Rotational Rheometry of Liquid Metal Systems: A Study with Al-Si Hypoeutectic Alloys

Rotational Rheometry of Liquid Metal Systems: A Study with Al-Si Hypoeutectic Alloys

By

Mohammad Minhajuddin Malik

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AUTHOR: Mohammad Minhajuddin Malik.
B.E (Aligarh Muslim University, U.P., India)

SUPERVISOR: Dr Mohamed Hamed
Department of Mechanical Engineering
Dr. Sumanth Shankar
Department of Mechanical Engineering

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ABSTRACT

Rheological property such as shear viscosity and flow curve for metallic liquid systems has been evaluated. Pure Al, pure Zn, Sn based solder alloy and various compositions of Al-Si hypoeutectic binary alloys were the metallic systems included in this study. The effect of 0.023 wt % Sr addition to various compositions of Al-Si hypoeutectic binary alloys was also included in this study. For the Al-Si alloys, the viscosity and flow curve were evaluated as a function of melt superheat temperature, Si composition and shear rate experience by the liquid. A rotational rheometer was developed with a high temperature environmental furnace for this study. Three types of measurement geometry were evaluated: *cone and plate, Din Coaxial and Double Concentric Cylinder (DCC)*. The DCC geometry has been proposed as the most practical geometry for liquid metal viscosity measurement in rotational rheometer. Analytical solution to evaluate viscosity with the rotational rheometer equipped with DCC measurement geometry has been proposed. Further, the critical maximum allowable angular velocity for reliable viscosity evaluation has also been proposed for this system. It has been concluded that contrary to popular belief, liquid metal systems are non-Newtonian and shear thinning fluids. The effect of Si on the viscosity of Al-Si hypoeutectic alloys have been quantified as a function of shear rate and melt superheat temperatures. Further, it has been concluded that Sr addition to Al-Si alloys significantly alters the viscosity and the melt at low melt superheat temperatures.

ACKNOWLEDGEMENTS

I thank Dr. Mohamed Hamed and Dr. Sumanth Shankar for their help, guidance and financial support Dr Shankar spent numerous nights in the lab as a friend, teacher and guide to troubleshoot problems during the experimental setup phase This work would not have been possible without his extra effort.

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I thank General Motors of Canada (GM of Canada) and National Science and Engineering Research Council (NSERC) for their financial support.

I extend my sincere thanks to the technicians, machinist and non-teaching staff in the department of mechanical engineering for their help and support. I thank Jim McLaren for his support in machining various components. I would also like to thank my collegues at the Light Metal Casting Research Centre (LMCRC) for all their help and insightful discussions I thank Dr Jeyakumar Manickaraj and Ahmad Omar for helping me with experiments and simulation.

I thank my family members for being patient throughout my research period and supporting me all the way At last and most, I thank God.

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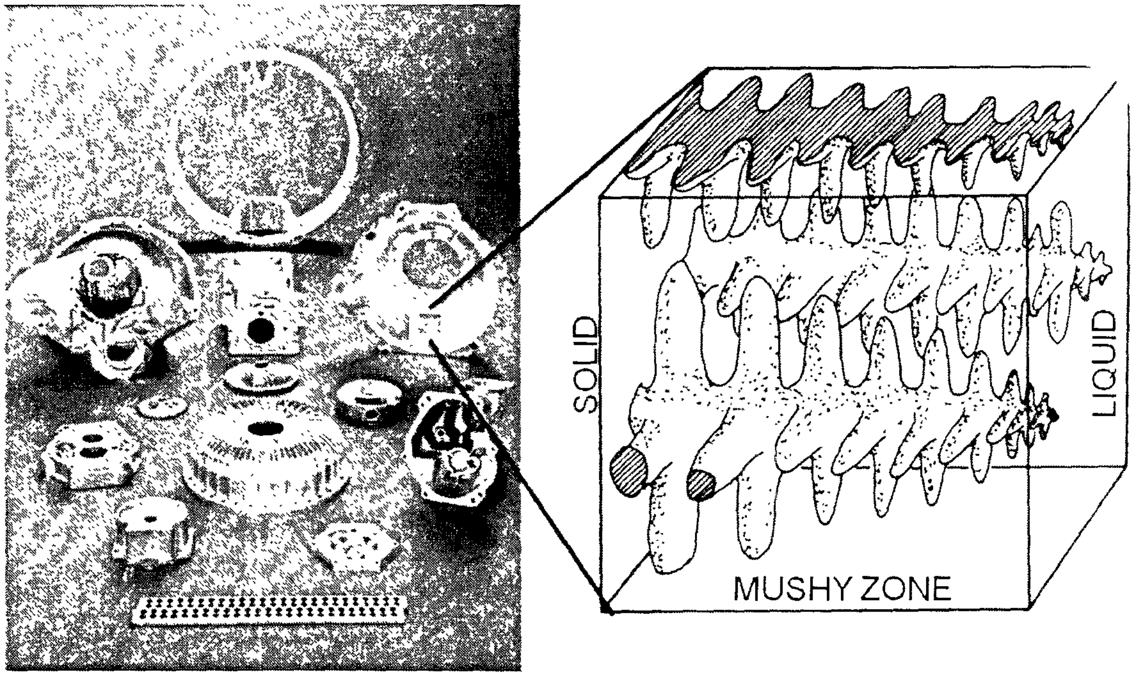
EXECUTIVE SUMMARY

Aluminum (Al) is the second most widely used metal other than Iron with increasing usage each year in the form of various Al based alloys [1]. Among Al alloys, Al-Si hypoeutectic alloys are most extensively used for casting components in Automotive and Aerospace industry The widespread application can be attributed to factors such as high strength to weight ratio, excellent castability and good performance properties. Canada is one of the key global players in Al industry. It had a market share of 15% of world exports in pure Al ingots in 1999. However the proportion of imported finished and semi finished goods is very high Al cast alloy products account for almost 25 % of the global Al products used in automotive industry. This leads to an increasing industrial demand for.

- Development of newer alloys with better mechanical and performance properties.
- New or improved casting process to increase the efficiency, productivity and reduce the wastage.



(a) (b)

Figure 1: Commercial application of Al-Si binary alloys (a) typical casting components and (b) schematic of the typical microstructure in these castings during solidification showing the solid on the left and the liquid on the right of the box with the two phase mushy zone in between.

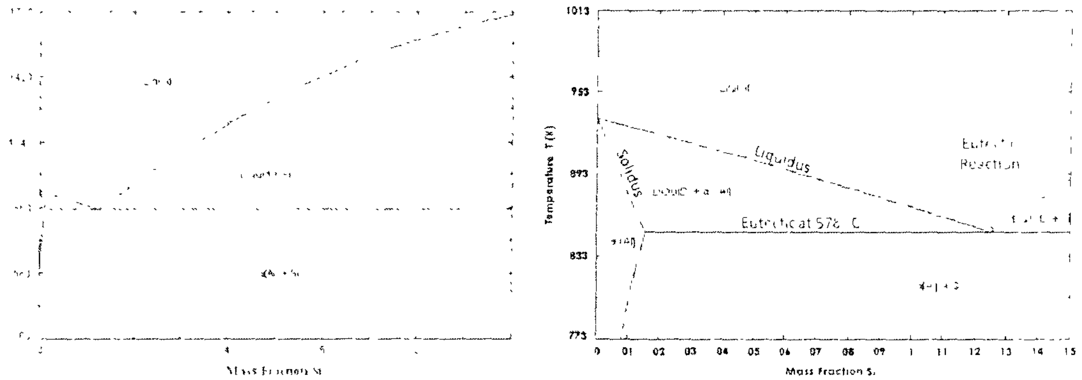
Figure 1(a) shows some typical cast components of Al-Si hypoeutectic alloys. During solidification of pure metals such as Al, the liquid transforms into solid at one constant temperature known as the melting point. However a binary or a multi-component alloy transforms from liquid to solid over a range over a range of temperature during which the solid and the liquid co-exist in a semi-solid state. Figure 1(b) shows a schematic of a

typical microstructure during solidification of a binary hypoeutectic alloy. The semi-solid region during solidification is known as the mushy zone. The mushy zone is bounded by the solid and the liquid and the heat is extracted from the liquid through the mushy zone and subsequently the solid phase.

