

Modelling the Semi-Solid Processing of Metallic Alloys

H.V. Atkinson

Department of Engineering, University of Leicester, University Rd., Leicester, LE1
7RH, UK.

Abstract

Semi-solid processing of metallic alloys and composites utilises the thixotropic behaviour of materials with non-dendritic microstructure in the semi-solid state. The family of innovative manufacturing methods based on this behaviour has been developing over the last twenty years or so and originates from scientific work at MIT in the early 1970s. Here, a summary is given of:- routes to spheroidal microstructures; types of semi-solid processing; and advantages and disadvantages of these routes. Background rheology and mathematical theories of thixotropy are then covered as precursors to the main focus of the review on transient behaviour of semi-solid alloy slurries and computational modelling. Computational Fluid Dynamics (CFD) can be used to predict die filling. However, some of the reported work has been based on rheological data obtained in steady state experiments, where the semi-solid material has been maintained at a particular shear rate for some time. In reality, in thixoforming, the slurry undergoes a sudden increase in shear rate from rest to 100s^{-1} or more as it enters the die. This change takes place in less than a second. Hence, measuring the transient rheological response under rapid changes in shear rate is critical to the development of modelling of die filling and successful die design for industrial processing.

The modelling can be categorised as one phase or two phase and as finite difference or finite element. Recent work by Alexandrou and co-workers and, separately Modigell and co-workers, has led to the production of maps which, respectively summarise regions of stable/unstable flow and regions of laminar/transient/turbulent fill. These maps are of great potential use for the prediction of appropriate process parameters and avoidance of defects. A novel approach to modelling by Rouff and co-workers involves micro-modelling of the 'active zone' around spheroidal particles. There is little quantitative data on the discrepancies or otherwise between die fill simulations and experimental results (usually obtained through interrupted filling). There are no direct comparisons of the capabilities of various software packages to model the filling of particular geometries accurately. In addition, the modelling depends on rheological data and this is sparse, particularly for the increasingly complex two-phase models. Direct flow visualisation can provide useful insight and avoid the effects of inertia in interrupted filling experiments.

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Glossary of Symbols in the Order in Which They Appear in the Text

(There is some overlap, particularly for constants, but confusion is avoided by identifying symbols with the equation in which they appear)

τ	Shear stress
$\dot{\gamma}$	Shear rate
η	Viscosity
τ_y	Yield stress
k	Constant related to the viscosity in equations (1)-(3)
n	Shear rate exponent in equations (2) and (3)
η_∞	Viscosity as the shear rate tends to infinity
η_0	Viscosity as the shear rate tends to zero
f_s	Fraction solid
λ	Structural parameter varying between 1 for completely built up and 0 for completely broken down
t	Time
a, b, c, d	Constants in equation (5)
k_1, k_2	Constants for breakdown and buildup in equation (6)
p, q	Exponents in equation (6)
N	Average number of links per chain in equation (7)
k_0, k_1, k_2	Rate constants in equation (7)
P	Number of single particles per unit volume in equation (7)
N_e	Average number of links per chain at equilibrium in equation (8)
η_e	Equilibrium viscosity
K, r	Constant and exponent in equation (10)
k, m	Material constants in equation (11)
η_p	Peak-stress viscosity in Table 2
η_{ss}	'First' steady-state viscosity in Table 2, i.e. after the 'fast' breakdown process as opposed to the 'slow'
τ_b	'First' breakdown time in Table 2 i.e. for the 'fast' breakdown process
$A(\lambda)$	Hydrodynamic coefficient as a function of λ in equation (12), Table 4 and also in equations (25) and (29), Table 5
c	Effective volume packing fraction solid in equation (12), Table 4 and in equation (25) and (29), Table 5
c_{\max}	Maximum effective volume packing fraction solid in equation (12), Table 4 and in equation (25) and (29), Table 5
η_f	Viscosity of fluid
$C(T)$	Exponential function of temperature in equation (12), Table 4 and in equation (25) and (29), Table 5
H	Agglomeration function in equation (13), Table 4 and in equation (26), Table 5
G	Disagglomeration function in equation (13), Table 4 and in equation (26), Table 5
\underline{u}	Velocity vector

ω	Inverse of the relaxation time in equation (14), Table 4
b_1, b_2	Constants in equation (15), Table 4
c	Constant in equation (16), Table 4
α	Rate constant for thinning in equation (18), Table 4
β	Rate constant for thickening in equation (18), Table 4 and also in equation (24), Table 4
B, k^*	Coefficients in equation (19), Table 4
κ	Structural parameter in equation (19), Table 4, varying between zero (fully broken down) and infinity (fully built up)
κ_e	Equilibrium value of κ
a, b	Constants in equation (20), Table 4
A, B	Coefficients in equation (23), Table 4
τ	Shear stress tensor in equations in Table 5
$\Delta \mathbf{u}$	Rate of deformation tensor in equations in Table 5
D_{II}	Second invariant of the rate of strain tensor in equations in Table 5
m	Coefficient in equation (27), Table 5
u	Velocity scalar
ρ	Density
K, G	Coefficients in equation (31), Table 5
τ_{ij}	Viscous stress tensor in equation (33), Table 5
D_{ij}	$u_{ij} + u_{ji}$ in equation (33), Table 5
m	Coefficient controlling the exponential rise in stress in equation (33), Table 5
K	Coefficient in equation (34), Table 5
a, b, c	Coefficients in equation (40), Table 5
λ_e	Equilibrium value of the structural parameter in equation (41), Table 5
D	Rate of strain tensor in equation (42), Table 5
σ	Flow stress in equation (45), Table 5 and subsequent equations
ε	Strain in equation (45), Table 5
$\dot{\varepsilon}$	Strain rate
a, b, m, n	Coefficients and exponents in equation (45), Table 5
T	Temperature
$\dot{\gamma}_0$	Strain rate cut-off in the PowerLaw Cut-Off model, equations (47) and (54), Table 5
K	Current yield stress in equation (48), Table 5
K_0	Yield stress in equation (48), Table 5
$\bar{\varepsilon}$	Effective strain in equation (48), Table 5
σ_0	True stress at the solidus temperature and a strain rate $\dot{\varepsilon}_0$ of 1 s^{-1} in equation (48), Table 5
τ_M	Maxwell time η/E where E is the Young's modulus at the temperature under investigation (equation (48), Table 5)
R_b	Bond radius in equation (48), Table 5
R	Average radius of the primary particles in equation (48), Table 5

	$(R_b / R \approx 0.25)$
Q	Activation energy for self-diffusion in equation (48), Table 5
R	Ideal gas constant in the exponential term in equation (48), Table 5
m	Material exponent in equation (48), Table 5
$\dot{\gamma}$	Strain rate tensor
η_0	Viscosity at a characteristic shear strain rate $\dot{\gamma}_c$ in equation (54), Table 5
$\dot{\gamma}_c$	Characteristic shear strain rate in equation (54), Table 5
$\bar{\sigma}$	Effective stress in equation (56), Table 6
S	Separation coefficient in equation (56), Table 6
K, m, β	Coefficients in equation (56), Table 6
$\bar{\varepsilon}_{cr}, \bar{\varepsilon}_{cr1}$	Critical strain I and critical strain II in equation (56), Table 6
b	'Breakage ratio' in equation (58), Table 6
f_A^s	Volume solid fraction of the 'active zone' in equation (60), Table 6
f^c	Critical fraction solid in equation (60), Table 6
D, n	Material parameters in equation (60), Table 6
Bi	Bingham number
Re	Reynolds number

1. Introduction to Semi-Solid Processing

Mascara, honey and certain kinds of paint are all thixotropic. When they are sheared they flow, when allowed to stand they thicken up again; their viscosity is shear rate and time dependent. Spencer et al. [1] first discovered such behaviour in semi-solid metallic alloys in the early 1970s when investigating hot tearing with a rheometer. If the material was stirred continuously during cooling from the fully liquid state to the semi-solid state the viscosity was significantly lower than if the material was cooled into the semi-solid state without stirring. Stirring breaks up the dendrites which would normally be present so that the microstructure in the semi-solid state consists of spheroids of solid surrounded by liquid (Fig.1). It is this microstructure which is a requirement for thixotropic behaviour and for semi-solid processing. When such a semi-solid microstructure is allowed to stand, the spheroids agglomerate and the viscosity increases with time. If the material is sheared, the agglomerates are broken up and the viscosity falls. In the semi-solid state, with between 30 and 50% liquid, if the alloy is allowed to stand it will support its own weight and can be handled like a solid. As soon as it is sheared, it flows with a viscosity similar to that of heavy machine oil. This is the behaviour which is exploited in semi-solid processing [2] and which is illustrated in Fig. 2, where the alloy can be cut and spread like butter.

Nearly 30 years of work and effort have been invested in the field of semisolid processing and the increase in interest in this field has been marked by seven international conferences [3-9] with an eighth planned in Cyprus in 2004. Semisolid processing is rivalling other manufacturing routes for military, aerospace and most notably automotive components [10-12]. In Europe, suspension parts, engine brackets

and fuel rails for automobiles are being produced. In the USA, examples include mechanical parts for mountain bikes and snowmobiles [13], while in Asia there is concentration on the production of electronic components such as computer notebook cases and electrical housing components, particularly in magnesium alloys via Thixomolding [e.g.12]. Fig. 3 shows some of the components produced by Thixoforming at Stampal for an Alfa Romeo car.

1.1 Routes to Spheroidal Microstructures

There are many different routes for obtaining non-dendritic microstructures. The main ones are described here.

