Abstract: Rheology of mixtures in the solidification range (semi-solid metallic alloys, magmas, corium, molten nitrates) has been studied during continuous cooling. For a given shear rate, two empirical relationships between viscosity and solid volume fraction have been proposed, based on either an exponential relationship proposed by Ramacciotti or a Krieger-Dougherty relationship. A study on molten nitrates showed the quantitative effect of the shear rate on the apparent viscosity. This relationship is also applicable to other types of solidifying mixtures. Visualization during solidification in a shear cell enabled the determination of the main physical phenomena and their relationship to rheology.

Keywords: Rheology, Solidification, Semi-solid, Suspensions, Visualization

1. Introduction

Rheology of solidifying alloys and mixtures is a key aspect of natural phenomena such as magmatic lava flows. It also occurs in the processing of metallic alloys in the semi-solid state. Finally, it controls the flow of the molten material (called corium) that would form in the hypothetical case of a nuclear reactor severe accident. This corium is mainly formed of UO₂, ZrO₂, FeOₓ, mixed with concrete decomposition products and can have a 1000°C interval between its liquidus and solidus temperature.

In this paper, the term semi-solid will be used to describe a slurry of crystals in a solidifying liquid subjected to a shear stress. Viscosity of these two-phase mixtures is a strong function of the solid fraction φ. Below 10 %vol, the presence of crystalline particles has a small effect on the rheology of the suspension, which remains close to that of the liquid phase [1]. Above a maximum solid fraction φm, known as the packing fraction, there is a continuous network of solid particles leading to a percolation regime. This threshold has been estimated by different authors as being between 25 %vol (for Holyoke basalt samples at rest studied by Philpotts et al. [2]) and 80 %vol (for sheared semi-solid alloys reported by Flemmings [1]). The transition from a viscous to a rigid behaviour varies according to crystal size dispersion [3] and strain rate [4, 5]: e.g. Sudduth [6] proposed a generalized modelling of the packing fraction showing that it increases from 64 % for monodisperse suspensions to 100 % for evenly-distributed polydisperse suspensions. The transition also depends on the particle shape which is controlled by the strain rate since high strain rates tend to produce rounder particles.

Between these two limiting cases, classical hard-sphere suspension models underestimate the apparent viscosity of semi-solids by at least one order of magnitude [7]. In order to focus on the main parameters, we limit our study to semi-solid materials for which there is only one liquid phase, which is Newtonian, and no inert materials are present.
Experimental analyses show that materials in the semi-solid state have a shear thinning behavior. As described by Vigneresse et al. [5], even if the completely molten material behaves as a Newtonian liquid, it becomes a multiphase (yield stress) material when crystals appear, and later behaves as a solid through which the remaining liquid phase percolates. When this stage is reached, the viscoelastic solid is several orders of magnitude more viscous than the above liquidus fluid.

Solid particle morphology has a crucial influence on the semi-solid rheology [1]. More spherical particles will lead to a lower semi-solid viscosity. It is classically known that high shear rates and/or low cooling rates lead to globular morphologies while, on the opposite, low shear rates and/or high cooling rates favour dendritic shapes.

Two limiting experimental approaches have been classically used for the rheology of semi-solid materials [1, 8]: either the semi-solid material rheology is studied at a constant temperature within the solidification interval or its viscosity is measured while it is cooled at a constant rate. In the former configuration, the effects of strain rate changes and of thixotropy are visible. This paper is mainly devoted to the latter case that is considered to be closer to what occurs during the continuous cooling of mixtures during natural or artificial processes.

Figure 1. Typical evolution of the semi-solid properties during one experiment. Temperature (solid line), shear rate (dashed line), solid volume fraction (dash-dot), relative viscosity (dotted line).

Figure 1 presents the typical sequence of a constant cooling rate semi-solid viscometry test. The mixture is first heated above the liquidus temperature to homogenize it. Then, shear is applied to the fluid and is maintained constant throughout the test. The temperature is lowered at a constant cooling rate, causing crystallization and an increase in the relative viscosity. The test is generally ended by a quench in order to freeze the microstructure for post-test analyses. Because of the continuous cooling, it is not possible to differentiate the effect of thixotropy from that of the ongoing solidification.

