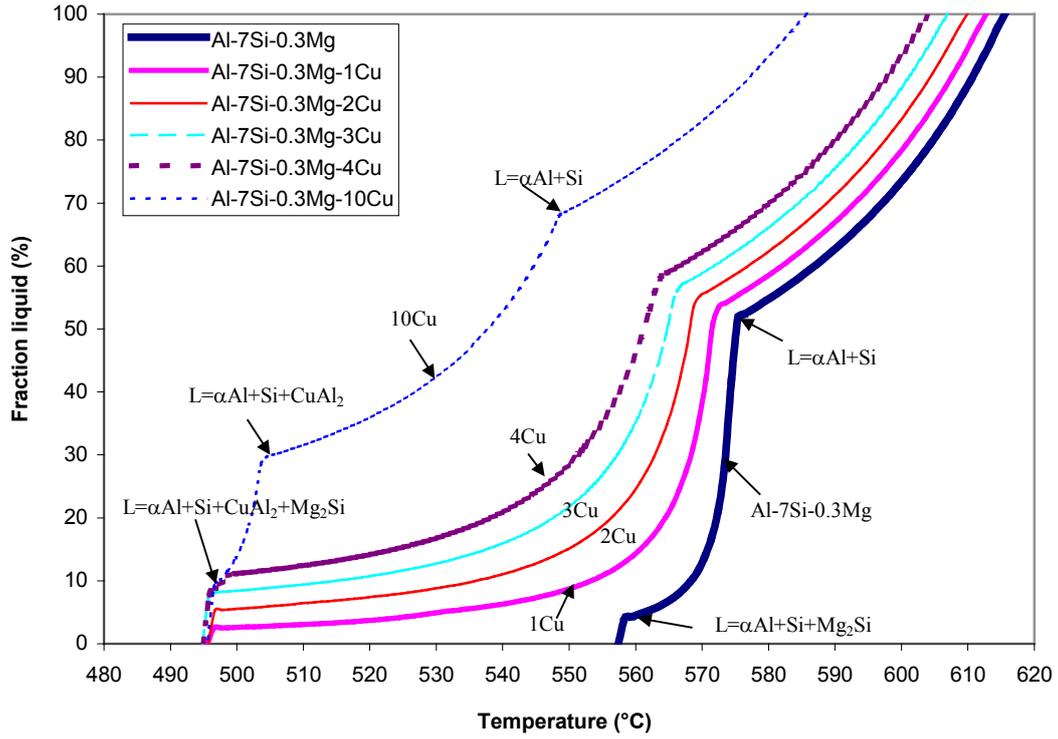


Fig. 3 Fraction liquid vs. temperature given by MTDATA/Scheil prediction for alloy A356 (Al-7Si-0.3Mg) and A356 modified with added Cu

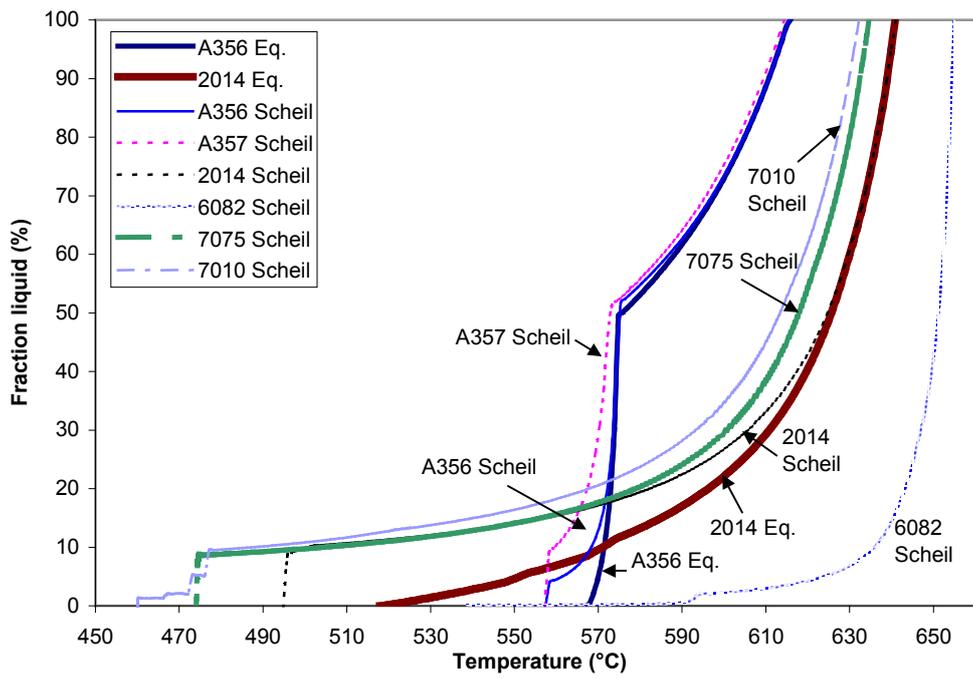


Fig. 4 Fraction liquid vs. temperature given by MTDATA/Scheil and MTDATA/Equilibrium for some cast and wrought aluminium alloys