- 1) MagnetoHydroDynamic (MHD) Stirring: This involves stirring electromagnetically (and hence without the contamination, gas entrapment and stirrer erosion involved in mechanical stirring) in the semi-solid state to break up the dendrites [e.g.14]. Much of the commercial production of aluminium alloy components to date has been based on MHD material supplied by Pechiney and SAG. There are some problems associated with this route including lack of uniformity and the fact that the spheroids are not completely round with some 'rosette' character remaining.
- 2) Sprayforming: Sprayforming is a relatively expensive route but one which can be used to produce alloys, which cannot be produced in any other way, such as aluminium-silicon alloys with greater than 20 wt.% silicon [e.g. 15]. Sprayforming essentially involves the atomisation of a liquid metal stream and collection of the droplets on a former. The resulting microstructure is fine and equiaxed. When heated into the semi-solid state it is ideal for thixoforming [16].

- 3) Strain Induced Melt Activated (SIMA)/ Recrystallisation And Partial Melting (RAP): These routes are similar but distinct. The material is worked, e.g. by extrusion. On reheating into the semi-solid state, recrystallisation occurs and the liquid penetrates the recrystallised boundaries so resulting in spheroids surrounded by liquid. The SIMA route [17] involves hot working and the RAP route [18] warm working. The advantages of these routes are that some alloys are supplied in the extruded state in any case and the spheroids are more fully rounded than those from the MHD route. The main disadvantages are that there may be variation in the amount of stored work across the section, resulting in inhomogeneity, and extrusion can be difficult and expensive with wider billet diameters.
- 4) Liquidus/Near-Liquidus Casting: There have been recent developments in producing feedstock by manipulating the solidification conditions. The UBE New RheoCasting (NRC) process [19,20] is based on this principle with the molten metal at near-liquidus temperature poured into a tilted crucible and grain nucleation occurring on the side of the crucible. The grain size is fine because the temperature is near liquidus. An allied technique is the Direct Thermal Method [21]. In the Cooling Slope method [22], liquid metal is poured down a cooled slope and collects in a mould. Nucleation on the slope ensures the spheroid size is fine. With liquidus casting, a high rate of nucleation can be achieved within the entire volume of undercooled melt [23, 24].
- 5) 'New MIT Process': This is a recently developed hybrid of stirring and near liquidus casting [25,26] (Fig. 4). A stirrer that also provides the cooling action is inserted into an alloy melt held a few degrees above the liquidus. After some

seconds of stirring, the melt temperature decreases to a value which corresponds to a fraction of solid of only a few percent and the stirrer is withdrawn.

- 6) Grain Refinement: Grain refined alloys can give equiaxed microstructures [e.g.26] but it is difficult to ensure the grain structure is uniformly spheroidal and fine and the volume of liquid entrapped in spheroids tends to be relatively high.
- 7) Semi-Solid Thermal Transformation: Spheroidal structure can also be produced by heating a dendritic structure to the semisolid temperature range for a period of time. This is known as semi-solid thermal transformation, or SSTT [27] The structures produced by this route tend to be relatively coarse (around 100 μm diameter particles).

Other methods are summarised in [2, 12, 28].

1.2 Types of Semi-Solid Processing

‘Semi-solid processing’ now covers a whole family of processes. The terminology is as follows.

‘Rheocasting’ refers to the process where the alloy is cooled into the semi-solid state and injected into a die without an intermediate solidification step. A typical rheocaster is shown in Fig. 5. The non-dendritic microstructure can be obtained by a variety of means during cooling (e.g. by mechanical stirring, by stimulated nucleation of solid particles as in the New RheoCasting NRC process recently patented by UBE [19,20] (see Fig. 6), or by electromagnetic stirring in the shot sleeve as in the New Semi-Solid Metal Casting process from Hitachi [30] (see Fig. 7). The NRC process involves pouring molten alloy, at a temperature slightly above the liquidus, into a steel

crucible and then controlled cooling to achieve a spheroidal microstructure before transfer to a forming machine. There is no need for specially treated thixoformable feedstock and scrap can be readily recycled within the plant. Hall et al [20] showed that the NRC route has a lower unit cost than Thixoforming, due to the lower starting material cost.

'Rheomoulding' is allied to polymer injection moulding, and uses either a single screw [31,32] or a twin screw [33,34] (Fig 8). Liquid metal is fed into a barrel where it is cooled while being mechanically stirred by a rotating screw. The semisolid material is then injected into a die cavity. Such processes are suitable for continuous production of large quantities of components and do not require specially produced feedstock material (at a price premium).

'Thixo' usually refers to processes where an intermediate solidification step does occur. There are exceptions to this e.g. 'Thixomolding'.

'Thixomolding' is the process licensed by the firm called 'Thixomat'[35,36]. It is now used by numerous companies, particularly in Japan and the US, to produce magnesium alloy components, e.g. for portable computers and cameras. As for rheomoulding, it is allied to injection moulding of polymers. Magnesium alloy pellets are fed into a continuously rotating screw (Fig. 9) and the energy generated by shearing is sufficient to heat the pellets into the semi-solid state. The screw action produces the spheroidal microstructure and the material is injected into a die. Although the process is highly effective with magnesium alloys, aluminium alloys in the semi-solid state attack the screw and the barrel. Strenuous efforts have been made to overcome these problems but it is not clear that a successful commercial outcome has yet been achieved.

'Thixoforming' can cover both 'thixocasting', 'thixoforging' and an intermediate process called 'thixoforming'.

'Thixocasting' usually means that the alloy is solid initially and has been treated in such a way that when it is heated into the semi-solid state it will have a non-dendritic microstructure. It is reheated into the semi-solid state and 'casting' is implying that the liquid content prior to forming is relatively high i.e. above about 50 vol. %. This is the type of process used by Magnetti Marelli in Italy to produce fuel rails [37].

'Thixoforging' describes the process where suitable material is heated into the semi-solid state and placed between dies halves [e.g.38]. The parts of the die are then brought together by a ram. The direct insertion of the slurry into the die reduces material use because of the lack of runners, gate and press discard.

'Thixoforming' is the process where suitable material is heated into the semi-solid state and injected into a die. Usually, the liquid content is between 30 and 50% prior to forming. This is the type of process used by Stampal in Italy to produce the Alfa Romeo suspension component and a number of other automotive components [39]. It is also the process used by Vforge in the US to produce master cylinders, anti-lock brake system valves and automotive steering pumps amongst others. A thixoforming press is shown in Fig. 10 and illustrates the steps in the process, although it is a vertically upwards acting press whereas most commercial presses are horizontal. The specimen is induction heated into the semi-solid state. When it has reached the appropriate proportion of liquid it is forced into the die. Usually in commercial thixoforming, the slugs are heated on a carousel. Cycle times are then very comparable with die casting, if not faster because the full solidification range does not have to be gone through.

The distinctions between rheocasting, thixocasting and thixoforging are illustrated in Fig. 11 [40].

Other processes include the shear-cooling roll (SCR) process [41,42] and the cooling slope process [43]. In addition, there is the possibility of using semi-solid slurries in Solid FreeForm (SSF) technology [44]. This method deposits a stream of slurry through a nozzle that moves relative to a substrate. Components are built by building up successive layers so as to rapidly fabricate dense metal structures.

1.3 Advantages and Disadvantages

As with any manufacturing process, there are certain advantages and disadvantages in semisolid processing. They are [2, 45-47]:

Advantages

The main advantages of semi-solid processing, relative to die casting, are as follows.

- 1) Energy efficiency: Metal is not being held in the liquid state over long periods of time.
- 2) Production rates are similar to pressure die casting or better.
- 3) Smooth filling of the die with no air entrapment and low shrinkage porosity gives parts of high integrity (including thin-walled sections) and allows application of the process to higher-strength heat-treatable alloys.
- 4) Lower processing temperatures reduce the thermal shock on the die, promoting die life and allowing the use of non-traditional die materials

[e.g.48] and processing of high melting point alloys such as tool steels and stellites [49] that are difficult to form by other means.

- 5) Lower impact on the die also introduces the possibility of rapid prototyping dies [48]
- 6) Fine, uniform microstructures give enhanced properties.
- 7) Reduced solidification shrinkage gives dimensions closer to near net shape and justifies the removal of machining steps; the near net shape capability (quantified, for example, in [50]) reduces machining costs and material losses.
- 8) Surface quality is suitable for plating.

Disadvantages

- 1) The cost of raw material can be high and the number of suppliers small.
- 2) Process knowledge and experience has to be continually built up in order to facilitate application of the process to new components.
- 3) This leads to potentially higher die development costs.
- 4) Initially at least, personnel require a higher level of training and skill than with more traditional processes.
- 5) Temperature control. Fraction solid and viscosity in the semisolid state are very dependent on temperature. Alloys with a narrow temperature range in the semisolid region require accurate control of the temperature.
- 6) Liquid segregation due to non-uniform heating can result in non-uniform composition in the component.

The economic advantages of thixoforming have been discussed [51,52], including the use of Quality Function Deployment (QFD) to evaluate the interrelationships between thixoforming characteristics (energy usage, near net shape capability, mechanical

integrity of product, short cycle time, reduced die wear, raw material cost, process development, skills/wages of work force) and product characteristics (weight, strength, geometry, tolerances, price premium, lead time, flexibility, finishing operations) and quantified in software (www.shef.ac.uk/~ibberson/thixo.html). The economics of the NRC process have been analysed [20]. The NRC process does not suffer from the disadvantage of 1). Such analysis is important for industries adopting novel manufacturing methods where the cost base is not yet established through 'custom and practice'.