The semi-solid rheology will be, in this paper, modeled as an extension of the simpler case of inert particle suspensions for which classical laws for the relative viscosity ($\eta/\eta_{\text{liquid}}$) are reported in Table I. Some of them have been obtained from first principles while others are simply correlations.

$$\eta_{\text{rel}} \approx 1 + 2.5 \phi$$

Einstein (1911) [11]

$$\eta_{\text{rel}} \approx \exp(2.5\phi)$$

Arrhenius (1917) [16]

$$\eta_{\text{rel}} \approx \left(1 - \phi / \phi_m\right)^{-2.5}$$

Roscoe (1952) [12]

$$\eta_{\text{rel}} \approx \exp\left(\frac{2.5\phi}{1 - \phi / \phi_m}\right)$$

Mooney (1951) [13]

$$\eta_{\text{rel}} \approx \left(1 - \phi / \phi_m\right)^{-2.5}\phi_m$$

Krieger and Dougherty (1959) [17]

$$\eta_{\text{rel}} \approx 1 + 2.75\phi + 10.05\phi^2$$

Thomas (1965) [30] + 0.00273 exp(16.6\phi)

$$\eta_{\text{rel}} \approx \left[1 + \frac{0.75 \cdot \phi}{1 - \phi / \phi_m}\right]^2; \phi_m = 0.55$$

Chong et al. (1971) [14]

$$\eta_{\text{rel}} \approx 1 + 2.5\phi + 6.2\phi^2$$

Batchelor (1977) [26]

$$\eta_{\text{rel}} \approx 1.3 \left(1 - \phi / \phi_m\right)^2$$

Brady (1993) [15]

Table I. Viscosity laws proposed for hard sphere suspensions; $\phi$: solid volume fraction, $\phi_m$: packing fraction, $\eta_{\text{rel}}$: relative viscosity ($\eta/\eta_{\text{liquid}}$).

In the first section, several experimental data on semi-solids, obtained during transient solidification, will be analyzed. Experiments with a mixture of semi-solid nitrates are analyzed to propose a simple empirical viscosity model. This approach will then be validated against literature data.

Finally a microscopic real-time visualization enables the observation of the effects of shear rate on semi-solid crystallization and on the solid particle behaviour.
2. Experimental data on semi-solid viscosity

The viscosity of a semi-solid mixture depends on its chemical composition, temperature and pressure as well as on the volume fraction, the shape of the solid particles and obviously shear rate and history. Ryerson et al. [9] and, independently, Seiler and Ganzhorn [10] proposed to estimate the viscosity of semi-solids by first determining the viscosity of the remaining liquid phase, and secondly by taking into account the solid phase as a suspension of crystals in the remaining liquid. In this approach, the solid volume fraction is estimated using a thermodynamic model of the solidification process. It must be underlined that, during the solidification process, the viscosity of the liquid phase varies, first because of cooling [the viscosity of the liquid, which is assumed here to be Newtonian, is generally a rate-controlled function of Arrhenius type, i.e. $\eta = \eta_0 \exp(E / RT)$], but also because its composition changes due to partial solidification.

In this section, published experimental data on semi-solid materials of various types (magmas, metallic alloys, corium-concrete mixtures, waxy oils) are analyzed. These data have been compared to two viscosity models:

- Ramacciotti [7] empirical model (extension of Arrhenius suspension model [16]):
  \[ \eta_{rel} = \exp(2.5 C \phi) \]
  where $C$ is an empirical factor. Ramacciotti et al. [7] have shown a very good agreement between this relationship and experimental data on semi-solid tin-lead by Joly and Mehrabian [8].

- Krieger and Dougherty [17] model (inert hard-sphere suspension) is better established for suspensions than Arrhenius model [16]. However, it largely underestimates the viscosity of semi-solid mixtures. Therefore, we propose to modify it with the adjunction of a corrective factor $K$ in the exponent:
  \[ \eta_{rel} = (1 - \phi / \phi_m)^{2.5} K \phi_m \]
  where $\phi_m$ is the maximal packing fraction. Some authors have determined the packing fractions $\phi_m$. In this case, this value is used in the modified Krieger-Dougherty relationship; otherwise, a value of 1 (due to the important polydispersity of the particles in semi-solids [7]) will be used.