Figure 2(a) shows the complete phase diagram for Al-Si binary alloy system. The eutectic reaction where in the liquid phase solidifies into a two phase solid alloy at an invariant point in temperature (578 °C) and Si mass fraction (0.125) is shown in Figure 2(a) and 2(b) The eutectic reaction for Al-Si binary alloy system is given by Equation (1)

$$Liquid \xrightarrow{578^{0}\text{ C and 0 125 mass fraction Si}} \alpha(Al) + Si \qquad (1)$$

The alloys with Si content less than eutectic composition are termed hypoeutectic and the alloys with Si content greater than eutectic composition are termed hypereutectic. Most commercial Al-Si alloys fall in the hypoeutectic region. Figure 2(b) shows the magnified phase diagram of the hypoeutectic alloy region. Si has a maximum solubility (0.015 mass fraction Si) in solid Al at 578 °C (eutectic temperature) and the alloy of Al with soluble Si is referred to as the primary α(Al).



(a) (b)

Figure 2: Al-Si binary alloy phase diagram. (a) the complete phase diagram for 0 to 1 mass fraction Si and (b) magnified region showing the hypoeutectic alloy between 0 and 0.125 mass fraction Si.

Let us consider the solidification of a typical Al-7mass% Si alloy. When the cooling liquid intersects the liquidus line (Figure 2(b)), the primary α(Al) phase evolves during start of solidification. As the liquid solidifies in the two phase mushy zone between the liquidus and eutectic lines (Figure 2(b)) the volume fraction of the primary aluminum phase increases with decreasing temperature; and at any specific temperature in the mushy zone, the liquid just ahead of the primary α(Al) phase will have a composition given by the liquidus line at that temperature and the composition of the solid α(Al) phase evolving is given by the solidus line (Figure 2(b)) at that temperature. At the end of solidification of the mushy zone (temperature at eutectic line) the composition of the last liquid just ahead of the solidifying primary Al phase is given by the eutectic composition and the composition of the last solidifying phase is given by the intersection of solidus and eutectic lines. Hence, during solidification of any hypoeutectic Al-Si alloy the mushy zone will have liquid compositions ranging from the eutectic composition at the interface of the mushy zone with the complete solid to the composition of the alloy at the intersection of the mushy zone with the complete liquid phase. Figure 3 shows a typical schematic of the microstructure of Al-Si hypoeutectic binary alloy.

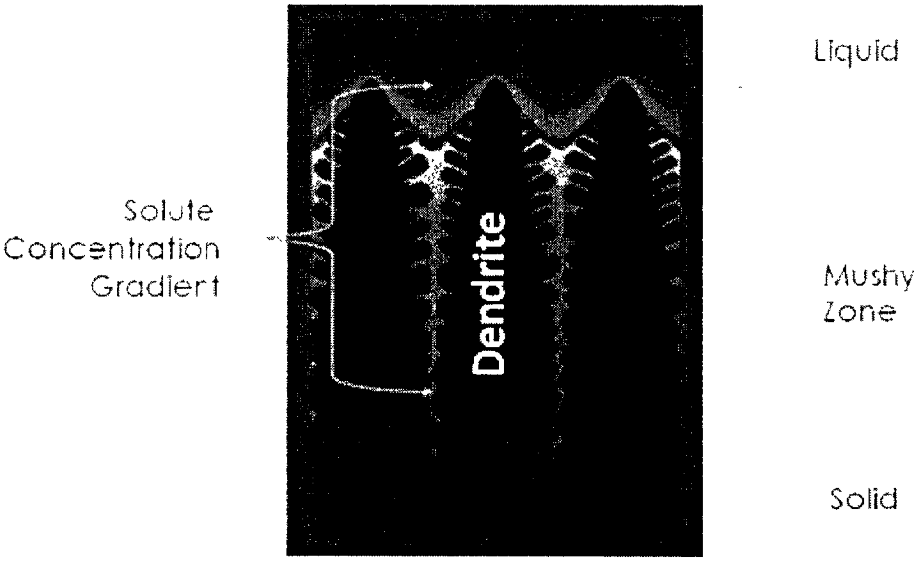


Figure 3: Typical schematic of the microstructure developed during solidification of Al-Si hypoeutectic binary alloy.

In Figure 3 the Si compositional gradient is shown from the solid to the liquid region between any two dendrites. The Si content near the solid phase is of eutectic composition and that near the liquid phase is the composition of the alloy solidifying. It is well known that volumetric shrinkage occurs during solidifying of the liquid to the primary α(Al) dendrite. The liquid in the inter-dendritic region fills this shrinkage to avoid cavities (defects) in the cast component. It is critical to fully understand the flow behavior of the inter-dendritic liquid to predict the evolution of the microstructure of the mushy zone during solidification and the evolution of defects such as porosity and shrinkage cavities. Simulation of microstructure and defect formation in these alloys will greatly enhance our predictability of casting component properties and performance.

The flow of liquid in the mushy zone is generated from various sources such as solidification shrinkage and buoyancy caused by thermal gradients and solute concentration gradients in the interdendritic liquid [2]. Viscosity is one of the critical parameters that quantify liquid flow behaviour.

Research has been ongoing to evaluate viscosity of Al and Al-Si alloys for the past sixty years [3]. However, there is a 400 % spread in the reported values of viscosity for these alloys [3]. The main reason for the spread is that most experiments were carried out in an Oscillation Vessel Viscometer (OVV) which inherently assumes that the Al-Si liquid sample has Newtonian flow behaviour. Newtonian fluids have a constant viscosity irrespective of the shear rate experienced by the liquid [4]. However, this assumption has not been verified or validated. Only few techniques such as rotational rheometry can evaluate viscosity for one specific shear rate experienced by the liquid. There have been recent fundamental simulation carried out using Non-Equilibrium Molecular Dynamics (NEMD) which have shown that liquid metal systems may exhibit non-Newtonian and shear thinning behaviour [5,6]. Shankar et al [7] have shown by experiments that Al - 12.5 wt% Si alloy may exhibit a non-Newtonian and shear thinning flow behaviour as well.

The aim of this project is to evaluate the rheological and atomistic characteristics of the Al-Si hypoeutectic alloys. The project has been initiated in two phases carried out in tandem: one to evaluate the rheological properties via rotational rheometry and the second to carry out atomistic characterization of the structure of liquid Al-Si hypoeutectic alloys by diffraction experiments with neutron and high energy x-ray (synchrotron) beams. The present thesis forms a part of the first phase of the project where in the viscosity values of these alloys were evaluated.

The following presents the objectives of this study:

- Design and develop a high temperature rotational rheometer equipped with an environmental furnace capable of reaching temperatures of over 1100 K.
- Develop measurement geometry to contain the sheared liquid such that the shear rate experienced by the liquid at a specific angular velocity is uniform throughout the liquid.
- Evaluate the viscosities of pure Al and Al-Si hypoeutectic alloys.
- Evaluate the effect of Sr addition of around 0.02 wt% to Al-Si hypoeutectic alloys.

In the first phase of the project an AR2000[*] rotational rheometer with an environment chamber was commissioned. A furnace capable of reaching 1100 K was designed and installed in the environment chamber. The chamber was purged with ultra high purity (< 2 ppm oxygen) Ar gas at 5 litre/min to minimize oxidation of the liquid metal

Three measurement geometry systems to contain the sheared liquid metal were considered: the cone and plate, DIN Coaxial Cylinder and Double Concentric Cylinder (DCC). Several of these geometries were machined from various metals and ceramics to ascertain the chemical reactivity with molten Al alloys. The cone and plate geometry is theoretically the most suitable to carry out experiments as the shear rate in the liquid at a specific angular velocity is uniform throughout. However, this geometry caused spillage of metal due to the absence of any wall to protect the rotating liquid [3] Only about ten percent of the experiments carried out with the cone and plate geometry were successful. The DCC geometry machined with the Cotronics 902[†] machinable ceramic proved to be the most practical Subsequently, viscosity experiments in this project were carried out with the DCC geometry. Details of the geometry selection and design are presented in subsequent chapters of this thesis.

The rheometer was evaluated for sensitivity of measurements and repeatability by using a standard Cannon S2000[‡] liquid Further, viscosities of Pure Al, pure Zn and a low melting

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[*] Advanced Rheometer, TA Instruments, New Castle, DE, USA http://www.tainstruments.com

[†] Cotronics Corporation, Brooklyn, NY, USA http://www.cotronics.com.