Much of the work on semisolid processing has been reported in the major series of conferences [3-9]. Some of these conferences have been refereed whilst others have not. It is therefore the policy in this review to give references as far as possible to refereed journal papers if the work has subsequently been published in that form. Previous reviews include those by Kenney et al [14], Flemings [45], Kirkwood [2], Quak [47], Collot [53] and Fan [12]. In addition, a book has recently been published edited by Figueredo [29]. The recent Fan review is comprehensive and the aim here is to complement that by providing a more detailed review of modelling of semi-solid processing and the transient rheological experiments required to provide data for that.

Millions of components are now made annually by semisolid processing. Aluminium alloy components produced by thixoforming and the NRC process are supplied to the automotive industry. Thixomolding is widely used, particularly in Japan, to produce lightweight magnesium components for mobile phones, laptop computers and cameras. New variants are still emerging (e.g. the 'new MIT process' [25]). The cutting edge research issues are now in developing the potential for producing high

performance alloys [54-60] and in modelling die fill with its concomitant requirement to obtain the experimental data which can support the modelling. This review focuses on the latter two areas.

2. Background Rheology

In a Newtonian fluid, the shear stress, τ is proportional to the shear rate, $\dot{\gamma}$, and the constant of proportionality is the viscosity, η . Thixotropic fluids are non-Newtonian i.e. the shear stress is not proportional to the shear rate. The viscosity is then termed the apparent viscosity and is dependent on shear rate, pressure, temperature and time. Some non-linear fluids also show viscoelasticity i.e. they store some of the mechanical energy as elastic energy. Thixotropic materials do not store energy elastically and show no elastic recovery when the stress is removed.

If a fluid exhibits a yield stress and then gives a linear relationship between shear stress and shear rate, it is termed a Bingham material (Fig.2). Then:

$$\tau = \tau_y + k\dot{\gamma} \quad (1)$$

where k is a constant related to the viscosity. The Herschel-Bulkley model is where behaviour is non-linear after yield i.e.:

$$\tau = \tau_y + k\dot{\gamma}^n \quad (2).$$

There is dispute over whether thixotropic semi-solid alloys display yield [eg.61] and whether they should be modelled as such (e.g. [62]). Barnes [63-65] concluded that the presence of a yield stress as reported by some workers for thixotropic materials (but not semisolid alloys) is probably due to the limitations of their experimental apparatus in not being able to measure shear stresses at very low shear rates. Koke

and Modigell [66] have used a shear stress controlled rheometer to measure yield stress directly on Sn 15%Pb. They distinguish between a static yield stress where the fluid is at rest prior to the application of a shear stress, and a dynamic yield stress where the fluid is being continuously sheared. Their results are shown in Fig. 13. The yield stress increases with rest time prior to deformation because of the increasing degree of agglomeration. In terms of modelling semi-solid alloy die fill, the use of a yield stress may be appropriate because a vertical billet does not collapse under its own weight unless the liquid fraction is too high. In addition, in rapid compression experiments to be described later (in Section 5.2) an initial peak in the load versus displacement curve is detected. Contrary to this though is the fact that at the ‘thixoforming temperature’ the initial peak is so small as to be undetectable.

The Ostwald de Waele relationship:

$$\tau = k\dot{\gamma}^n \quad (3)$$

is used to describe fluids which do not have a yield point and where there is a power law relationship between the shear stress τ and the shear rate $\dot{\gamma}$. If the exponent $n = 1$, this reduces to the expression for a Newtonian fluid with the constant k equal to the viscosity η . In Fig. 12, the shear thinning material (whose viscosity decreases as the shear rate increases) would have a value of n of less than 1 and the shear thickening material would have n greater than one. Thixotropic materials are essentially shear thinning but also thicken again when allowed to rest (i.e. all thixotropic materials are shear thinning but not all shear thinning fluids are thixotropic).

It is thought that at very high shear rates and at very low shear rates, thixotropic fluids effectively become Newtonian. This is expressed in the Cross model [67]:

$$\eta = \eta_{\infty} + \left[\frac{\eta_0 - \eta_{\infty}}{1 + k\dot{\gamma}^n} \right] \quad (4)$$

where as the shear rate $\dot{\gamma} \rightarrow 0, \eta \rightarrow \eta_0$ and as $\dot{\gamma} \rightarrow \infty, \eta \rightarrow \eta_{\infty}$. Fig. 14 shows data from a number of studies [67-70] for Sn 15% Pb alloys with various fractions of solid f_s . The data obey the Cross model, but information on the extremes is sparse. These data are for steady-state viscosities and, as will be discussed below, it is the transient behaviour which is of importance for the modelling of thixotropic die fill.

Viscosity is highly dependent on temperature. For a Newtonian fluid (e.g. the liquid matrix in a semisolid slurry), the viscosity decreases with increase in temperature. Temperature also affects the microstructure. Thus in semisolid slurries, the fraction solid decreases with increase in temperature, with a consequent effect on viscosity (see Fig. 14). In addition, over time, the microstructure will coarsen by diffusion and this will be accelerated as the temperature increases. Fig. 14 is for Sn 15%Pb alloy. There is little data on aluminium alloys because there are few commercially available rheometers that operate above about 500°C.

For a thixotropic material at rest, when a step increase in shear rate is imposed, the shear stress will peak and then gradually decrease until it reaches an equilibrium value for the shear rate over time (Fig. 15). The higher the shear rate after the step, the lower the equilibrium viscosity. The peak viscosity encountered will increase with

increasing rest time before it recovers back to the equilibrium viscosity of the shear rate specified.

3. Origins of Thixotropy

What is the microstructural origin of thixotropic behaviour? The importance of the spheroidal microstructure which results on stirring has already been mentioned. The semisolid metallic systems have much in common with flocculated suspensions (Fig. 16). At the shear rate $\dot{\gamma}_1$ corresponding to point 'a', the microstructure consists of a series of large flocs. If the shear rate is increased from $\dot{\gamma}_1$ to $\dot{\gamma}_2$, the flocs break up until the size corresponds to the flow curve which passes through point 'b'. If the shear rate is then reduced back to $\dot{\gamma}_1$, the individual particles begin to collide and agglomerate until an equilibrium size is reached appropriate to the lower shear rate. In semisolid metallic systems, the agglomeration occurs because particles are colliding (either because the shear brings them into contact or, if at rest, because of sintering) and, if favourably oriented, form a boundary. By 'favourable orientation' is meant the fact that if the particles are oriented in such a way that a low energy boundary is formed, it will be more energetically favourable for the agglomeration to occur than if a high energy boundary is formed. If a 3-D network builds up throughout the material, the semisolid will support its own weight and can be handled like a solid. As the shear rate is increased, these bonds between particles are broken up and the average agglomerate size decreases. Once the bonds are formed, the agglomerated particles sinter, with the neck size increasing with time.

The viscosity in the steady state depends on the balance between the rate of structure buildup and the rate of breakdown. It also depends on the particle morphology. The closer the shape to that of a pure sphere, the lower the steady state viscosity [45...summarising much earlier work]. In addition, if liquid is entrapped within particles, it does not contribute to flow. Thus, although the fraction liquid may take a certain value, governed by the temperature (and indeed kinetics as the thermodynamically predicted fraction liquid is not achieved instantaneously on reheating from the solid state), in practice, the effective fraction liquid may be less as some is entrapped within spheroids.

There are similarities and differences between thixotropy in semi-solid metallic systems and that in other thixotropic systems. These are associated with the nature of the forces between the particles. Table 1 summarises the phenomena which are occurring during structural buildup and structural breakdown in a variety of systems. In general, the forces between particles include:- Van der Waals attraction; steric repulsion due to adsorbed macromolecules; electrostatic repulsion due to the presence of like charges on the particles and a dielectric medium; electrostatic attraction between unlike charges on different parts of the particle (e.g. edge/face attraction between clay particles). In semisolid metallic slurries, none of these forces apply. What must actually be occurring in structural buildup is a process akin to adhesion in wear. As shear occurs, particles are forced into contact with each other. If it is energetically favourable for a solid-solid boundary to be formed, the two particles will stay in contact. If not, they will separate again. The process will be influenced by the rate of shear in two opposing ways. Increasing the rate of shear will increase the possibility of particle-particle contact but it will decrease the time of contact and the

formation of a new solid-solid boundary is a time dependent process. When the slurry is at rest, gravity will bring the particles into contact. In addition, if the solid fraction is sufficiently high, the packing density will be such that particles touch each other. Structural breakdown requires the breakdown of particle-particle bonds and this will depend on the cross-sectional area of the bond and the radius of the neck which generates a stress concentrating effect.

Can this process be represented by a force-distance curve for the particle-particle interaction as has been assumed in other systems? If it can, the forces are very short range (perhaps <1 nm) and the potential well is deep because many bonds do form.

In many thixotropic systems, the Brownian (thermal) randomising force is significant. For particles of all shapes, this constant randomisation influences the radial distribution function (i.e. the spatial arrangement of particles as seen from the centre of any one particle). The Brownian force is strongly size dependent, so that below a particle size of $1\ \mu\text{m}$ it has a big influence. In semisolid alloy slurries though, the individual particle size tends to be at least $20\ \mu\text{m}$ and so the Brownian force does not play a strong part. The other force which acts on the particles is the viscous force, which is proportional to the local velocity difference between the particle and the surrounding fluid.

Many thixotropic systems show 'reversibility' i.e. the slurries have a steady state viscosity characteristic of a given shear rate at a given fraction solid regardless of past shearing history. However, in semisolid alloy slurry systems, the evolution of particle shape (and size) with time and stirring (Fig.17) is irreversible. The measured viscosity

is then expected to depend on the shearing and thermal history. These dependencies contribute to the difficulty in modelling.