The use of a coefficient $C$ or $K$ can be considered as a way to introduce in a simplified form an effective solid fraction proposed by Quemada [18] and applied to semi-solids by Perez [19].

It must be noted that both formulations are equivalent for solid fraction tending to zero, and that Ramacciotti’s relationship is no longer valid in the vicinity of the maximal packing fraction (but, at this packing fraction, the viscosity is anyhow very high, for our applications).

2.1 Semi-solid metallic alloys

Ramati et al. [20] have proposed to describe the relative viscosity $\eta_{rel} = \eta / \eta_{liquid}$ of a semi-solid metal slurry at volume fractions greater than 20 %vol with an exponential function of the solid fraction. Taha et al. [21] proposed the following expression for the apparent viscosity of semi-solid Bi-17 %w Sn alloy in function of the solid volume fraction $\phi$ and of the shear rate $\gamma$:

\[ \eta = 0.34 \exp(13.08 \phi) \gamma^{-4} \]

Turng and Wang [22] have proposed, for high cooling rates (> 1000°C/mn) of Sn-15 %w Pb and Zn-27 %w Al-2 %w Cu semi-solid alloys, the following experimental law:

\[ \eta_{rel} = \exp(16 \phi) \]

This corresponds to the Ramacciotti relationship (Eq. (1)) with $C = 6.4$.

As proposed by Lewis and Nielsen [23], $\ln(\eta_{rel} / 2.5 \phi)$ has been plotted on Figure 2. It corresponds to the local evaluation of the $C$ multiplying factor in Eq.(1). For data by Joly and Mehrabian [8] on semi-solid Sn-15 %w Pb alloys at various shear and cooling rates, this $C$ factor remains independent of the solid fraction above 25 %vol for each experimental condition and lies between 4 and 8.

Figure 3 presents, for one typical set of Joly and Mehrabian [8] data on lead-tin alloys, the fitting of the experimental relative viscosities with various modified suspension laws. The fits are good ($r = 0.996$) for Ramacciotti and the modified Krieger-Dougherty relationships.

Considering the case of adhesive particles, Cichocki and Felderhof [25] have proposed a modified form of the Batchelor [26] formulation in order to apply it to adhesive spheres:

\[ \eta_{rel} = 1 + 2.5 \phi + \left(5.913 + \frac{1.899}{\tau_B} \right) \phi^2 \]

where $\tau_B$ is the Baxter [27] interaction parameter which is infinite in the case of non-adhesive spheres.
and defines an infinitely narrow and deep attraction-well at the sphere surface.

![Figure 2](image)

Figure 2. Evaluation of $\ln \eta_{rel}/2.5\phi$ for solidifying Sn-15 % Pb at various shear rates and cooling rates (data from Joly and Mehrabian [8]). The viscosity of the remaining liquid is almost constant in the solidification range, around 1.5 mPa.s [24].

![Figure 3](image)

Figure 3. Fitting of semi-solid Sn-15 % Pb data from Joly and Mehrabian [8] for a cooling rate of 25°C/min and a shear rate of 230 s⁻¹ (circles) by various modified suspension laws.

Fitting Joly and Mehrabian data [8] with this model, in view of taking into account adhesion between neighbouring particles as suggested by Wang et al. [39] requires very large adhesivities. Anyhow, as shown in Figure 3, the fit is poor. So it can be concluded that these experimental data on semi solid alloys are not adequately explained by the adhesive particle suspension model.

The modified Krieger-Dougherty formulation can also be fitted to the experimental data. Table II shows the fitted values for experimental data by Joly and Mehrabian [8]. It appears that the least-square fitting requires taking a value of 100 %vol for the packing fraction, which is the value for evenly-distributed polydisperse suspensions [6]. The values of the exponent are 4.5 to 5.3 times higher than the 2.5 $\phi$ coefficient introduced by Krieger and Dougherty [17] for spheres.

In conclusion, the best fits of experimental data are found for metallic semi-solids with the Ramacciotti and modified Krieger-Dougherty relationships.