[‡] Cannon S2000 is a certified viscosity fluid developed and marketed by Cannon Instrument Company State College PA, USA http://www.cannoninstrument.com

Sn based solder alloy were evaluated to verify the repeatability of the rheometer Subsequently, Al-Si alloys of various hypoeutectic compositions were prepared and cast into hollow cylinders for viscosity evaluation. The experiment materials and procedures along with the results and discussion are presented in subsequent chapters of this thesis.

This study is part of a collaborative project among Light Metal Casting Research Center (LMCRC) at the McMaster University, General Motors of Canada and National Science and Engineering Research Council (NSERC) of Canada

This thesis is presented as a consolidation of four publications that were written as a part of this project

Author's Contribution to Publications

The following are the contributions by the author of this thesis to all the four publications included

- Review prior-art.
- Design and assemble rotational rheometer.
- Design, develop and manufacture measurement geometries
- Prepare and cast alloys; and subsequently prepare samples for rheometry
- Carry out rotational rheometry experiments.
- Review and consolidate rheometry data.
- Analyze results.
- Write discussions.
- Prepare publication manuscripts.

The details of each publication are given below:

PUBLICATION A

Title:	How to measure viscosity of liquid aluminum ALLOYS?
Authors:	Mohammad Minhajuddin Malik[§], Guillaume Lambotte[**], Mohammed S Hamed[§], Patrice Chartrand[**] and Sumanth Shankar[§]
Publication:	: 2nd International Symposium Edited by Paul N. Crepeau, Murat Tiryakioğlu and John Campbell TMS (The Minerals, Metals & Materials Society), 2007
Objectives:	Introduce rotational rheometer as viable technique to evaluate viscosity of liquid Al alloys.
Details:	• Compared Experimental efforts to evaluate viscosity of Al alloys
Conclusion:	• Oscillating Vessel Viscometer (OVV) is unsuitable to evaluate viscosity of liquid metals. • Liquid Al-Si eutectic alloy seem to exhibit non-Newtonian and shear thinning behaviour.

PUBLICATION B

Title:	Rotational Rheometry of Liquid Metal Systems: Measurement Geometry Selection and Flow Curve Analysis.
Authors:	Mohammad Minhajuddin Malik[§], Manickaraj Jeyakumar[§] Mohammed S Hamed[§], Michael J Walker[‡‡], Sumanth Shankar[§]
Publication:	Shape CastingJournal of Non-Newtonian Fluid Mechanics, (Submission in September 2008)
Objectives:	▪ Optimize the measurement geometry design. ▪ Evaluate flow behaviour and viscosity of liquid Al, Zn and Sn solder alloy.

Details:	• Three measurement geometries were evaluated
	  • Cone and Plate
	  • DIN Coaxial Cylinder
	  • Double Concentric Cylinder (DCC)
	• Flow curves and viscosities of liquid Al, Zn and Sn solder alloy were evaluated.

Conclusion:	▪ DCC is most practical measurement geometry. ▪ Liquid Al, Zn and Sn solder alloy exhibit non-Newtonian and shear thinning behaviour

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[§] Centre for Solidification & Thermal Processing (CSTP), McMaster University Hamilton, ON Canada L9H 2E8

[**] Centre for Research in Computational Thermochemistry Department of Chemical Engineering Ecole Polytechnique, Montréal, QC Canada H3C 3A7.

[‡‡] General Motors Michigan, USA

PUBLICATION C

Title:	Rheology of liquid Al and Al-Si Hypoeutectic alloys
Authors:	Mohammad Minhajuddin Malik§, Manickaraj Jeyakumar§, Mohammed S Hamed§, Michael J Walker, Sumanth Shankar§
Publication:	Material Science Engineering, (Submission in September 2008)
Objectives:	▪ Evaluate viscosity of Al and Al-Si hypoeutectic alloy as a function of shear rate and melt temperature.
Details:	▪ Viscosity of Hypoeutectic Al-Si alloys were evaluated for 3wt%, 7wt%, 10wt% and eutectic (12.5wt%)Si composition at four individual melt superheat temperatures using the DCC measurement geometry. ▪ Shear rates between 0.16 and 467 s^{-1} were used in the study
Conclusion:	▪ Liquid Al-Si eutectic alloys exhibit non-Newtonian and shear thinning behaviour. ▪ Al-7 wt% Si show the least viscosity at all shear rates and temperatures among the alloys investigated. ▪ Viscosity of each alloy decreases with temperature for all shear rates and agreed with Andrade's equation.

PUBLICATION D

Title:	Effect of Sr Addition on the rheology of Liquid Al-Si Hypoeutectic Alloys
Authors:	Mohammad Minhajuddin Malik§, Manickaraj Jeyakumar§, Mohammed S Hamed§, Michael J Walker, Sumanth Shankar§
Publication:	Scipta Materialia, (Submission in September 2008)
Objectives:	▪ Evaluate the effect of Sr addition on Al-Si hypoeutectic alloys.
Details:	▪ Rotational rheometry with DCC geometry was used to evaluate effect of 0.02 wt% Sr of viscosity of Al-Si alloys with 7 wt%, 10 wt% and 12.5 wt% (eutectic) Si content at four individual melt superheat temperatures. ▪ Shear rates between 0.16 and 467 s-1 were used in the study.
Conclusion:	▪ Sr addition to Al-Si alloys increased the melt viscosity significantly at low melt superheat temperatures. ▪ Sr addition does not affect viscosity of pure Al ▪ Al-7wt% Si alloy showed the highest viscosity and the highest change in viscosity after Sr addition to the melt.

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Shape Casting: 2nd International Symposium *Edited by Paul N. Crepeau, Murat Tiryakioğlu and John Campbell*
TMS (The Minerals, Metals & Materials Society), 2007

HOW TO MEASURE VISCOSITY OF LIQUID ALUMINUM ALLOYS?

Mohammad Minhajuddin Malik[1], Guillaume Lambotte[2], Mohammed S Hamed[1], Patrice Chartrand[2], Sumanth Shankar[1],

[1]Centre for Solidification & Thermal Processing (CSTP), McMaster University, Hamilton, ON, Canada L9H 2E8.

[2] Centre for Research in Computational Thermochemistry, Department of Chemical Engineering, École Polytechnique, Montréal, QC, Canada H3C 3A7.

Keywords. Viscosity, Rheometer, Aluminum, and Al-Si alloy

Abstract

Viscosity of liquid Al and Al-Si alloys are critical to better understand the solidification and porosity formation in the mushy zone towards the end of solidification of the alloy. In this paper, viscosity data from the literature for Al and Al-Si alloys are presented along with the drawbacks of the most prevalent technique used to evaluate viscosity – the oscillating vessel viscometer. Experimental techniques using an alternative rotational rheometer equipped with a cone and plate measuring geometry are presented along with results of flow characterization of molten Zn and Al-Si alloys. The results show that molten Zn exhibits Newtonian flow characteristics and molten Al-Si eutectic alloy exhibits a non-Newtonian behavior at various melt superheats and low shear rate regimes

Introduction

Al-Si alloys are the most widely used alloys in the automotive and aerospace casting industry. It is critical to fully understand the flow characteristics of these alloys since the rheological properties of the liquid influences the filling of the mold cavity and feeding the mushy zone during solidification. Understanding the rheological properties of Al-Si alloys will help develop robust predictive models simulate the evolution of microstructure, porosity formation and hot tearing tendencies in the mushy zone during the final stages of alloy solidification. One of the key rheological properties of liquid metals is apparent viscosity.