4. Mathematical Theories of Thixotropy

Barnes [65] has summarised current mathematical theories of thixotropy. Some detail on these is given here to enable work on semisolid slurries to be put in the context of the wider understanding of thixotropy. The theories fall into three groups:

- 1) Those that use a general description of the degree of structural buildup in the microstructure, denoted by a scalar parameter, typically λ , and then use $d\lambda/dt$ as the working parameter;
- 2) Those that attempt some direct description of the temporal change of microstructure as for instance the number of bonds or an attempt at describing the real floc architecture using fractal analysis;
- 3) Those that use viscosity time data itself on which to base a theory.

4.1 Models Based on a Structural Parameter λ

A completely built structure is represented by $\lambda = 1$ and a completely broken down structure by $\lambda = 0$. In the simplest case of a typical, inelastic, non-Newtonian fluid with upper and lower Newtonian viscosity plateaus (e.g. see Fig.14), $\lambda = 1$ corresponds to η_0 and $\lambda = 0$ to η_∞ . Thixotropy is usually then introduced via the time derivative of the structure parameter, $d\lambda/dt$. This is the sum of the breakdown and buildup terms and in the simplest theories these are only controlled by the shear rate and the current level of structure λ . The most general description of the rate of breakdown due to shearing is given by the product of the current level of structure and the shear rate raised to some power and the driving force for buildup as controlled by

the distance the structure is from its maximum value i.e. $(1-\lambda)$, raised to another power. Then

$$\frac{d\lambda}{dt} = a(1-\lambda)^b - c\lambda\dot{\gamma}^d \quad (5)$$

where a , b , c , and d are constants for any one system. Overall, if the value of $d\lambda/dt$ is negative, the system is breaking down towards equilibrium and if it is positive it is building up towards equilibrium. The Moore model [72] is a simplified version of equation (5) with b and d set to one. Cheng and Evans [73] set $b=1$ but allowed d to vary. The next step is to relate the structure λ , (as calculated using the equations above), to the stress τ or viscosity η in some flow equation. This has been done in a variety of ways which range from a simple Bingham equation (see equation (1) in Section 2), through the Cross model to a Cross-like model (equation (4) in Section 2) containing a yield stress.

4.2 Direct Structure Theories

Denny and Brodkey [74] applied reaction kinetics to thixotropy via a simple scheme that examined the distribution of broken and unbroken bonds. The number of these bonds was later linked to viscosity. The rate of structure breakdown was then:

$$-\frac{d(\text{unbroken})}{dt} = k_1(\text{unbroken})^p - k_2(\text{broken})^q \quad (6)$$

where k_1 and k_2 are the rate constants for the breakdown and buildup respectively. This can be solved to give the viscosity by assuming that viscosity is linearly proportional to the amount of unbroken structure, with a maximum value when completely structured of η_0 and a minimum value when completely destructured of

η_∞ . The rate constant k_2 is assumed to be independent of shear rate, being merely a description of Brownian collisions leading to restructuring (but note that for semisolid alloy slurries build up is not due to Brownian collisions- Section 3), while k_1 is related to the shear rate by a power law expression.

The Cross model [67] was derived using such considerations. Assuming that a structured liquid was made up of flocs (agglomerates) of randomly linked chains of particles, Cross obtained a rate equation of the form:

$$\frac{dN}{dt} = k_2 P - (k_0 + k_1 \dot{\gamma}^m) N \quad (7)$$

where N was the average number of links per chain, k_2 was a rate constant describing Brownian collision, k_0 and k_1 were rate constants for the Brownian and shear contributions to breakdown, P was the number of single particles per unit volume and n was a constant less than unity. At equilibrium, dN/dt is zero, so:

$$N_e = \frac{k_2 P}{k_0 \left(1 + \frac{k_1}{k_0} \dot{\gamma}^n \right)}. \quad (8)$$

Assuming that the viscosity was given by the constant η_∞ plus a viscous contribution proportional to the number of bonds N_e ,

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \frac{k_1}{k_0} \dot{\gamma}^n} \quad (9)$$

which is equivalent to the expression given earlier in equation (4) but with $k = k_1 / k_0$.

Lapasin et al [75] used a fractal approach to describe flocculated suspensions. In the relationship they predicted, the viscosity is related to: the number of primary particles in a floc when the shear stress becomes infinite, a yield stress and the fractal dimension of the floc.

4.3 Simple Viscosity Theories

Mewis and Schryvers [76] have devised a theory that circumvents the use of any structural parameter such as λ , and instead uses the viscosity as a direct measure of the structure. The rate of change of viscosity is then related to the viscosity difference between the steady state η_e and the current values of viscosity (not the structure difference) i.e.:

$$\frac{d\eta}{dt} = K[\eta_s(\dot{\gamma}) - \eta]^n. \quad (10)$$

Thixotropic breakdown has also been described [77, 78]

$$(\eta - \eta_\infty)^{1-m} = [(1-m)kt + 1](\eta_0 - \eta_\infty)^{1-m} \quad (11)$$

where η_0 and η_∞ are the asymptotic values of viscosity η (representing the fully structured and fully destructured states, respectively) measured at time t for any particular shear rate, and k and m are material constants.

5. Transient Behaviour of Semi-Solid Alloys

Computational Fluid Dynamics (CFD) can be used to predict die filling [see Section 6]. However, some of the work reported has been based on rheological data obtained in steady state experiments, where the semi-solid material has been maintained at a particular shear rate for some time. In reality, in thixoforming the slurry undergoes a sudden increase in shear rate from rest to 100s^{-1} or more as it enters the die. This change takes place in less than a second. Hence, measuring the transient rheological response under rapid changes in shear rate is critical to the development of modelling of die filling and successful die design for industrial processing. It can be investigated with two types of experiment. Firstly, via rapid shear rate changes in a rheometer and secondly, for higher fractions solid (where the torque capability of a rheometer is not sufficient), with rapid compression experiments, for example, in the thixoformer itself or in a drop forge viscometer.

5.1 Rapid Shear Rate Changes in Rheometers

Studies of transient behaviour have included those by Kumar [79], Quaak [47], Peng and Wang [80], Mada and Ajersch [81,82], Azzi et al [83] Koke and Modigell [66] Modigell and Koke [84,85] and Liu et al. [71,86]. Two relaxation times were quantified: (1) breakdown time and (2) buildup time. The breakdown time is the characteristic time for the slurry to achieve its steady-state condition after a shear rate

change from a lower value to a higher value, while the buildup time is for a change from a higher shear rate to a lower shear rate. These workers found that the times for breakdown are faster than those for buildup. This would be expected, as the breaking up of 'bonds' between spheroidal solid particles in agglomerates is likely to be easier than the formation of bonds during shear-rate drops. Quaak [47] proposes two characteristic times to describe a shear rate jump. He suggests that during a shear-rate change, the slurry undergoes an initial rapid breakdown/buildup followed by a more gradual process dependent on diffusion. This can be described by a double exponential expression. Quaak gives Fig.18 as the microstructural basis. Immediately after a change in shear rate, the structure remains the same ('iso-structure'). This is followed by a very fast process and then a slow process, associated with diffusion, giving coarsening and spheroidisation. It is the 'very fast process' which is relevant to modelling die fill.

In a rheometer, great care must be taken to ensure that inertial effects do not interfere with the results [e.g. see 86]. In addition, instrumental effects must be carefully separated from those of the material itself, particularly when attempting to examine behaviour that occurs in less than a second. For example, electronic switching may occur during the shear rate jump. This can be allowed for by only analysing results after the shear rate has reached ~90% of the specified final shear rate (see [86]). The work of Liu et al. [86] involves the fastest data collection rate so far (~1 kHz capture rate). This is significantly faster than that used by other workers (200 Hz in [79], 9 Hz in [47], 200 Hz in [80]) and enables the capture of the very fast process. The results for shear rate jumps from 0 to 100 s^{-1} after different rest times are shown in Fig.19. With longer rest times, the peak stress recorded increases. The breakdown times in

Table 2 were obtained by fitting an exponential to the data obtained during the second after 90% of the final shear rate was achieved. In Table 2, η_p is the peak-stress viscosity, η_{ss} is the ‘first’ steady-state viscosity (given that there are at least two processes going on as mentioned earlier) and τ_b is the ‘first’ breakdown time. Table 2 shows that the longer the rest time prior to the shear rate jump, the lower the breakdown time. This is consistent with microstructural evidence (Fig.20) showing that increasing the rest time increases the solid-particle sizes and the degree of agglomeration. This increase would impede the movement of the particles upon the imposition of the shear stress. The ease with which particles are able to move past each other depends on the fraction of liquid medium present, the size of the particles and the degree of agglomeration. The data show that during a change in shear rate, in about 0.15 seconds the semisolid structure would have broken down from its initial state. Regardless of the initial shear rate, the breakdown time decreases with increasing final shear rate [47, 81-83, 85, 86].

As far as the existence of ‘iso-structure’ during the jump is concerned, Turng and Wang [69] and Peng and Wang [80] observed an overshoot in the measured stress during a rapid increase in shear rate. They found that this overshoot (or undershoot in the case of a decrease in shear rate) is proportional to the change in shear rate. Therefore, they argue, for that instant, the material is behaving in a Newtonian way. The viscosity, and hence the structure, is constant, during the change. Peng and Wang [80] observed that the overshoot increases with increasing solid fraction. Horsten et al. [87] and Quak and co-workers [40,47] argued that during this transient period structure evolution has not had time to occur and the structure corresponds to that of the previous shear rate. Kumar et al [88] and Koke and Modigell [66] however, find

shear thickening ‘iso-structural’ flow behaviour (e.g. Fig.21). In [66], after each shear rate jump, the substance is sheared at $\dot{\gamma}_0$ to obtain equilibrium before the next jump. The plot of shear stress versus shear rate can be fitted with a shear thickening Herschel-Bulkley model with a flow-exponent $n = 2.07$. Koke and Modigell [66] argue that this finding is of high importance for simulation of the industrial process.