![Table II](image)

Table II. Least-square fitting of Ramacciotti and modified Krieger-Dougherty relationships on the experimental viscosity data for 0.33 K.mn⁻¹ cooled semi-solid Sn-15 %wt Pb [8].

2.2 Data on solidifying lavas and basalts

Figure 4 presents viscosity data on a Hawaiian tholeitic basalt semi-solid studied by Shaw et al. [28]. The relative viscosity has been estimated by dividing the experimental viscosity of the solidifying melt by the viscosity of the liquid, which has been extrapolated from the above-liquidus viscosity. It appears that these results cannot be described by suspension models, which are indeed dedicated to non-interactive hard spheres.

On the contrary, a good agreement is found with an exponential relationship between the relative viscosity and the solid volume fraction, corresponding to Ramacciotti formulation (Eq. (1)) with $C = 18.8/2.5 \approx 7.5$. The modified Krieger-Dougherty relationship (Eq. (2)) fits also very well the experimental data points.

These relationships are also verified on the Etna lava viscosity measured in laboratory by Pinkerton and Norton [32], if a multiplying factor $C = 3.1 \pm 0.3$ is used for Ramacciotti relationship or $K = 2.45 \pm 0.15$ for the modified Krieger-Dougherty formulation. Table III presents, for these data, the relative viscosity and the value of $C$ necessary to approximate it with equations (1) and (2). It appears that such formulations can provide an estimate of the apparent viscosity with a precision at least similar to that of the method described by Pinkerton and
Stevenson [33] which is based on the Roscoe [12] formulation:

\[
\eta_{rel} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5}
\]

Table III. Analysis of the viscosities of 1983 Etna lava measured during cooling for a unit shear strain rate by Pinkerton and Norton [32]. The viscosity of the remaining liquid and the crystal fractions had been estimated in the original paper. This lava’s main constituents are SiO$_2$ (47 %wt), Al$_2$O$_3$ (17 %wt), Fe$_2$O$_3$ (11 %wt), CaO (10 %wt) and MgO (6 %wt).

On the contrary, Lejeune and Richet [34] have measured the viscosity of a pyrope garnet (Mg$_3$Al$_2$Si$_3$O$_{12}$) melt in which aluminous enstatite crystals were suspended. At the experiment temperature, pyrope garnet crystallizes metastably to aluminous enstatite at kinetics slow enough to allow viscometric measurements with an a priori determined crystal volume fraction. In this case, the Roscoe [12] relationship gives a better fit than Ramacciotti one (Fig. 5). Similar results are found for the modified Krieger-Dougherty relationship.

In summary, the measured viscosities from solidifying lavas and basalts can be described with the Ramacciotti relationship with values of factor $C$ between 3 and 7.5 or with modified Krieger-Dougherty models with factor $K$ in the same range. Fits are obtained with an acceptable correlation ($r^2 > 0.85$). This is not the case for the data from Lejeune and Richet [34] that are indeed out of the scope of this study on semi-solid materials, since the solids have been artificially added to the melt instead of being formed by solidification under shear.

2.3 Corium-concrete mixtures in the solidification range

Similar rheological behavior has also been observed for oxidic melts, prototypic of the mixture that would be formed by a hypothetic corium-concrete
interaction [35]. For example, let us analyze the data that Roche et al. [36] obtained for a mixture of the following composition:

56.55 %\text{w} UO\text{2}, 19.95 %\text{w} ZrO\text{2}, 21.51 %\text{w} SiO\text{2}, 1.26 %\text{w} Al_2O_3, 4.2 %\text{w} CaO, 0.22 %\text{w} MgO

at temperatures between 2444 K (slightly above liquidus) and 2004 K (about 45 % vol solid fraction) with a Brookfield RVRH viscometer in which the stainless steel spindles have been replaced by molybdenum or molybdenum-tungsten spindles of the same geometry.

The viscosity of the liquid phase has been estimated using the methodology proposed by Seiler and Ganzhorn [10] where the liquid fraction is estimated assuming a quick cooling according to the Schell [37] hypothesis (infinite diffusion in the liquid phase, infinitely slow diffusion in the solid phases). The apparent viscosity can here also be well fitted to the Ramacciotti and modified Krieger-Dougherty relationships, with correlations coefficients above 0.85.