Figure 1 presents a comprehensive graph tabulating most of the available date for the viscosity of pure Al. It is evident in Figure 1 that there is a 400% spread in the data available in the literature today [1]. Figure 2 presents similar tabulation of viscosity data for various compositions of Al-Si alloys. Figure 2 shows a 100% spread in the data from literature [1]. Over ninety percent of the data shown in Figures 1 and 2 were obtained using the oscillating vessel viscometer. Although the data was acquired by critically controlled experiments, there is a large spread in the reported values of melt viscosity. This may not be fully attributed to differences in the mathematical formulation and experimental errors. The shear rate experienced by liquid metal in the oscillating vessel viscometer is not uniform both in spatial and temporal regimes. However, the viscosity is measured over a range of shear rates and reported as one value for the liquid metal over the entire spatial and temporal regimes for the experiments. This reported value of melt viscosity is meaningful if and only if the liquid exhibits Newtonian flow behavior. In other words, the reported values of viscosity in Figures 1 and 2 [2] are valid only if the viscosity is independent of the shear rate experienced by the molten metal. However, if the liquid metal exhibits non-Newtonian behavior, a singular value of viscosity for an entire shear rate regime is not accurate. Therefore, we believe that the spread in reported viscosity values shown in Figures 1 and 2 may be due to an innate flaw in the assumption that liquid Al and Al-Si alloys exhibit Newtonian flow behavior. Further, there is no experimental evidence in the literature to justify an assumption of Newtonian or non-Newtonian flow behavior of Al and Al-Si alloys. Hence, the use of the oscillating vessel viscometer may not lend itself to accurate evaluation of melt viscosities of liquid metals exhibiting non-Newtonian flow characteristics.

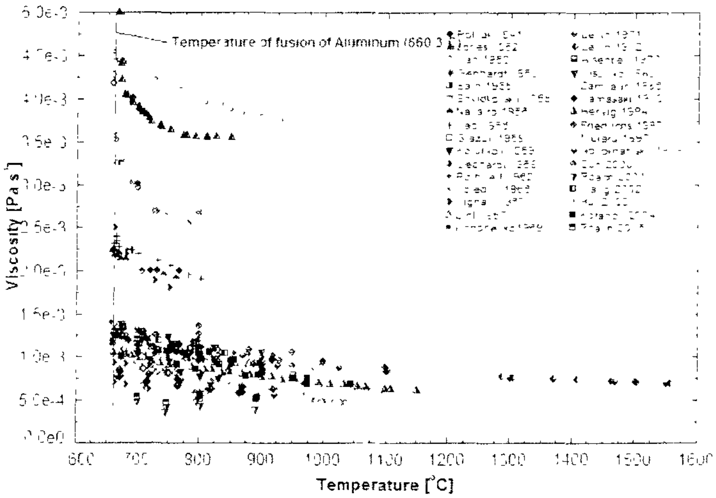


Figure 1: Reported viscosity data of pure liquid aluminum at various temperatures [2]

In this paper, we will present experimental evidence to show that, contrary to popular belief, pure Al and Al-Si alloys exhibit non-Newtonian flow behavior. Further, an alternate experimental scheme using a rheometer fitted with a cone and plate measurement geometry will be presented to evaluate, more accurately, viscosities of molten metals exhibiting non-Newtonian flow characteristics.

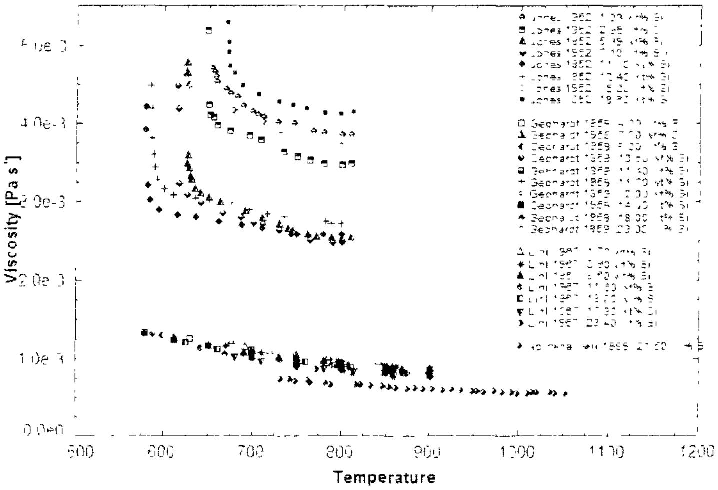


Figure 2: Viscosity data of liquid Al-Si alloys [2]

Viscosity of Molten Metal

Prevalent viscosity measurement techniques for molten metals and alloys include the capillary method, oscillating vessel method, rotational method, oscillating plate method, and acoustic method. The oscillating vessel viscometer is the most popular among these techniques accounting for over 90% of the reported data for Al alloys shown in Figures 1 and 2. [1]

In the oscillating vessel viscometer the fluid sample in the crucible or vessel is set in oscillatory motion about a vertical axis by applying a set torque pulse. The torque will create an oscillatory motion of the vessel, which will eventually damp out, primarily by frictional energy absorption and viscous dissipation within the liquid. The viscosity of the liquid is then calculated by solving the governing second order differential equation of motion shown in Equation (1) as presented by Wang et al [3].

$$I_0\omega_0\left(\frac{d^2\beta(\tau)}{d\tau^2} + 2\Delta_0\frac{d\beta(\tau)}{d\tau} + (1+\Delta_0)^2\beta(\tau)\right) = 0 \qquad (1)$$

Where I_0 is the moment of inertia of the empty vessel or crucible. ω_0 is the angular frequency, $\beta(\tau)$ is the angular displacement, Δ_0 is the damping parameter and τ is dimensionless time.

It is the most preferred method for viscosity measurement of liquid metals due to the ease and accuracy in measuring the time period and decrement of oscillations. In addition, the geometry of the cylindrical crucible used is in range of 50 mm to 125 mm in height and 14 mm to 50 mm in internal diameter, which also leads to a relatively stable temperature profile throughout the sample [1][4].

Despite simplicity of construction, the mathematical equations used to describe the oscillatory movement of the crucible are complex and presently there is no reliable mathematical procedure available for solving them [5]. One of the major reasons for the spread in viscosity could be differences in mathematical models used to relate the experimental parameters to viscosity. The major mathematical models are Knappwost's Equation [6], Shvidovskii's Equation [7], Roscoe's Equation [8] and the Kestin & Newell model [9]. Among these mathematical models for the oscillating vessel viscometer, according to Iida et al [4], the Roscoe Equation provides the most accurate values of viscosity. However, the absolute Roscoe equation needs further modification by means of correction factor to account for the end effects caused by the curvature of the liquid metal at the free surface [4].

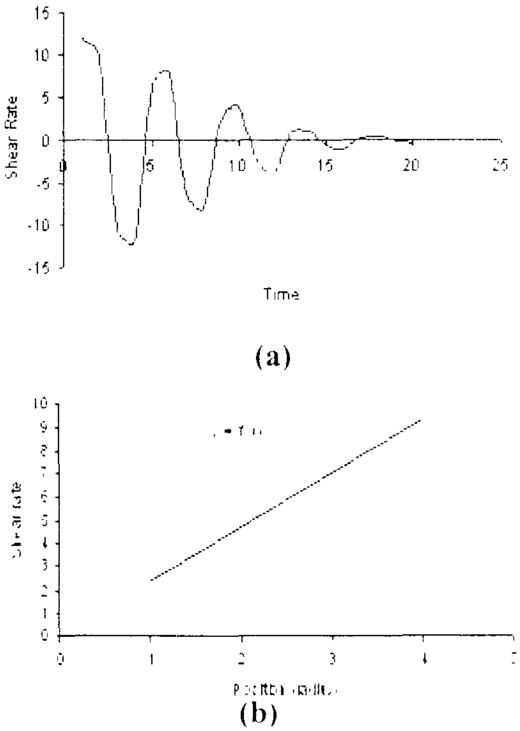


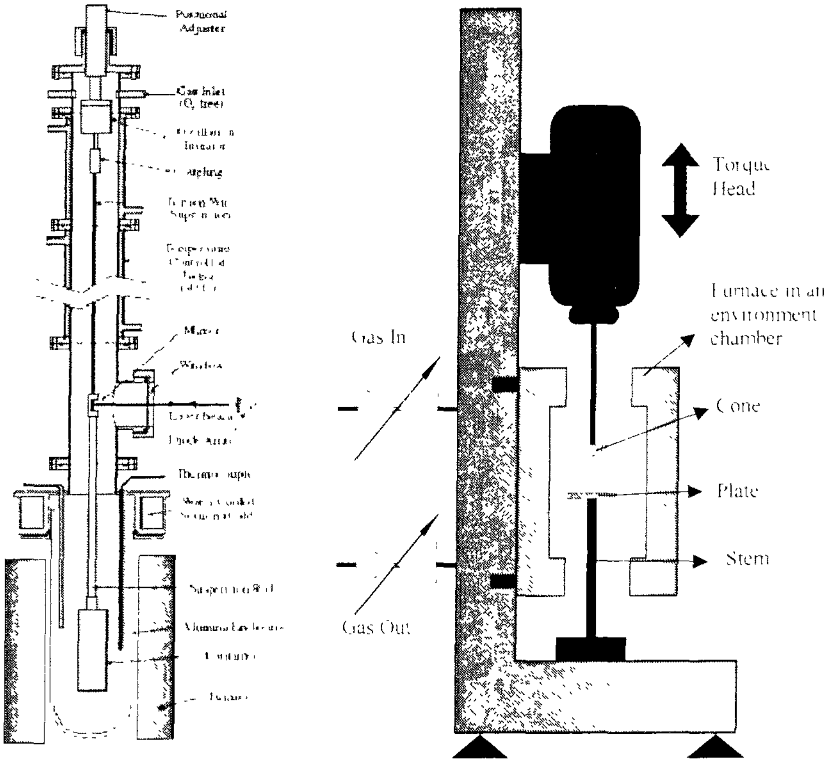
Figure 3: Schematic graphical representation of the variation of shear rate in an oscillation vessel viscometer. (a) Temporal variation and (b) Spatial variation.