Data on the transient behaviour of aluminium alloys is sparse because the majority of the commercially available rheometers do not operate at semisolid aluminium alloy temperatures.

5.2 Rapid Compression

For high solid fractions, above about 0.5, conventional rheometers do not have sufficient torque capability. Other methods must then be used, introducing complexity because the shear rate is no longer constant throughout the material (as it can be assumed to be in a concentric cylinder rheometer). Laxmanan and Flemings [68] measured the force and displacement for Sn 15%Pb compressed between parallel plates at low strain rates. The resulting load was not measured directly (but rather, derived from the pressure on the ram) and the rate of compression was much slower than in the industrial process. The work of Loué et al [89], carried out at higher shear rates by backward extrusion on aluminium alloys, resembles industrial thixoforming more closely. However, the specimens were heated to temperature over a long period of time (~ 10 minutes) and then held isothermally for 30 minutes before compression. Such time periods would be considered long in industrial thixoforming. Yurko and Flemings [90] designed a drop forge viscometer (Fig.22) to study fluid flow behaviour

at transient high shear rates. It consists of a lower platen and an upper platen, with an attached platen rod to track platen motion with time. It is similar to a parallel plate compression viscometer but the upper plate is allowed to fall under the influence of gravity. A high speed digital camera images the rod as it falls. The force is calculated from the second derivative of the displacement data allowing calculation of viscosities at shear rates in excess of 1000 s^{-1} . A typical experiment yields instantaneous, volume-averaged viscosity first under rapidly increasing shear rate and then under rapidly decreasing shear rate. Segregation of liquid from solid did not occur at the high shear rates. Liu et al. [91] have carried out rapid compression in the thixoformer itself using a load cell to record the load versus time signals. The compression rate is then akin to industrial thixoforming and the load is measured directly. A typical signal response is shown in Fig.23. The peak is believed to originate from the three-dimensional skeletal structure built up in the solid phase at rest, which breaks down under load. The width of the peak (or, more accurately, the downward part of it) is a measure of the time taken to destroy this skeletal structure. A rough estimate then gives a breakdown time of about 10 ms, an order of magnitude less than the relaxation times obtained from shear rate jumps in rheometer experiments (see Section 5.1) and must therefore be related to a different mechanism. The height of the peak falls with temperature as the skeletal structure is consumed, and the minimum load beyond the peak also decreases with increasing temperature, both because a more spheroidal microstructure is developed and the fraction liquid increases (see Fig.24). In practice, successful thixoforming takes place at temperatures where there is little or no peak. Viscosity versus shear rate can be derived from the load-displacement data using a method based on that outlined in Laxmanan and Flemings [68]. This does however assume a Newtonian fluid at one stage in the analysis and this may introduce errors.

Data on viscosity versus shear rate for Al-Si alloys is summarised in Fig. 25. It is important to be aware that small changes in silicon content can affect the results quite considerably by changing the solid fraction. The lower values recorded by Yurko and Flemings [90] in comparison with those of Liu et al. [91] are derived for an alloy with higher silicon content and also one which has been soaked for longer (giving a larger particle size and consequently lower viscosity). Included in the figure is the steady-state viscosity determined by Quaak [47] for a 7% Si aluminium alloy, extrapolated to 0.5 fraction solid; this is well below the other results, emphasizing that the steady state is not achieved in those experiments, nor in industrial thixoforming.

6. Modelling

The recent commercialisation has highlighted the need to model slurry flow into die cavities. Die design and processing conditions such as ram speed, dwell time and pressure have, to some extent, been a matter of trial and error. In particular, die design rules from die casting are not transferable to thixoforming. This is illustrated in Fig.26, where attempts were made to produce a generic demonstrator consisting of a round plate with three bolt holes and a central boss. In preliminary trials, there was difficulty in filling the die. Therefore, partial filling experiments were carried out which demonstrated that the design of the die, particularly the in-gate, which was narrow as for die-casting, led to some jet flow across the cavity (Fig.26(a)) instead of the smooth progressive filling which is the aim in thixoforming. FLOW3D (a Computational Fluid Dynamics Programme produced by FLOWSCIENCE, Los

Alamos) was used to model the flow into the die, trying out different viscosities in order to find the range in which the experimental behaviour was mimicked (e.g. Fig.26(b)). The agreement was promising given that the work did not take into account heat transfer in the die nor friction at the die surface. In addition, the model did not, in the version used, incorporate thixotropic behaviour as such (i.e. it assumed the fluid had a constant viscosity, independent of the shear rate and time, which in practice is not the case). Changing the design of the die in the light of the findings of this 'simple' modelling led to improved filling (e.g. Fig.26(c)). There is, therefore, real potential commercial benefit to be obtained from better understanding of flow of semi-solid material in dies, alongside the academic interest.

In this section modelling is reviewed. Previous reviews include those by Kirkwood [92], Atkinson [93] and Alexandrou [chapter 5 in 28]. Table 3 summarises the main papers on modelling [94-125]. The papers are given in year order and this is carried over into Tables 4, 5 and 6 which give further information. These Tables are not exhaustive and, where authors have published in journals in addition to conferences, it is the journal papers which are cited. The papers are classified as to whether the modelling is finite difference or finite element, one-phase or two-phase. There is in addition, a paper on micro-modelling [125] which does not strictly fit any of these categories. A major aim here is to draw out the similarities and the differences between the flow and viscosity equations which modellers are using. In Tables 4, 5 and 6, this is done by quoting the equations from the papers but converting the symbols as far as possible to be common. A Glossary of Symbols is given. Where the equations are given in complex terms they are then reduced to simple shear which allows more direct comparison. It must be assumed, since this is not made explicit in

most papers, that where a derivative, for example with respect to t is given as $\partial / \partial t$ or d / dt , that this is in fact the substantive derivative D / Dt following the material as it moves. Tables 4, 5 and 6 identify the main features of the models and also observations on simulation results and whether these have been validated. Where commercial code has been used this is identified with the reference. The main threads in the development of each of the categories are discussed below, with an initial section on the model of Brown and co-workers since this has been used by a number of researchers. Thus, the finite difference papers are grouped as to whether they are based on:- The Model of Brown et al. (Section 6.2.1); FLOW3D (Section 6.2.2); MAGMAsoft (Section 6.2.3); Adstefan (Section 6.2.4); Two-Phase Modelling (Section 6.2.5). For the one-phase finite element papers (Section 6.3.1) in some cases it makes sense to group the papers according to author. Thus, the headings are:- Zavaliangos and Lawley; Backer; Alexandrou, Burgos and co-workers; Viscoplastic constitutive models; Power Law Cut Off (PLCO) Model of Procast; Model Based on Viscoelasticity and Thixotropy. The two phase finite element papers are sensibly dealt with as a single section (Section 6.3.2) but highlighting the distinctive features of the papers. The work of Rouff et al. [125] on Micro-Modelling is covered in section 6.3.3.

6.1 Model of Brown and Co-Workers

Brown and co-workers [127-129] presented a constitutive model based on the 'single internal variable' concept (see Section 4.1), where the structural parameter λ varies between 0 and 1, depending on whether the structure is fully broken down or fully built-up respectively. Their model assumes that flow resistance is due to hydrodynamic flow of agglomerates and deformation of solid particles within the

agglomerates. It has been used by a number of workers both for finite difference and for finite element modelling (Ilegbusi and Brown [94]), Ilegbusi et al. [102], Zavaliangos and Lawley [103], Backer [104]). Ilegbusi and Brown [94] used it in their finite difference work but also introduced a yield stress τ_y . The second term on the right hand side in equation (12) (at the top of Table 4) represents the hydrodynamic interaction among agglomerates, with $A(\lambda)$ a hydrodynamic coefficient depending on the size, distribution and morphology of the particle agglomerates. The term is linear in shear rate and increases non-linearly with the solid fraction, f_s (the effective volume fraction of solid $c = f_s(1 + 0.1\lambda)$). It depends weakly on f_s for $f_s < 0.5$ but then increases at an increasing rate towards an infinite asymptote at a given solid fraction and state of agglomeration. The third term on the right hand side represents the deformation resistance due to energy dissipated in the plastically deforming particle-particle bonds. Under isothermal conditions and at constant structure this term indicates a shear rate thickening response with $n > 1$ - during rapid shear rate transients, the deformation resistance increases with increasing shear rate (consistent with experimental work by Kumar et al [129]). There is debate as to whether shear rate thickening is the constant structure response (e.g. see [84]). The term exhibits a strong inverse dependence on temperature through $C(T) = C_0 \exp(nQ/RT)$, which brings in the temperature dependence of diffusional processes and the temperature dependence of the solid deformation.

Equation (13) (the second equation in Table 4) represents evolution of the structure parameter as a function of flow conditions and state variables. H is an agglomeration function and G a disagglomeration function representing the shear-induced rupture of the particle-particle bonds.

Overall the model of Brown et al predicts an increase in deformation resistance with the solid fraction and this becomes rapid between 0.5 and 0.6 f_s . Brown et al. state that it is not valid beyond this sharp increase in deformation resistance and is applicable only for $f_s < 0.5 - 0.6$.

6.2 Finite Difference Modelling

6.2.1 One Phase Finite Difference based on the Model of Brown et al.

Ilegbusi and Brown [94] use the Brown et al. model (see Section 6.1), but with a yield stress, to examine flow into a chisel shaped cavity. This showed the importance of heating the die and the heat transfer coefficient, as a solid shell formed at the mould wall leading to 'jetting' in the centre of the cavity.