Figure 6 shows the evolution with the shear rate of Ramacciotti C factor determined for this data set by fitting Eq. (1). This factor, which integrates the semi solid behavior over the solidification range, decreases from 5.3 at low shear rates (2,25 s\text{\textsuperscript{-1}}) to 3,25 at 40 s\text{\textsuperscript{-1}}. For the modified Krieger-Dougherty relationship, the exponent K varies from 3,9 at 5 s\text{\textsuperscript{-1}} to 2.4 at 40 s\text{\textsuperscript{-1}}. This characterizes the shear thinning behavior of this semi-solid mixture.

The viscosity data from another viscometry test performed on a 34.11 %\text{w} SiO\text{2}, 26.7 %\text{w} UO\text{2}, 13.5 %\text{w} FeO, 9.8 %\text{w} ZrO\text{2}, 6.3 %\text{w} Al_2O_3, 5.85 %\text{w} CaO, 2.1 %\text{w} Fe_2O_3, 1.6 %\text{w} MgO corium-concrete mixture [38] also fit the Ramacciotti relationship with $C = 4.8$ at the shear stress of measurement (Figure 7). It also fits well the modified Krieger-Dougherty relationship with $K = 4.15$. These measurements were performed in a custom-made tungsten Couette viscosimeter, installed in a high temperature induction furnace.

Figure 7: Viscosity of a corium-concrete mixture (data from Skoutajan et al. [38] compared to estimation of the liquid phase and semi-solid mixture viscosity estimations)

2.4 Discussion

The Ramacciotti and modified Krieger-Dougherty relationships fit relatively well the experimental data on semi-solid mixtures, either metallic alloys, natural silicates or oxidic corium mixtures. It has also been noted that the relationship is not applied to the case of inert suspensions, even if the suspended particles have the chemical composition of what should crystallize from the melt, as in the experiment by Lejeune and Richet [34]. It is assumed that it is the characteristics of the particles solidified under shear that causes the large relative viscosity in comparison with the inert sphere suspension models.

It is recognized that, when crystallization occurs in a viscometer, precision is not optimal. The solid volume ratio estimation, which is based on thermodynamic solidification models, is also subject to some errors. Nevertheless, evidence for the proposed relationships comes from different types of experiments performed by six independent teams on semi-solid materials with a wide range of compositions.

It must be noted that a different behavior has been reported for isothermal semi-solid mixtures [8]. In this case, thixotropic effects are significant. During a continuous cooling, which is similar to the natural or artificial processes we are interested in, it is not
possible to distinguish between the effects of the increase in solid fraction and those of thixotropy. For both relationships, multiplicative factors are a decreasing function of the shear rate and an increasing function of the cooling rate.

3. Viscosity of solidifying nitride mixtures

In order to reach a better understanding of the semi-solid behavior, and in particular the effect of the shear rate, we have conducted a series of rheological experiments with low temperature transparent materials.

3.1 Experimental set-up

All our investigations have been conducted on a mixture of anhydrous silver and ammonium nitrides (81 %mol AgNO₃-NH₄NO₃) which has a large diphasic range at practical temperature (T_{solidus} = 110°C and T_{liquidus} = 170°C, see Figure 8), and is transparent, enabling the microscopic observations reported in Section 4. The liquid phase behaves similarly to a Newtonian fluid for the studied shear rates. Its viscosity is of 10 ± 1 mPa.s and is almost not modified throughout the range of temperatures and liquid phase compositions encountered during the solidification tests.

A Couette rheometer made of two concentric cylinders (30 mm mobile inner cylinder diameter, 32.6 mm static outer cylinder diameter) has been used for these experiments. It has been calibrated with silicone viscosity standards (from Brookfield Engineering Laboratories). The annular gap is about 40 times larger than the particle average size, in order to limit the experimental errors due to the presence of solids (wall effects and formation of local rigid networks). Shear rates in the range from 65 s⁻¹ to 1200 s⁻¹ have been studied in this set-up.

The nitride mixture is heated by electrical resistors. Cooling rate is set by natural convection to 1.8°C.min⁻¹. Sample temperature is measured by a thermocouple attached to the outer cylinder wall. The semi-solid temperature inhomogeneities are smaller than 4°C in tests without shearing. They are smaller when shear is applied.