One of the main assumptions in using the oscillation vessel viscometer and developing the mathematical models is that the liquid metal exhibits Newtonian flow behavior. Figure 3 shows a typical schematic graphical representation of variation of shear rate of the liquid metal as a function of time and position within the oscillating vessel. Figure 3 (a) shows that the shear rate periodically decreases over the entire time of experiment due to the viscous damping of the liquid. Figure 3 (b) shows that shear rate continuously increases from the centre of the oscillating vessel to the wall of the vessel. Hence, the shear rate of the liquid in the oscillating vessel is not a constant at any instant in time or position in space. To present a singular value of viscosity for such an experimental set up will entail the assumption that viscosity of the liquid metal is independent of the shear rate (Newtonian flow behavior). Hence, to accurately evaluate viscosities of liquid metal showing non-Newtonian dependence on shear rate an alternate experiment technique will have to be adopted. A suitable technique is the rotational rheometer apparatus equipped with cone and plate measurement geometry.

Rotational Rheometer

The basic principle is to apply a known rotational torque to a fixed volume of liquid metal and measure the angular velocity attained by the liquid volume The value of angular velocity is then converted to shear rate experienced by the liquid volume by a simple mathematical evaluation. The shear stress distribution in the known volume of liquid metal is evaluated from the rotational torque applied in the experiment. A graphical plot between the shear stress and the shear rate termed as the 'flow curve' is obtained as output from the rotational rheometer experiments [10] The slope of the flow curve represents the 'apparent viscosity' of the liquid metal sample. The term 'apparent viscosity' was used instead of 'viscosity' because of the dependence of viscosity on the shear rate. The flow curve for liquids exhibiting Newtonian flow behavior is a straight line with slope (apparent viscosity) independent of shear rate. However, the flow curve for liquids exhibiting non-Newtonian flow behavior is not a straight line and the slope (apparent viscosity) varies as a function of shear rate.

Figure 4 compares schematics of an oscillating viscometer and a rotational rheometer equipped with cone and plate measurement geometry [11]. Table 1 lists governing mathematical equations for this measurement geometry and for two others, the cone and plate, and the cup and bob.



(a) (b)

Figure 4: Schematics of (a) Oscillating vessel viscometer [11] and (b) Rotational rheometer equipped with a cone and plate measurement geometry.

A predetermined volume of metal is subjected to shear between the measurement components of the rotational viscometer. Shear can be held constant or varied with time depending on rheometer and desired experimental conditions. This shear causes a laminar flow in the liquid sample [12]. The measured torque, T and the measured angular velocity, ω are then converted to shear stress, τ and shear rate, γ, respectively. (Equations (2) to (5) show the mathematical formulations for a cone and plate measuring geometry.

$$T = \frac{2}{3}\pi R^3 \tau \qquad (2)$$

$$\gamma = \frac{\omega \times r}{r \times \tan\theta} \cong \frac{\omega}{\theta} \qquad \text{(For small } \theta\text{)} \qquad (3)$$

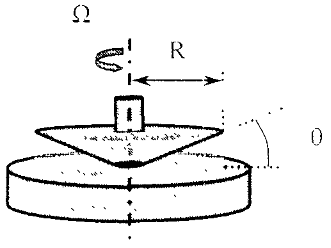
$$\text{Newtonian fluids} \rightarrow \tau = A\gamma \qquad (4)$$

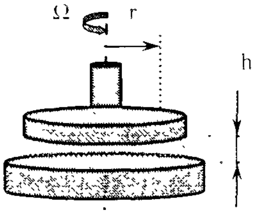
$$\text{Non-Newtonian fluids} \rightarrow \tau = A\gamma^{n} \qquad (5)$$

The slope of the plot between τ and γ (flow curve) represents the apparent viscosity of the liquid metal. For Newtonian fluids, A in Equation (4) is the apparent viscosity and for non-Newtonian fluids ($A\gamma^{n-1}$) in Equation (5) represents the apparent viscosity. Table I and Equation (3) show that the cone and plate measuring geometry is unique when compared to the other two geometries in that the value of shear rate, γ is constant across the volume of the liquid metal. It is only dependant on the angular velocity and the angle of the cone. In the cone and plate geometry, shear rate is constant in both the spatial and temporal regimes of the experiment.

The cone and plate measuring geometry in a rotational rheometer is considered as the ideal measuring geometry for evaluating flow behavior of liquid metals and alloys [12][13]. Apart from the advantages of evaluating the entire flow characteristics of the liquid metal, the mathematics in a rotational rheometer with cone and plate geometry is simpler than that in an oscillating vessel viscometer and presents an exact analytical solution for of the governing equations.

Table I: Measuring geometries and respective governing equations for rotational rheometer. γ is the shear rate experienced by the fluid sample, θ is the cone angle, ω is the velocity with which the cone is rotated, R is the radius of the cone, T is the torque and, τ is the shear stress.

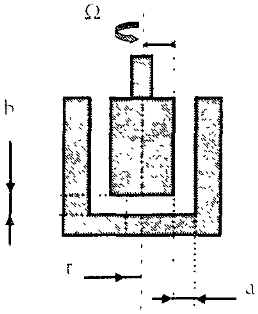
Measuring Geometry	**Governing Equation**
 *Cone and Plate Setup*	$\gamma = \frac{\omega \times r}{r \times \tan\theta} \cong \frac{\omega}{\theta}$ For small θ $T = \frac{2}{3}\pi R^3 \tau$



Parallel Plate Setup

$$\gamma = \frac{\omega \times r}{h}$$

$$T = \frac{\pi R^4 \mu\omega}{2h}$$



Cup and Bob Setup

For annular gap

$$\gamma = \frac{\omega \times R}{a}$$

$$T = \frac{2\pi R^3 \mu\omega H}{a}$$

For bottom gap

$$\gamma = \frac{\omega \times r}{b}$$

$$T = \frac{\pi R^4 \mu\omega}{2b}$$

Experiments and Results

Shankar et al [14] carried out experiments to evaluate the flow curves of pure Zn and Al-12.5wt%Si alloy using a rotational rheometer equipped with cone and plate. The alloy was made from 99.999% purity raw materials by melting and casting. The aim of this work was to evaluate the flow characteristics of the interdendritic eutectic liquid at the final stages of solidification of the mushy zone.

The time dependency of the flow behavior of near eutectic composition Al-Si alloys was characterized by measuring the shear stress produced at a given shear rate as a function of shear time and calculating the corresponding torque. Figure 7 shows that shear stress at constant shear rate was constant during the experiment which verifies that the measurement sample remained 100 % liquid.

Figure 8 shows the flow cures and apparent viscosity data for 99.99% purity zinc. Figure 8(a) shows that the relationship between shear stress and shear rate at constant superheat is linear, thus demonstrating Newtonian behavior. In Figure 8 (b), the plot for apparent viscosity versus temperature (evaluated by Equation (4)) agreed with published values. Figure 8(b).