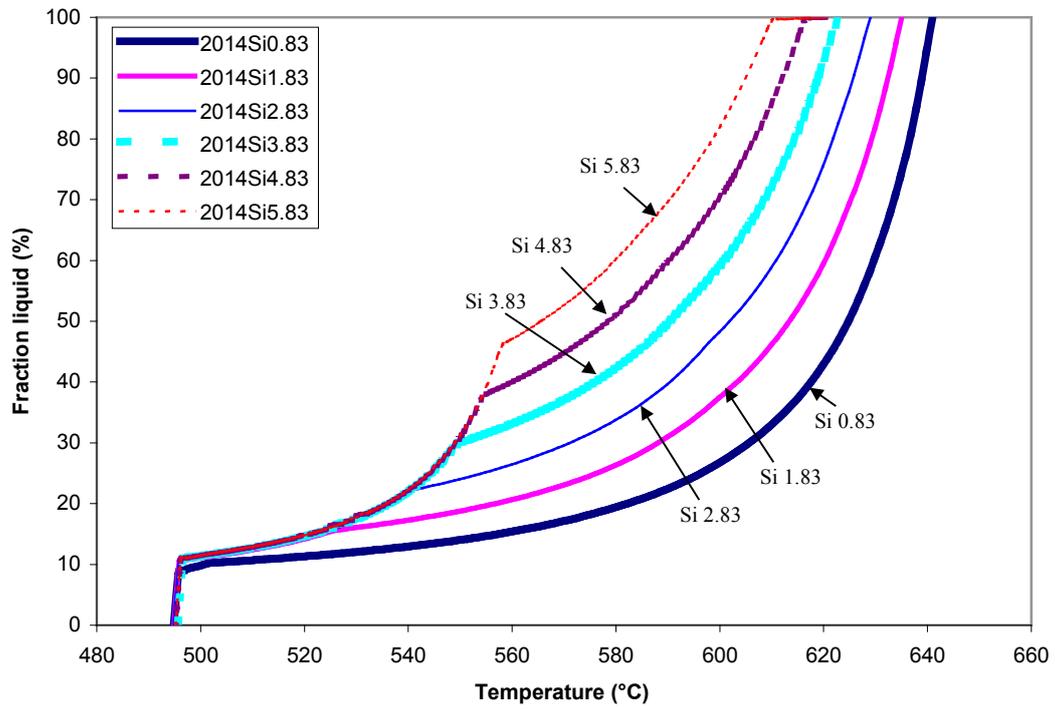


Fig. 5 Effect of element Si on fraction liquid vs. temperature for alloy 2014 (Al-3.91Cu-0.47Mg-0.83Si-0.29Fe-0.55Mn, wt%) given by MTDATA/Scheil