The viscometer response time is small enough to guarantee that viscosity remains constant during measurement, even in case of continuous solidification. Viscosity has been measured every 0.5 s (i.e. every 0.015°C) while the procedure described in Figure 1 was applied.

3.2 Experimental results

The experimental data at 65 s⁻¹ and 841 s⁻¹ are plotted on Figure 9. It is then possible to reconstruct a virtual rheogram (Fig. 10) for a given solid fraction (or temperature since we assume thermodynamic equilibrium). It must be stressed that each point from the rheogram has been extracted from data measured during constant shear-rate experiments.
For solid volume fractions below 10 %vol, the behaviour is close to that of a Newtonian fluid. At higher concentrations, a peculiar rheological behavior is observed, showing a local maximum of the shear stress and a threshold shear-rate value (around 800 s⁻¹), above which the dynamic viscosity remains constant.

Figure 10. Virtual rheograms reconstructed at constant solid volume fractions.

Wang et al. [39] have reported the same behaviour on tin-lead and aluminium-zinc semi-solid alloys. They considered that the fluid was initially pseudoplastic, then “transient” and dilatant, before having again a pseudoplastic behaviour.

Both Ramacciotti and modified Krieger-Dougherty relationships fit satisfactorily \((r^2 > 0.94)\) the experimental data (Fig. 9). The \(C\) and \(K\) factors decrease when the shear rate is increased, as observed for all semi-solids presented in Section 2.

In the limit of very low shear rates, the viscosity of the solidifying mixture will be very high [2]. On the opposite, for infinite shear rate, the rheology will tend to that of a suspension of rigid spheres. From these asymptotic behaviours, relationships of the following form have been determined by least-square fit:

\[
C \text{ or } K = 1 + \left( \frac{\dot{\gamma}_c}{\dot{\gamma}} \right)^n \tag{7}
\]

The following fits have been determined on our data on silver – 10 %wt ammonium nitrates:

\[
C = 1 + \left( \frac{942}{\dot{\gamma}} \right)^{0.77} \tag{8}
\]

\[
K = 1 + \left( \frac{760}{\dot{\gamma}} \right)^{0.79} \tag{9}
\]

Critical shear rates \(\dot{\gamma}_c\) in the numerators of equations (8) and (9) are close to the threshold shear rate observed on Figure 10. Exponents (0.77 and 0.79) are close for both Ramaccio and extended Krieger-Dougherty relationships.

3.3 Generalization to bibliographical data

We have seen in Section 3.2 that the modified Krieger-Dougherty and Ramacciotti relationships fit very well \((r^2 > 0.94)\) our experimental data on semi-solid nitrates.

The modified Krieger-Dougherty and Ramacciotti relationships fit quite well \((r^2 between 0.85 and 0.99)\) all the published experimental data, dealing with several different materials and experimental conditions (lead-tin [22, 39] or aluminum-copper-magnesium alloys [40], volcanic lavas [28, 32] and corium [36]) that were discussed in Section 2.

The fitted factors \(C\) and \(K\) are increasing functions of the cooling rate. For equivalent cooling rates \((1.8°C/s)\) [experimental data from our work on nitrates, Tung and Wang [22] work on Sn-Pb and Kattamis and Piccone [40] measurements on Al-Cu-Mg semi-solids], \(C\) and \(K\) values are close even for different materials (at least for these three studied materials). However, the published data do not encompass enough data points (in terms of solid fractions and shear rates) to enable a reliable fit for \(K\) and \(C\) against shear rate.

The only exception is Roche et al. [36] data on corium. It covers a large enough set of shear rates to fit \(C\) and \(K\). In this experimental configuration, for which the cooling rate has not been reported, Ramacciotti relationship gives the best fit \((r^2 > 0.95)\). It leads to the following relationship:

\[
C = 1 + \left( \frac{325}{\dot{\gamma}} \right)^{0.31} \tag{10}
\]

3.4 Discussion

The two studied relationships fit satisfactorily the viscosity data on semi-solid mixtures, whatever their nature. The factors \(C\) and \(K\) are a function of the cooling and shear rates: they increase when the cooling rate is increased and/or the shear rate is decreased. Correlations have been proposed that link these factors to the shear rate, using two free parameters: a critical shear rate and an exponent. This expression is close to that proposed by Ito et al. [41] for the effective volume fraction, as estimated from "post-test" observations:
\[ \phi_{eff} = \phi + \phi_{	ext{entrapped liquid}} = \phi \left[ 1 + \left( \frac{121}{\dot{\gamma}} \right)^{0.76} \right] \]  

(11)

Effective volume fraction takes into account the liquid entrapped in clusters that thus do not participate to the flow.