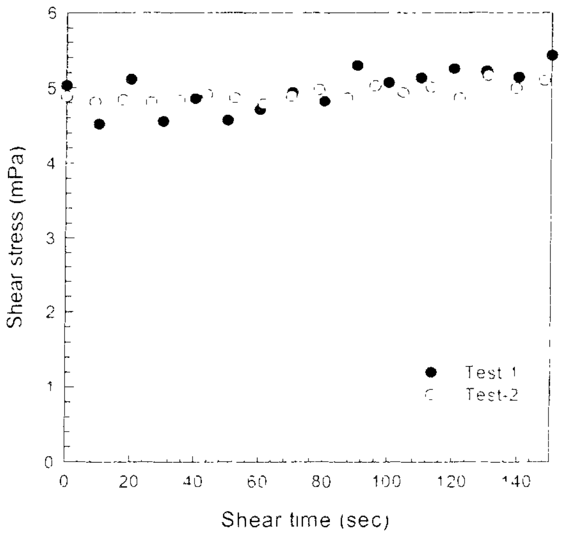


Figure 7: Relationship between shear stress and shear time for the Al-12.5wt%Si alloy tested at $\gamma = 0.5$ s^{-1} and 598°C.

Figure 9 shows measured data and power-law fits of flow curves and apparent viscosity data (evaluated using Equation (5)) for Al-12.5 wt% Si alloys measured with a rotational rheometer equipped with cone and plate, thus demonstrating, contrary to popular belief, that molten Al-12.5wt% Si exhibits non-Newtonian flow behavior. Figure 9 also shows that Al-Si eutectic alloy is a shear thinning liquid.

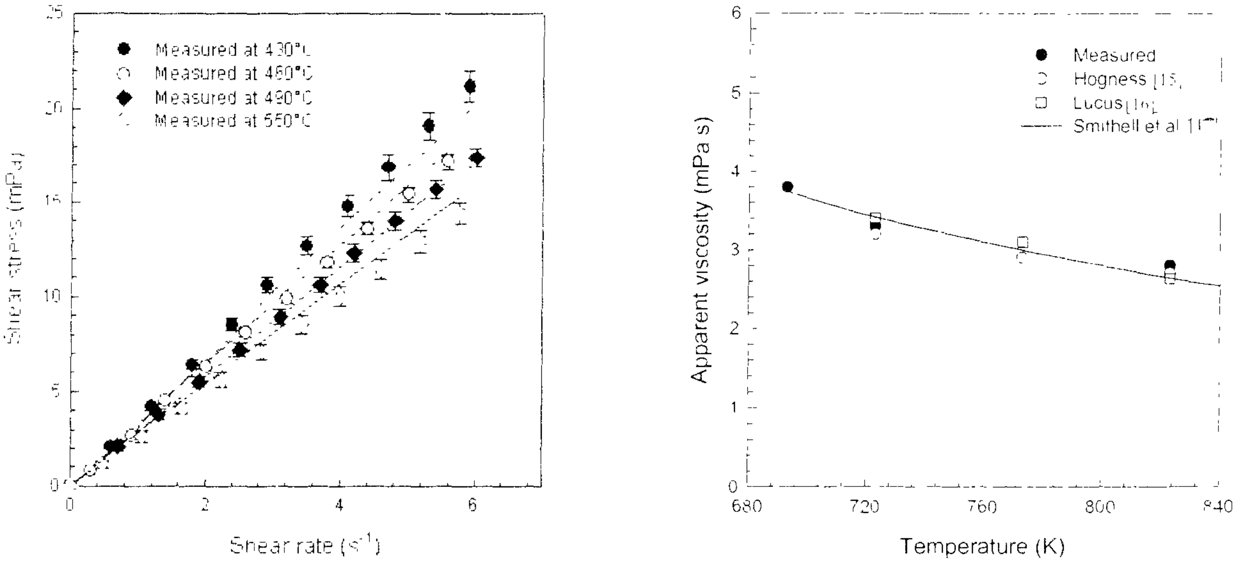
Figures 8 and 9 illustrate the difference in experimental results for Newtonian and non-Newtonian fluids. It is to be noted that the measured data shown in Figures 8 and 9 are in the low shear rate regimes characteristic of the interdendritic regions of the mushy zone during the final stages of solidification.

Fundamental physics suggests that if a binary alloy exhibits non-Newtonian flow behavior then one of the pure components should also behave similarly In Figure 10, it is evident that 99.999% pure Al liquid metal exhibits a non-Newtonian behavior at a given melt superheat in the low shear rate regimes [15]. Moreover, in Figure 10, pure Al shows a shear thinning behavior in apparent viscosity as a function of shear rate and also shows a hysterisis in the ramp up and ramp down stages of shear rate cycle.

Summary

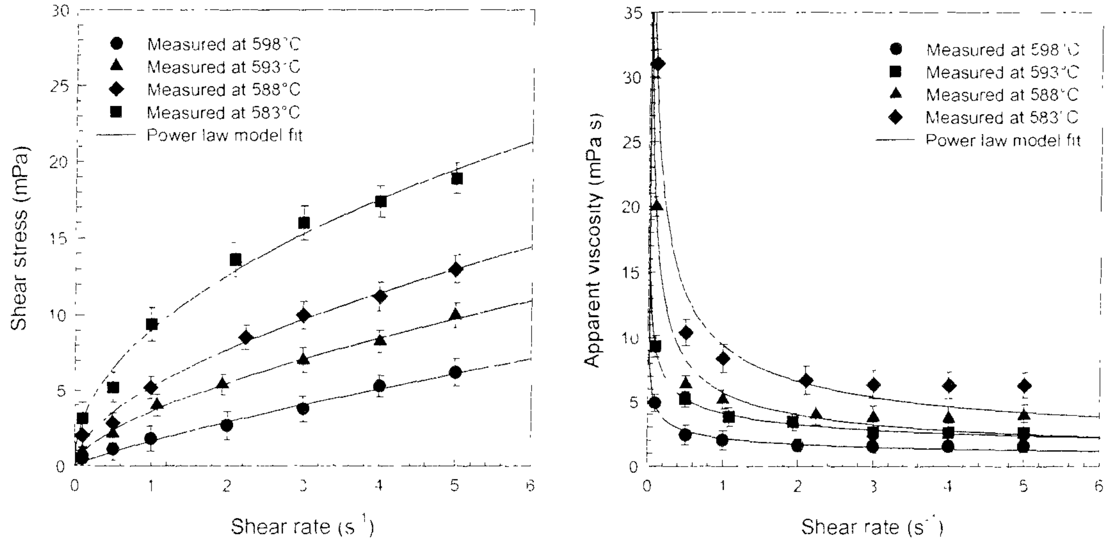
The following can be summarized from this publication.

- Viscosity data for molten metals and alloys using the oscillation vessel viscometer is valid if and only if the liquid has been proven to be a Newtonian fluid, unlike in the case for Al and Al-Si alloys.
- Pure Al and Al-Si alloys are non-Newtonian fluids with shear thinning behavior. Hence, only experiments which measure viscosities as a function of shear rates will present accurate data for viscosities of these alloys.
- Rotational rheometer with a cone and plate geometry has been shown to be reliable equipment to measure viscosity of molten metals (both Newtonian and non-Newtonian) because the measurement technique does not assume a fluid behavior.



(a) (b)

Figure 8: Results from rotational rheometer experiments with cone and plate for 99.99 % purity molten Zn. (a) Flow curves and (b) Apparent viscosity as a function of temperature [16,17,18].



(a) (b)

Figure 9: Results from rotational rheometer experiments with cone and plate for molten Al-12.5 wt% Si alloys. (a) Flow curves at four melt superheats. (b) Apparent viscosity data as a function of shear rate and melt superheats.

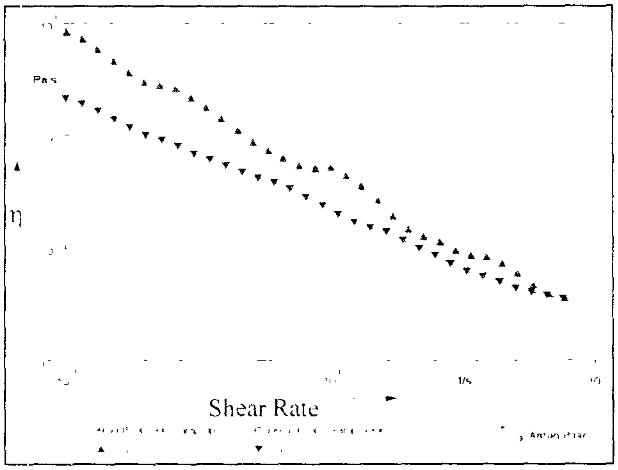


Figure 10: Apparent Viscosity curve for 99.999 % pure Al melt showing non-Newtonian (shear thinning) behavior [18].