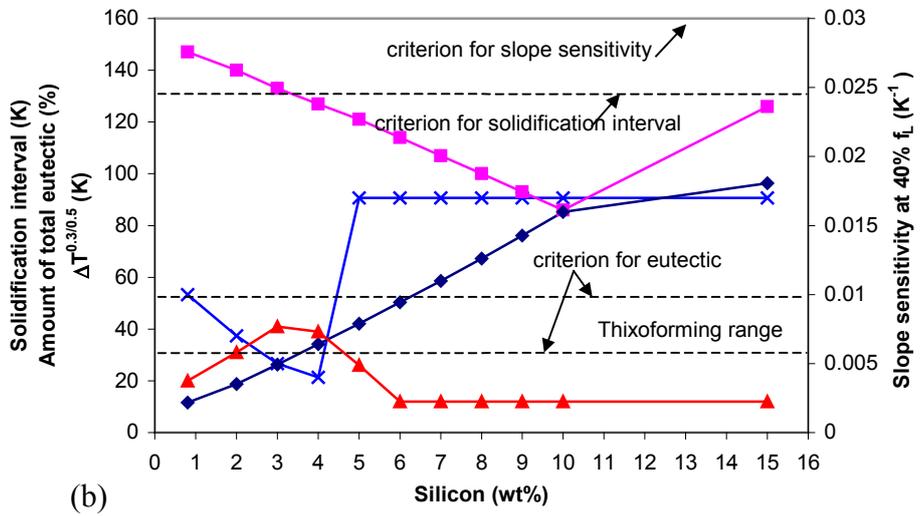
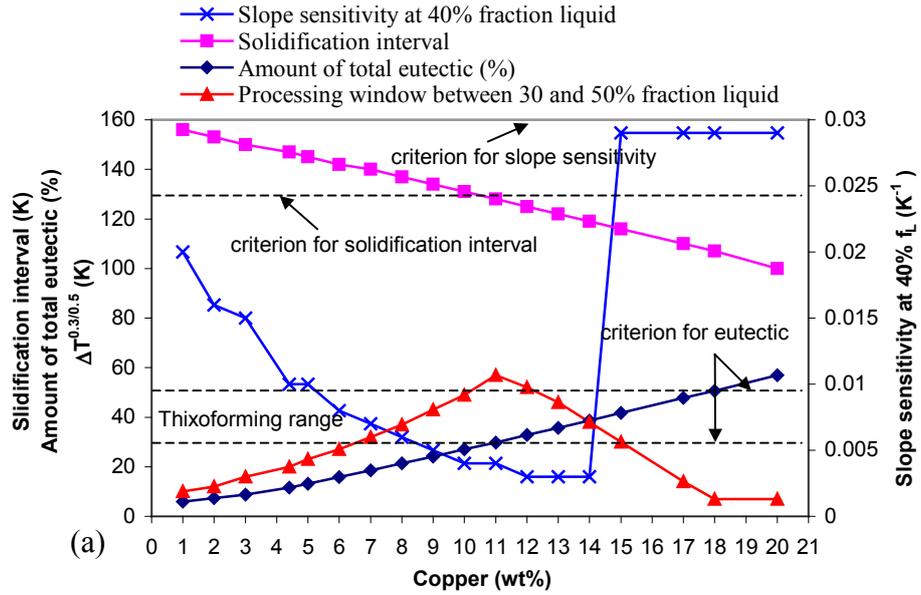


Fig. 6 Solidification parameters estimated by MTDATA/Scheil for (a) alloys Al-xCu-0.5Mg-0.8Si (wt%) and (b) alloys Al-4.4Cu-0.5Mg-xSi (wt%). The criteria are those defined at the end of Section 1.

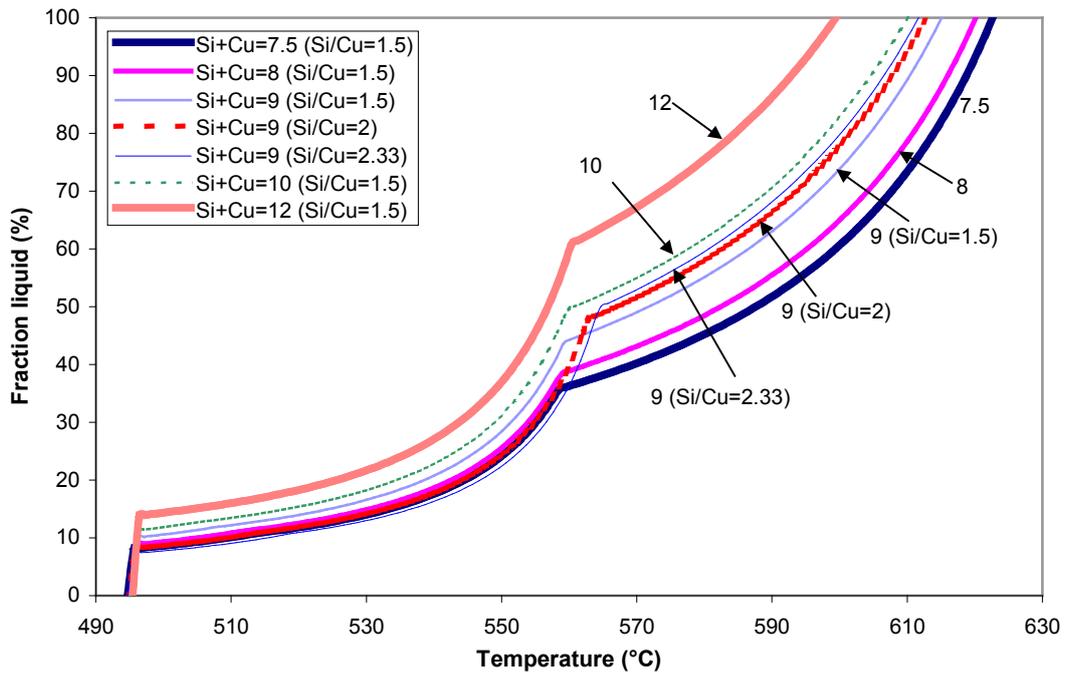


Fig. 7 Fraction liquid vs. temperature given by MTDATA/Scheil for Al-Si-Cu-Mg alloys showing the effects of Cu+Si and Si/Cu on the curves