6.2.2 One Phase Finite Difference Based on FLOW3D

The approach to thixotropic modelling in the FLOW3D code is outlined in Barkhudarov et al. [95] and Barkhudarov and Hirt [96]. Barkhudarov et al. [95] use a transport equation (equation (14) in Table 4) for the viscosity η rather than a transport equation for λ because this is more convenient for CFD, which requires a value for η . This is therefore reminiscent of the simple viscosity theories in Section 4.3. The transport equation includes an advection term and a relaxation term which accounts for the thixotropy of the material. The relaxation term is based on two variables, the steady state viscosity η_e and the relaxation time $1/\omega$, both of which

may be functions of shear rate and solid fraction. No yield stress, wall slip or elastic or plastic behaviour at high solid fractions are included. This simple model therefore applies for $f_s < 0.6 - 0.7$. It can be related to the Moore model (see Section 4.1 and [72]) and $\partial\lambda/\partial t$ then includes agglomeration and disagglomeration terms. Here disagglomeration is dependent on $\dot{\gamma}$ and not $\dot{\gamma}^n$ as in the Model of Brown et al. [127-129]. Barkhudarov et al. [95] used their model to predict hysteresis curves for Sn 15%Pb with reasonable accuracy and to predict die swell when the relaxation time is similar to the time it takes for the metal to flow through the nozzle. The equation in Barkhudarov and Hirt [96] (equation (18) in Table 4) is an extension of that in Barkhudarov et al. [95]. If the local viscosity is greater than the equilibrium viscosity η_e then the local viscosity is driven towards η_e at the thinning rate α , if the local viscosity is less than the equilibrium viscosity then it is driven towards η_e at the thickening rate β . In this work it is assumed that α and β are constants, but practically it is likely that they are dependent on shear rate. The test problem is one of Sn-15%Pb droplets impacting on a flat plate. The results show that droplet shape is influenced by relaxation time. The approach outlined here is essentially the basis for the thixotropic module in the FLOW3D code, which is the basis of thixotropic modelling by a number of workers including Modigell and Koke [84], Modigell and Koke [85], Ward et al. [98], Messmer [99].

Modigell and Koke [84] fitted the steady state flow curve for Sn-15%Pb to a Herschel-Bulkley model (see Section 2 equation (2)) with a yield stress τ_y dependent on the fraction solid. The second term on the right hand side in the expression for shear stress (equation (19) in Table 4) includes a structural parameter κ which

describes the current state of agglomeration but differs from λ in that it varies from zero (fully broken down) to infinity (fully built-up) rather than zero and one. The time evolution of κ is described with first order reaction kinetics (equation (20) in Table 4) with $a \exp(b\dot{\gamma})$ the rate constant for the approach of κ to the equilibrium value κ_e . After parameter evaluation, the model fits step-change of shear rate experiments with Sn-15%Pb quite well. Simulation of die fill involved a cavity with a cylindrical obstacle, highlighting the different behaviour of Newtonian and thixotropic fluids (see Fig. 27).

The equation for shear stress τ in Modigell and Koke [85] (equation (22) in Table 4) appears to be slightly different from that in Modigell and Koke [84] in that the yield stress τ_y is now multiplied by the structural parameter κ and the exponential in the second term in equation (19) in Table 4 is no longer present. This may have been rolled into the consistency index k^* as the text states ‘ k^* ...increased exponentially with the solid fraction’. The experimental rheological data was for Sn-15%Pb but the material used for die filling simulation was A356 aluminium alloy. The parameters used for the model were adjusted empirically during the simulation study (but are not given in the paper). Modigell and Koke found that above a critical inlet velocity the filling was not laminar any more. The transition between laminar and turbulent filling (in the sense of a smooth flow front and one that is starting to break up) could be represented reasonably well.

Ward et al [98, 140, 141] found that, in modelling force versus time for a rapid compression test (see Section 5.2), the implicit solver tended to give an initial peak regardless of whether the viscosity was Newtonian or thixotropic, especially if the

software was allowed to choose its own time step and if the model started with a gap between the slug and the platen. Provided the time step was small enough not to be a factor in determining the results, the implicit solver could reproduce the downward slope of the initial peak and the subsequent force profile. The explicit solver could accurately model shear rate jumps in a rotational viscometer (see Section 5.1) but was inordinately slow. FLOWSCIENCE have therefore produced a new Alternating Direction Implicit (ADI) solver to cope with the large ranges and changes of pressure associated with thixotropic slurries. Fig. 28 shows the ADI result for a shear rate jump in Sn-15%Pb compared with experimental results (three repeats of the same experiment) and the results from a one dimensional spread sheet calculation. The contrast between implicit and explicit solvers is not mentioned elsewhere and it is not clear whether workers have tested their modelling against the artefacts found with the implicit solver. Ward et al. [98] found that to model the shear rate jumps, an initial viscosity was required which was 2-5 times lower than the experimental values. This suggests that the initial breakdown of the slurry is very rapid, possibly beyond the limits of the viscometer data collection system, even though the system used in this experimental work has the fastest data collection rate of any existing system (see Section 5.1 and [86]).

Messmer [99] used FLOW3D to simulate thixoforging rather than thixoforming i.e. the slurry is inserted directly into open dies and the parts of the die are then brought together by a ram. In simulating the thixoforging process, moving dies must therefore be modelled. The apparent viscosity depends on fraction solid f_s , shear rate $\dot{\gamma}$ and time t . The fraction solid is calculated using the Scheil equation (i.e. assuming a simple binary). The equilibrium viscosity is given by equation (23) in Table 4 and the

time dependent thixotropic effects in equation (24). The viscosity parameters were obtained by fitting the simulation to experimental results with A356 aluminium alloy. Comparison between forming forces, measured on the lower die at the end of the punch stroke, and simulated forces suggests that the initial thinning rate is much higher than that in the final stages. This is consistent with the results of Ward et al. [98] and with the proposal by Quaak [47] that at least two different relaxation processes are operating, with different characteristic relaxation times. The die filling for a suspension part was modelled where the material has to flow around a core and weld on the opposite side. The die was modified to ensure this welding occurred in the area of the overflow as required.

6.2.3 One Phase Finite Difference Based on MAGMAsoft

MAGMAsoft and FLOW3D are commercial competitors in the simulation of flow processes. It is not the intention here to discuss the relative merits of various commercial codes but rather to identify how those codes have been used. Kim and Kang [97] compared the output from MAGMAsoft with a Newtonian fluid and assuming the viscosity of the fluid obeyed the Ostwald-de-Waele power law with n varying between -0.48 and $+0.45$ depending on the temperature. The data for this is from MAGMAsoft. It is not clear in the text what relationship between n and f_s is being used to obtain this temperature relationship or how this relates to the experimental findings for A356 by Quaak et al. [142], who found n values of -0.2 and -0.3 for solidified fractions between 0.2 and 0.4 (i.e. temperatures of 605 and 589°C respectively) and by Loué et al. [143] who found n of -1.0 almost independent of temperature for temperatures between 603°C and 590°C . A value of n of -0.2 does

fit the curve in Fig. 15 in Kim and Kang [97] at 605C but the other values are a long way off. It is also of note that values of n of less than zero imply that the shear stress decreases with increasing shear rate. This is not easily explained (see discussion in [142] and also [61]). Notwithstanding these comments about the basis for the curve of n versus temperature, the Newtonian analysis does not agree well with the experimental results of partial filling experiments, whereas the results using the Ostwald-de-Waele power law are closer to the experimental findings.

Seo and Kang [100] also used MAGMAsoft, comparing the Ostwald-de-Waele power law model, which has a limited range of shear rates over which it is applicable, with the Carreau-Yasuda equation, which allows viscosity at very low and very high shear rates to be considered. In the paper, only results of simulation with the Ostwald-de-Waele model are presented and show reasonable agreement with partial filling results for an automotive component (but one that does not involve parting and rewelding of flow fronts or very big changes in section thickness).

6.2.4 One Phase Finite Difference with Adstefan

Itamura et al. [101] compares simulation for die casting, squeeze casting and rheocasting for both metal flow and solidification. Few details are given. The results indicate that air entrapment would occur for die casting, in contrast with squeeze casting and rheocasting. There would be fewer shrinkage defects in rheocasting than with the other processes.

6.2.5 Two Phase Finite Difference

There appears to be only one paper using a finite difference model for a two phase analysis, that by Ilegbusi et al. [102]. The single phase equations are solved for the whole filling phase. Trajectories of a given number of particles are computed, assuming they will ‘disappear’ when they hit a wall or are trapped in a recirculation zone. A measure of segregation is obtained by comparing the number of particles at a given distance from the inlet to the total number of injected particles.

6.3 Finite Element Modelling

The consideration of finite element modelling is divided into one-phase and two-phase treatments. A number of different commercial and other codes are used.

6.3.1 One Phase Finite Element

Zavaliangos and Lawley

Zavaliangos and Lawley [103] use identical equations to Ilegbusi and Brown [94] from the Brown et al Model (see Section 6.1) but without a yield stress. The analysis is for Sn-15%Pb and, for fractions solid less than about 0.5, it is predicted that a free standing billet will collapse. The thixoforming of a simple shape is simulated. No experimental validation of the results is given. Zavaliangos and Lawley deal with a two phase analysis in the same paper (see Section 6.3.2).