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PUBLICATION B

Rotational Rheometry of Liquid Metal Systems: *Measurement Geometry Selection and Flow Curve Analysis*

Mohammad Minnajuddin Malik[1], Manickaraj Jeyakumar[1], Mohammed S Hamed[1], Michael J Walker[2], Sumanth Shankar

[1]Centre for Solidification & Thermal Processing (CSTP), McMaster University Hamilton ON
Canada L9H 2E8
[2]General Motors, Michigan, USA.

ABSTRACT

In the present study rotational measurement technique was used to evaluate viscosities of liquid metals and metallic alloys Three types of measurement geometries in a high temperature rotational rheometer were evaluated: *cone and plate, Din Coaxial and Double Concentric Cylinder (DCC)* The DCC geometry proved to be the most effective. An analytical solution has been presented to evaluate the shear viscosity as a function of shear rate for DCC geometry The flow curves and shear viscosities of pure Al, pure Zn and $Sn_{95.8}Ag_{3.28}Cu_{0.92}$ solder alloy has been evaluated as a function of shear rate and melt superheat temperature. It is proposed that liquid metal systems are non-Newtonian and shear thinning in flow behavior.

INTRODUCTION

Viscosity of liquid metal system is one of the key transport properties affecting solidification processes such as welding and casting. Further, understanding viscosity and rheological properties will enable a more in-depth understanding of the structure of liquid metal systems[1]. Current understanding of the viscosity of liquid metal systems is insufficient to understand their atomic structure. Prior art[2, 3 4, 5] reveals that that Oscillating Vessel Viscometer (OVV) is the most extensively used apparatus to obtain liquid metal viscosity data. The underlying assumption in using an OVV is that liquid metal systems behave as Newtonian fluids. The definition of Newtonian fluids[6] suggests that viscosity of such fluids is independent of shear rate and shear history. The fundamental assumption that liquid metal systems behave as Newtonian fluids[1] has not been verified or validated. Hence, there is a lack of understanding for the rheological behavior (flow behavior) of liquid metal systems.

The shear rate experienced by liquid metal in an OVV is not uniform: both in the spatial and temporal regimes. However the viscosity measured over the range of shear rates is reported as one value for the liquid metal systems[2, 3 4, 5]. This reported value of melt viscosity is meaningful if and only if the liquid exhibits a Newtonian flow behavior. Lately, it has been reported that certain metal systems may not behave as Newtonian fluids[7,8,9]. Hence there is an urgent necessity to re-evaluate our understanding of the viscosity of liquid metal systems This may be achieved only by a thorough understanding of the rheological properties of such systems. Rheological evaluation by rotational rheometer is a viable technique to evaluate viscosities of liquid metal systems. However not all measuring geometries that contain and shear the sample liquid in a rotational rheometer are viable. Only measuring geometries that present a nearly uniform shear rate (in both spatial and temporal regimes) in the liquid that is contained and sheared is viable to evaluate rheology. With a suitable measuring geometry viscosity can be evaluated for specific shear rates and shear history. Such evaluations are not possible in an OVV. There are three viable geometries to evaluate viscosity and flow behavior of liquid metal systems in a rotational rheometer: cone/plate, DIN co-axial cylinder and Double

Concentric Cylinder (DCC). In this publication, these three measuring geometries have been critically analyzed and it has been proposed that the Double Concentric Cylinder (DCC) geometry is the most practical option to measure rheological properties of liquid metal systems, especially for low viscosity liquids. Experiment results for rheological properties for water S2000 standard liquid, pure Zn, pure Al and solder alloy (Sn-Ag-Cu) systems using the DCC measuring geometry are presented in this publication.

BACKGROUND

There are many experimental methods available for viscosity measurements, however, for liquid metal systems we are limited by the high melting temperature chemical reactivity, oxidation characteristics and low viscosity values. The most prevalent techniques for measuring liquid metal viscosity are Capillary, Rotational, Acoustic, Oscillating Vessel and Oscillating-plate Methods. Iida et al[1] have explained the details of each of these various methods The Oscillation and Rotational methods are elaborated in this section

Oscillating Vessel Viscometer (OVV)

Figure 1 (a) represents the schematic of the OVV [7]. In the OVV a preset torque pulse is applied to the fluid sample in the container shown in Figure 1 (a). The liquid then experiences a continuously dampening oscillatory motion about a vertical axis The viscosity of the liquid is then evaluated by solving the governing second order differential eauation of motion [10] given as Equation (1).

$$(I_o\omega_o)\left(\frac{d^2\beta(\tau)}{d\tau^2}+2\Delta_o\frac{d\beta(\tau)}{d\tau}+(1+\Delta_o)^2\beta(\tau)\right)=0 \qquad (1)$$

In Equation (1), I_0 is the moment of inertia of the empty vessel or crucible, ω_0 is the angular frequency, $\beta(\tau)$ is the angular displacement Δ_0 is the damping parameter and τ is dimensionless time.

Despite simplicity of construction, the mathematical equations used to describe the oscillatory movement of the crucible are complex and presently there is no reliable mathematical procedure available for solving them[1] Some of the popular mathematical models are the Knappwost Equation[11], Shvidovskii Equation[1] Roscoe Equation[12] , and Kestin & Newell model[2]. Among these mathematical models, a modified version of the Roscoe Equation provides the most accurate values of viscosity for Newtonian fluids [1] Modifications to the Roscoe equation involve a correction factor to account for the end effects caused by the curvature of the liquid metal at the free surface

The graphical schematics of the variation of shear rate experience by the continuously dampening oscillating liquid in an OVV are shown in Figure 1 (b) and (c) wherein, the shear rates are non-uniform in both the spatial and temporal regimes respectively. If the measuring liquid exhibits a Newtonian flow behavior, then these variations in the shear rates are acceptable and will not haven any influence on the viscosity value of the liquid. However, when the measuring

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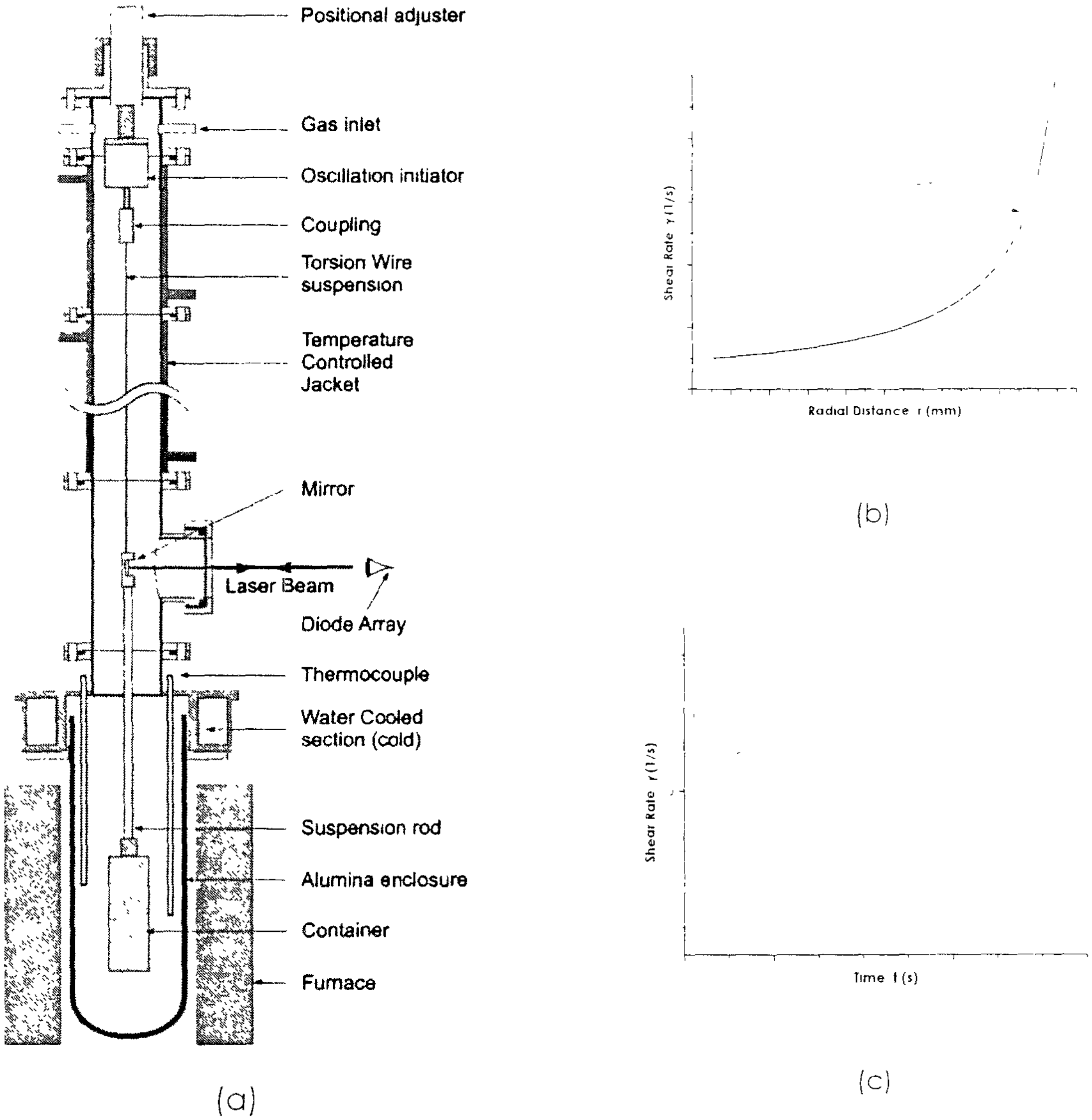
[1] Cannon S2000 is a certified viscosity fluid developed and marketed by Cannon Instrument Company, State College. PA, USA http //www cannoninstrument com