The analogy between relationships (8), (9) and (11) suggests that the factors \( C \) or \( K \) could be interpreted as a corrective factor for the volume fraction, similarly to the suggested viscosity law by Perez [19]. However, such interpretation would lead to non-physical effective volume fractions (\( C\phi > 1 \)). A microscopic examination is thus needed to interpret these factors.

4. Microscopic observations under shear

In the previous section, it has been observed that viscosity was tightly related to cooling and shear rates. Flemmings [1] linked this to the observation that solid particles get more globular when cooling slows and/or shear increases. Two essential topics remain open: the globularisation mechanism, for which two hypotheses are present in the literature (dendrite arm fragmentation [42] or thermosolutal effect [43]), and inter-particular interactions (cluster formation, effective volume fraction).

4.1 Limitations of the classical observation technique

Up to now, semi-solid microstructure has been observed with a “post-test” approach: at a given temperature in the solidification range, a sample is quenched. The liquid phase solidifies with a very fine microstructure, so that it can be easily discriminated from the solid particles present before quenching. This approach provides useful information but is unable to show the morphological evolution of particles or clusters. Moreover, even if it shows the presence of contacts between particles, it is not possible to evaluate the nature of interactions (e.g., collisions between particles or strong bonds).

4.2 Real-time direct observations

To understand particle globularisation and clusterization, it is necessary to observe continuously the behaviour of semi-solid material. This is the rationale for our choice of a material that is transparent in the liquid state and translucent as a solid, enabling observation by optical microscope.

The experimental set-up [44] is designed for the observation of a sheared sample during its cooling (Fig. 11). The use of polarized light provides a better contrast between liquid and solid phases. This set-up comprises a Leica microscope connected to a video acquisition system (camera, monitor, recorder) and a Linkam CSS40 shear cell. This device enables to shear the sample while controlling its temperature. The upper glass is static while the lower part of the cell rotates. The molten pool is positioned thanks to capillary forces, since the lower cavity walls are far from the pool sides. Velocity gradient \( \dot{\gamma} = \omega r / h \) is inversely proportional to the gap thickness \( h \), which can be set by vertical translation of the cell upper-plate. At a given radial position, shear rate is constant over the sample thickness. Heating elements are in contact with the two plates. The small window for observation (diameter 1 mm) is located at 7.5 mm from the rotation axis. Due to the window small size, the shear rate is constant in the entire observation window.

4.3 Experimental results

In the absence of shear, solid phase appears as unidirectional columnar dendrites. This microstructure is classically found during the solidification of metallic alloys [1]. The formation of a columnar structure is due to the presence of a unidirectional heat flux leading to a macroscopic thermal gradient and a solute concentration gradient in the liquid phase.

Even a small shear rate (1 s\(^{-1}\)) changes dramatically the solidification structure (Fig. 12). With shear, the molten salt crystallizes then tends to be equiaxed (at least in the shear rate range of our tests, between 1 and 50 s\(^{-1}\)). These observations confirm Doherty [45] and Flemmings [1] hypothesis that the solid phase always appears as dendrite.
However, the particle evolution, in terms of size, number and shape, varies with the flow conditions. Dendrite size diminishes when shear rate is increased (Figs. 13a and 13c), in accordance with Doherty [45] and Flemings [1] findings on metallic semi-solids. During cooling, the number of particles (and especially the number of particles below 100 microns) increases with shear (Figs. 13b and 13d). This confirms Wang et al. data [39]. Also, the particles have a rounder shape for high shear rates.