Backer

Various rheological models were programmed into the WRAFTS software by Backer [104] including:- a Newtonian; a Herschel-Bulkley model (i.e. combining a yield stress with a power law-see equations (27) and (28) in Table 5); and a Bingham fluid (see Section 2) combined with a power law dependence (see equations (29) and (30) in Table 5). Note that it is not clear that the description of “a Bingham fluid combined with a power law dependence” is correct here as there is no yield stress in equation (30) but rather one term dependent on $\dot{\gamma}$ and one on $\dot{\gamma}^n$. An internal variable model is also used (viz. Brown et al in Section 6.1). In this the structural parameter λ (which varies between 0 and 100% rather than 0 and 1) is perceived as a chemical concentration and a convective transport equation is written for its spatial and temporal variation (equation (31) in Table 5). When this equation is simplified by assuming the fluid density is constant and the velocity does not vary spatially, it can be compared to that due to Barkhudarov et al. [95]. There is a strong similarity but with a factor of λ^2 in the second term on the right hand side rather than λ as in equation (15) in Table 4. This reduces the contribution of disagglomeration.

With the Newtonian rheological model, due to the relatively low viscosity of the liquid metal, there are a number of locations behind cores in a complex die that remain unfilled while the liquid flows past them. Such locations would increase gas entrapment and would show flow lines in a casting. For the power law rheological model, the fluid fills behind the cores. With the internal variable model, a larger percentage of the flow into the cavity arises from the runner at the side of the die cavity, in contrast with the Newtonian and Bingham/power law models which predict a larger flow rate from the bottom runner. The reason for the larger flow rate from the side runner is that the structural parameter (‘agglomeration variable’) λ is reduced as

the mixture flows through the runner system from a maximum value of 100% in the shot sleeve to less than 20% at the end of the side runner. The value at the bottom runner is 40%; thus, the material in the side runner is less viscous and can flow into the cavity more readily. Experimental validation is not presented in the paper.

Alexandrou, Burgos and co-workers

There are several papers by Alexandrou, Burgos and co-workers [105-109,114] sometimes with Alexandrou and Burgos working together and sometimes in cooperation with others. The papers have similar threads running through and therefore are treated together here.

In [105], Alexandrou et al. use the commercial code PAMCASTSIMULOR to compare Newtonian and Bingham filling of a three-dimensional cavity with a core. The yield stress τ_y is a function of the fraction solid f_s . Temperature dependence is introduced through this relationship. Equations (33) and (34) in Table 5 give the viscous stress tensor and the viscosity expression. D_{II} is the second invariant of the deformation rate tensor. In simple shear, $\sqrt{D_{II}}/2 = \dot{\gamma}$. When the local stress is larger than τ_y , the slurry behaves as a Non-newtonian fluid. m controls the exponential rise in the stress at small rates of strain and, depending on the value of the power law coefficient n , the behaviour is either shear thinning ($n < 1$) or shear thickening ($n > 1$). The continuous Bingham law in equation (33) is based on that introduced by Papanastasiou [131] to avoid the discontinuity at the yield stress. In [105], the value of n is taken to be 1. In the simulation, firstly pipe flow was studied, demonstrating that the flow at the outlet was identical with the analytical solution. Due to the finite

yield stress, the Bingham case shows a large unyielded area where the material in the centre flows like a solid. For a three dimensional cavity with a cylindrical core, there is a strong contrast between Newtonian and Bingham behaviour (Fig.29). In the Newtonian case, the velocity vectors at the rewelding front (i.e. where flow fronts must remerge beyond a core) point towards the core, whereas in the Bingham case, they point away from the core, allowing oxide skins to be transported into overflows.

Burgos and Alexandrou [106] examined the flow development of Herschel-Bulkley fluids in a sudden three dimensional square expansion, using again the Papanastasiou model [131]. The results show that during the evolution of flow, two core regions and dead zones at the corners are formed. The extent of the core regions decreases with the pressure gradient and the Reynolds number and increases with the power-law index.

The relative importance of the inertial, viscous and yield stress effects on the filling profile in a two-dimensional cavity with a Bingham fluid is examined in Alexandrou et al [107]. The analysis is as for the previous two papers. The results identify five different flow patterns (see Fig. 30): ‘shell’ (large Reynolds numbers but small Bingham numbers), ‘mound’ (low Reynolds and Bingham numbers), ‘bubble’ (larger Bingham numbers), ‘disk’ (occurs between shell and bubble filling), and ‘transition’. These can be plotted using the Saint-Venant number, (which is defined as the ratio of the Bingham number $\tau_y H / \eta V$ to the Reynolds number $\rho V H / \eta$, where H and V are characteristic length and velocity scales), which indicates the importance of the yield stress relative to the inertia forces, and the Reynolds number (see Fig. 31). This is a very helpful approach to schematising the different types of behaviour,

particularly in identifying the vulnerability to defects. Transition flow occupies a narrow region between the disk and bubble patterns. Since the flow initially starts as disk and then switches to bubble filling, this region may be prone to instabilities.

In Burgos et al [108], the Herschel-Bulkley model in equation (33) in Table 5 and the approach of the previous papers [105-107] is expanded to include the effect of the evolution of microstructure via an equation for $\partial\lambda/\partial t$ very similar to equation (15) in Table 4 [95] but including an exponential factor in the second term on the right hand side (i.e. the disagglomeration term). This exponential dependence is included to account for the fact that experimentally [e.g. 80-82, 86] the shear stress evolution for shear-rate step-up experiments is faster than that for the step-down case. (It is not clear why this is not taken into account by the constants a and b or whether this is, in fact, a way of introducing two relaxation processes as in Quaak [47]). In addition, the yield stress, consistency index K and power law index n are now all assumed to be functions of the volume fraction solid f_s and the structural parameter λ . There are then six material parameters in the model: $a, b, c, K(f_s, \lambda), n(f_s, \lambda), \tau_y(f_s, \lambda)$. Burgos et al. [108] obtain these using data on Sn-15%Pb from Modigell et al. [133]. The behaviour of the material is shear thickening for isostructure during a shear rate jump. The power law index decreases with the structural parameter while the consistency index and the yield stress increase. For flow through a straight square channel, disagglomeration is small in the corners and in the core region of the channel.

Alexandrou et al [109] analysed a simple compression test assuming a Bingham fluid and not taking account of the evolution of the internal structure. The viscosity and

yield stress were obtained from fitting a load versus time curve. There is unyielded material at the top and at the bottom of the compressed cylinder, in stagnant layers.

The identification of flow regimes prone to instabilities in [107] has led to a more recent paper (Alexandrou et al [114]) analysing two dimensional jets of Bingham and Herschel-Bulkley fluids impacting on a vertical surface at a distance from the die entrance. A bubble pattern gives an unstable jet, whereas shell, disk and mound are all stable, along with most transition cases. Instabilities are the result of finite yield stress and the way yielded and unyielded regions interact. Plots of Bingham number versus Reynolds number identify stable and unstable regions. This identification of instability provides an important explanation of the common defect in semi-solid processing sometimes termed the ‘toothpaste effect’ (Fig. 32)

Viscoplastic Constitutive Models

Ding et al. [110] established a rigid viscoplastic constitutive model for AlSi7Mg alloy through compression tests. They neglected the flow stress during the initial breakdown stage and only fitted the flow stress in the steady state. In the simulation, they assumed that the deformation of semi-solid materials is governed by the Levy-Mises flow rule. They used DEFORM-3D software with a six-fingered die heated to the initial temperature of the billet, i.e. the conditions are quasi-isothermal. The die fingers are of different cross-sectional areas. It appears from the diagrams that the material is initially in position in the die and is then compressed by the punch. Metal in the larger orifice fingers flows faster, contrary to what would be expected with thixotropic breakdown. The simulation and the experimental results agree well but

there is no analysis of whether liquid phase has segregated out from the solid, and whether it is this which is giving the results which are contrary to expectations.

Rassili et al. [112] also obtained a viscoplastic constitutive model from force recordings of extrusion tests. Their simulation is aimed at thixoforging steels. There is no time dependence in the constitutive equation (equation (49) in Table 5) in contrast with the Ding et al. equation (46) in Table 5 which does include a $\dot{\gamma}$ term. This is therefore essentially a forging simulation. The friction is assumed to be very low. There are several combinations possible for the tool displacement. If the ejector goes up and the punch starts to go down when the ejector stops, buckling occurs and leads to a lap. If the punch and ejector move simultaneously, or the punch goes down first and then the ejector goes up, the buckling disappears but a lap is formed on each 'ear' of the part. The simulation agrees reasonably with a lead prototype but thixoforging results with steel are not presented.

Power Law Cut-Off (PLCO) Model of Procast

Jahajeeah et al. [111] and Orgeas et al [115] have both used the Power Law Cut Off (PLCO) model in Procast commercial software [134]. The major assumption of the PLCO model is that the material is a purely viscous isotropic, incompressible fluid. The versions used are slightly different. In the Jahajeeah et al. work, the demonstrator component is divided into different regions each with different cut-off values $\dot{\gamma}_0$. It is not clear how these values are determined. If $\dot{\gamma} \leq \dot{\gamma}_0$ then $\eta = \eta_0 \dot{\gamma}_0^n$, whereas if $\dot{\gamma} > \dot{\gamma}_0$ then $\eta = \eta_0 \dot{\gamma}^n$ i.e. shear thinning is only occurring if the cut-off value is exceeded. If it is not exceeded, the viscosity is not affected by local shearing and is calculated using

$\dot{\gamma}_0$. There is reasonable agreement between the simulation and the results of interrupted filling tests with A356 aluminium alloy. With less than optimum runner design, defects are predicted and these were found in the identified areas in practice.

In the work by Orgeas et al. [115], there is only one value of the cut-off $\dot{\gamma}_0$ and this is determined by geometry. The shear rate cut-off $\dot{\gamma}_0$ was initially used in finite element codes to improve numerical convergence for shear thinning materials ($n < 1$) when the shear rate decreased towards zero. Orgeas et al. adopt a different point of view. Firstly, they assume that agglomeration and coalescence of grains probably does not take place over the very short injection times characteristic of thixoforming. Therefore, a decrease of $\dot{\gamma}$ will not lead to an increase of the viscosity η . Secondly, a sudden increase of the shear rate $\dot{\gamma}$ will lead to a decrease in viscosity. In effect, an increase of $\dot{\gamma}$ beyond the largest shear rate $\dot{\gamma}_0$ experienced so far will lead to a decrease in viscosity (and modify the maximum shear rate $\dot{\gamma}_0$). A decrease of $\dot{\gamma}$ below $\dot{\gamma}_0$ will not modify the viscosity (and leaves $\dot{\gamma}_0$ unchanged). This ‘ratchet-type’ behaviour could be fully modelled, but in the work by Orgeas et al. they have assumed only one value of $\dot{\gamma}_0$ because their experiments involve a transition between a shot sleeve and a small injection aperture and most of the change in viscosity is occurring at that point. The calculation of the value of $\dot{\gamma}_0$ is given in the paper.

Orgeas et al. obtain the parameters for their model from experiments measuring the pressures and temperatures in a tube with a shaft in it. They then use the model to simulate the filling of a reservoir. Comparison between the simulations and interrupted filling experiments for A356 aluminium alloy are shown in Fig. 33. It

should be noted that Orgeas et al. found eutectic-rich concentric rings in the tube in a Poiseuille type experiment (Fig. 34(a)). These were due to veins of liquid formed in the shot sleeve as a result of mechanical instabilities generated in a solid skeleton which is not uniformly sheared (see Fig. 34). The vein of eutectic liquid at 45 was due to the 'dead' zone at the bottom right corner of the shot sleeve i.e. a zone which is almost not sheared and only compressed. The compression of the dead zone induces a 'sponge-like' effect. Such complex behaviour cannot be predicted with a one-phase model. It should be noted that this highlights the need for such dead zones to be avoided in die design for semi-solid processing.

Model Based on Viscoelasticity and Thixotropy

Wahlen [113] presents a model based on viscoelasticity and thixotropy. Thixotropic materials do not normally display viscoelasticity. It would seem that this could only really occur if the fraction solid is relatively high. In equation (30) in Table 5, the first term in brackets is the viscoelastic term and the last term in brackets is essentially a creep term. It is not clear why these terms have been multiplied rather than being treated as additive. There is good agreement between the model and the curve of flow stress versus true strain but this is for a temperature of 570C where the A356 would be expected to be almost fully solid (see Differential Scanning Calorimetry data in [59]). The simulation results are compared with backward extrusion samples for various temperatures. There is a transition at around 570C, which is interpreted as the transition between plastic deformation of a connected-particle network and the viscous flow of a suspension of solid particles.

6.3.2. Two Phase Finite Element

Some of the two-phase finite element modelling papers are presented in Table 6 but that approach is less useful when the equations are so complex. (Gebelin et al. [144] have presented a useful mathematical comparison of one phase and two phase approaches). Others are discussed here in a more general background section. Orgeas et al. [115] have reviewed two-phase approaches. In the two-phase models, the semisolid material is considered as a saturated two-phase medium i.e. made of the liquid and solid phases. Each phase has its own behaviour, which can be influenced by the presence of the other phase via interfacial contributions. The conservation equations can be written within a mixture theory background [145] and the solid phase (solid skeleton) can be modelled as a purely viscous and compressive medium [146,147]. Momentum exchanges between the solid and the Newtonian liquid are handled by a Darcy-type term appearing in the momentum equations [148]. These models are able to predict phase separation [e.g.118,149]. However, the determination of the rheological parameters which are required is not straightforward [e.g. 146, 147]. Two-phase models also usually require the simultaneous calculation of a solid fraction field, a pressure field, two velocity fields (for the liquid and the solid) and a temperature field (although in most cases the simulation is isothermal). Such simulations therefore require very high computation time.

The distinctive features of the papers identified in Table 6 are as follows:

- Zavaliangos [116] The degree of cohesion is represented by an internal variable which evolves with deformation (cf. the internal variable in the Brown et al. Model [127-129] in Section 6.1). The permeability equation

implies that solid-liquid segregation decreases as the grain size decreases.

Behaviour is not symmetric under tension and compression.

- Koke et al. [117]: The solid phase is assumed to be a pseudo-fluid with a Herschel-Bulkley viscosity.
- Kang and Kung [118] treated the solid phase as compressible and introduced a separation coefficient expressing the actual separation of the particles in relation to their initial separation. The higher the strain rate the more homogeneous the distribution of the solid fraction. In compression forming, macroscopic phase segregation occurred with densification of the remaining solid in the central region.
- Binet and Pineau [119] adopt a mixture approach where the hydrodynamic part is the same as for most incompressible CFD codes but the velocity field represents the velocities of the mixture. A source term is added to the momentum equations to take account of the diffusion velocities of the individual phases.
- Choi et al. [120] The solid is assumed to be viscoplastic. Kuhn's yield criterion is used for the solid phase. (i.e. behaviour is symmetric for tension and compression and the hydrostatic component of stress is included).
- Yoon et al. [122] used Von Mises yield criterion (i.e. symmetric in tension and compression). The semisolid is treated as a single incompressible phase.
- Kopp and Horst [123] adopt the Drucker-Prager yield criterion (i.e. non-symmetric in tension and compression).
- Modigell et al. [124] use the pseudo-fluid approach for the solid phase [117]. All the non-Newtonian properties of the material are shifted to the solid phase and the liquid is treated as Newtonian. Two-dimensional contour maps

showing the transitions between laminar, transient and full turbulent filling are plotted (Fig.35). The dimensionless groups used for this mapping are not given in detail in this short paper. The three-dimensional process window for A356 aluminium alloy, based on laminar filling, is also identified (Fig.36). These results are highly significant.

6.3.3 Micro-Modelling

Rouff et al. [125] present a novel and interesting approach. Spherical inclusions (i.e. particles) containing entrapped liquid are assumed to deform very little and can slip relative to each other if the restriction between them is released. They are surrounded by solid bonds and the 'not entrapped' liquid where deformation generally takes place. This 'active zone', associated with the strain localization, is gathered in a layer surrounding the inclusions (Fig. 37). The volume solid fraction of the active zone, f_A^s , is the internal variable. During deformation, the bonds are broken and liquid is released. Thus, the bimodal liquid-solid distribution changes with the strain rate. Both the liquid and the solid are assumed isotropic and incompressible. The liquid and solid are then embedded in a homogeneous equivalent medium having the effective properties of the inclusion or the active zone. The viscosity of each inclusion and the viscosity of the active zone can then be determined and the effective viscosity of the semi-solid is a mixture of these. This approach enables very accurate prediction of the viscosity of Sn-15%Pb as a function of shear rate and shows great promise for further development.

7. Flow Visualisation

Virtually all the experimental validation of die filling patterns reported in Section 6 involves interrupted filling. The difficulty with this is that the effects of inertia compromise the results, with the material continuing to travel even when the ram has stopped. The most appropriate way of checking the position of the flow front during die fill is with *in situ* observation. The main recent work with transparent sided dies is that by Petera et al.[150] and Ward et al. [98]. Petera et al. [150] use a T-shaped die, covered with a glass plate on one side. The die is integrated into an oven to ensure that conditions are isothermal. Experiments have been carried out with Sn-12%Pb. The effect of piston velocity on the flow front is shown in Fig.38. At low piston velocity (Fig.38 (a)), no detachment of material from the walls of the die could be observed. At much higher piston velocity (Fig.38(c)), there is significant detachment, with the potential to form cavities in the final product. Ward et al. [98] established an arrangement which could be used with both SnPb and with aluminium alloys. Various obstacle shapes were placed in the path of the flowing material to observe flow fronts remerging. Fig.39 illustrates the results for Sn15%Pb and Fig.40 for A357 aluminium alloy. The die entrance was either parallel sided or splayed. Obstacles included cylinders of various diameters and 'spiders' used in the manufacture of PVC pipe. Remerging was sensitive to ram velocity and obstacle shape.

8. Concluding Remarks

The main focus for this review has been the modelling of semisolid processing. As background for that, routes to spheroidal microstructures, types of semi-solid processing and the advantages and disadvantages have been summarised.

Groundwork on rheology and the origins of thixotropy have been laid and mathematical theories of thixotropy introduced. Experimental data for input into modelling is crucial and depends on measuring behaviour during rapid transients, either through rapid shear rate jumps in rheometers or through rapid compression testing. The review of modelling has then been divided into those models based on finite difference methods and those based on finite element. In addition, some models are one-phase and some are two-phase. Papers on modelling are summarised in Tables 4, 5 and 6 and in the text are dealt with in sections, grouped together where there is common ground.

There are a multiplicity of approaches to the modelling of semisolid forming. What emerges clearly here is the lack of quantitative measures of the accuracy of the results and a lack of direct means of comparison. There is also a serious need for more rheological data, both for Sn-15%Pb (the classic 'model' alloy for semisolid thixotropic studies), for aluminium alloys used in commercial forming, and for other materials such as steels where there is significant interest in commercial use. This rheological data is difficult to obtain and great care has to be taken to avoid artefacts and to ensure the data is appropriate for the application. For example, thixoforming is essentially a rapid transient rather than a steady state process. Despite these difficulties, accurate modelling can be a great aid in die design, predicting appropriate processing conditions and minimising defects. The recent development of 'maps' by Alexandrou and co-workers [114] and by Modigell et al. [124] is highly significant in this respect.

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