Particle morphologic evolution during cooling is not important, even though a strong shear rate seems to favour a decrease of the interdendritic spacing (distance between dendrite arms), so that a quasi-smooth envelope can be defined (Fig. 13). Dendrite arm deformation or fragmentation was never observed in the studied shear rate range. Cluster formation (Fig. 13b) was only observed for very small shear rates (below 5 s\(^{-1}\)). In some tests, bubbles that had been entrapped in the shear cell were able to break clusters: the links between particles in such clusters must be weak. Above 5 s\(^{-1}\), the particle contact time after a collision is very short, so there is no bonding between particles.

It was also noted that when the volume fraction reached a “percolation threshold” (appearance of a continuous solid network), there were still some particles with a few degrees of freedom.

4.4 Discussion

These observations confirm that semi-solids crystallize initially as dendrites.

Interactions between particles during continuous cooling have been observed to be weak: for the studied material (nitrate mixture) no solid bond has been observed. Therefore, in the absence of cluster, the notion of effective volume fraction only encompasses the interdendritic liquid that is entrapped between the dendrite arms. Nevertheless, it has not been possible to derive from these observations a quantitative relationship between structure and the multiplicative coefficients C or K.

Neither deformation nor breakage of dendrite arms has been observed in our tests. Particle globularization under shear seems thus to be due to a thermostolutal effect. Actually, a higher shear rate clearly leads to rounder dendrites that tend to be equiaxial: a continuous envelope is formed around the particle. Shear tends to lower the concentration gradient, so it prevents constitutional undercooling [46], leading to a plane-front solidification (at the particle scale).

Even though this visualization was only possible with one transparent/translucent semi-solid, we assume that these results can be transposed to opaque semi-solids exhibiting similar rheological behaviour.

5. Conclusions

General relationships (Ramacciotti or modified Krieger-Dougherty relationships) have been proposed for solidifying mixtures viscosity. Both lead to a satisfactory description of the measured relative viscosities for intermediate volume fractions Actually this modelling has been neither validated for low volume fractions, where the relative viscosity is close to 1, nor for volume fractions above the packing fraction, where another phenomenology occurs. Nevertheless, this intermediate range is of practical interest for many practical applications.
The C and K factors modify Einstein coefficient 2.5. They express the solid particle morphological evolution (from dendrites to globules by a shear-controlled thermosolutal effect). Novel empirical laws linking these exponential factors to shear rate have been proposed and validated on a wide range of materials (nitrates, semi-solid metallic alloys, lavas, corium-concrete mixtures).

Microscopic observations of a mixture solidifying under shear have experimentally confirmed that mixtures crystallize under shear first as dendrites and then form rounder particles and clusters, depending on the shear and solidification rates. It also showed that solid particle clusters were mostly weakly bond. Therefore, the effective volume notion does not seem to explain satisfactorily the factors C and K introduced in the viscosity laws.

In conclusion, empirical laws, coupled to direct microscopic observations under shear flow, are proposed to estimate the viscosity of mixtures solidifying under shear, depending on both the solid volume fraction and the shear rate. Effect of the cooling rate, which affects the solid particle shape, must still be analyzed in subsequent studies.

6. References


Version française abrégée

La rhéologie de mélanges en cours de solidification sous cisaillement (alliages métalliques semi-solides, magmas, corium, nitrates fondu) a été étudiée durant un refroidissement continu. On propose d’utiliser des versions modifiées des modèles de suspensions de sphères rigides d’Arrhenius (relation de Ramacciotti) ou de Krieger-Dougherty, avec un facteur multiplicatif fonction du taux de cisaillement. Cette approche est d’abord établie sur des expériences déjà publiées. La rhéologie d’un mélange de nitrates fondu en cours de solidification a été étudiée expérimentalement. On en a déduit une relation empirique entre le facteur multiplicatif introduit dans les modèles de suspensions et le taux de cisaillement. Une visualisation en cours de solidification dans une cellule de cisaillement nous a permis de déterminer les phénomènes physiques en cours et de les relier à la rhéologie. Ceci nous a permis de confirmer que les semi-solides cristallisent d’abord sous la forme de dendrites qui globularisent sans qu’il n’y ait de bris des bras des dendrites, vraisemblablement par un effet thermosolutal local dépendant du cisaillement.