liquid is non-Newtonian, the shear rate variations in the OVV will affect the evaluation of the viscosity values, since viscosity varies as a function of applied shear rate in the liquid



(a)

(b)

(c)

Figure 1: Schematic of a typical (a) Oscillating Vessel Viscometer (OVV) (b) the spatial variation of shear rate, and (c) the temporal variation in shear rate

The OVV technique is not a suitable technique to evaluate whether the liquid is Newtonian or not Hence, using the OVV technique inherently assumes the measuring liquid to be Newtonian We have shown [7] in our recent publication that the measured values of viscosity of liquid Al by various researchers during the second half of the 20th century exhibits a 400% variation in the evaluated viscosity data and all the data were measured by the OVV technique Similar variations have been reported for liquid Fe, Zn and Cu as well [3,4,5]. One of the main reasons for this variation is that it has been a prevalently accepted assumption is that liquid metals are Newtonian in nature[1]. This assumption had not been experimentally verified Contrary to this popular assumption, recent atomistic simulations of shear viscosity of liquid metals and alloys under various shear rates have shown that liquid metals may not be Newtonian in nature [9] Further, a few recent experiments on shear viscosity of liquid metals have also shown that these systems are not Newtonian fluids. Hence, OVV technique is not suitable to measure viscosities of liquid metals The rotational technique is more suited for measuring liquid metal viscosities because the technique makes no assumptions about the nature of the fluids and evaluates the viscosity as a function of shear rate experienced by the liquid.

Rotational Rheometer

The principle of rotational rheometer involves filling a measurement container geometry with the liquid sample of pre-determined volume exposing it to specific angular velocity for given lengths of time and measuring the resultant torque. A specific torque can also be applied to the liquid and the resultant angular velocity measured. The applied angular velocity or torque can be constant or function of time depending upon the rheometer and the experiment The shear stress τ, and the shear rate, γ are evaluated from the measured torque, T and the measured angular velocity, ω, respectively It must be ensured that the applied angular velocity or torque should only result in a laminar and stable flow of the measured liquid Depending on the measurement geometry, there are specific mathematical expressions to evaluate the shear stress and shear rate from the measured torque and angular velocity respectively The shear viscosity of the liquid is evaluated as the ratio between the shear stress and the shear rate. In the case of liquid metals and alloys, where in the assumption of Newtonian behaviour is not valid, the ideal geometry for any rheological study is one which imparts constant shear rate to the test liquid. There are three geometries, which approximately lend themselves to the constant shear rate criteria with various levels of accuracy, repeatability ease of measurement and shear rate regimes: *the cone and plate, DIN coaxial cylinder and the Double Concentric Cylinder* The specific details and the mathematical expressions for the three geometries are presented in the following sections.

Cone and Plate Measurement Geometry

Theoretically, the cone and plate is the ideal measurement geometry for rotational rheometry wherein a constant shear rate in the liquid is desired: Figure 2 shows a schematic of a typical cone and plate measurement geometry. In Figure 2, R is the radius of the base of the cone, z is the truncation of the cone tip, θ is the cone angle The cone tip truncation should be about 50 to 100 μm and the cone angle should be less than 4°[15]. The mathematical expressions to evaluate the shear stress and shear rate from torque and angular velocity, respectively, are presented in Equation (2).

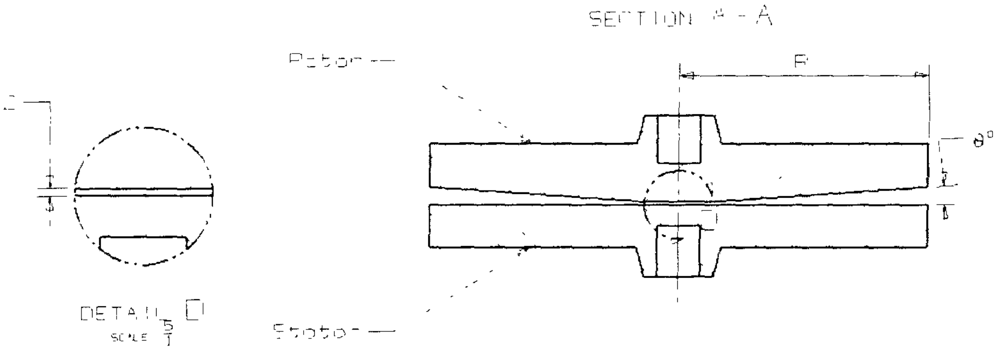


Figure 2: Cross-section of Cone and Plate measurement geometry. The liquid is contained between the rotor and stator

$$T = \frac{2}{3}\pi R^3 \tau \qquad and \qquad \dot{\gamma} = \frac{\omega}{\tan\theta} \approx \frac{\omega}{\theta} \tag{2}$$

Where $\dot{\gamma}$ is the shear rate experienced by the fluid sample, θ is the cone angle ω is the velocity with which the cone is rotated R is the radius of the cone, T is the torque and τ is the shear stress. Shear viscosity is evaluated as the ratio of shear stress over shear rate at a particular value of shear rate. Although the cone and plate is the most accurate method to evaluate viscosity, there are two major practical issues in carrying out reliable experiments with this geometry Firstly, manufacturing a cone which is chemically inert to the sheared liquid metal precise in the measured cone angle and precise in the tip truncation is quite tedious Further accurate measurements of the cone dimensions are not easily possible [13] Secondly, loading and containment of a liquid metal sample in the cone and plate geometry is also practically tedious. Liquids exhibiting a low viscosity value further exacerbate this problem In experiments carried out with the cone and plate measuring geometry, the success rate in obtaining a reliable sample loading and containment with the cone and plate geometry is about ten percent Even after a successful loading of the sample, the experiments will be limited to only low shear rate regimes

DIN Coaxial Cylinder Measurement Geometry

The disadvantages in the cone and plate geometry were marginally overcome by the DIN Coaxial Cylinder design. Figure 3 shows the typical cross-section of the DIN Coaxial Cylinder measurement geometry. In Figure 3, the problems of containment and loading in the cone and plate geometry were overcome by creating an outer vertical wall on the plate to form a cup (annular region).. This method is particularly suited for low viscosity liquids measured at low shear rate regimes. Experiments showed that the sample spillage was considerably alleviated but not eliminated. Experiments with various cone angles (2° to 4°) of the rotor showed that there was always a persistent centrifugal force on the liquid sample in contact with the cone surface thus eventually pushing the liquid out of the geometry to cause spillage. The main constraint of this measurement geometry is that the spillage was unpredictable and that experiments could not be carried out for extended periods of time due to eventual spillage of sample.

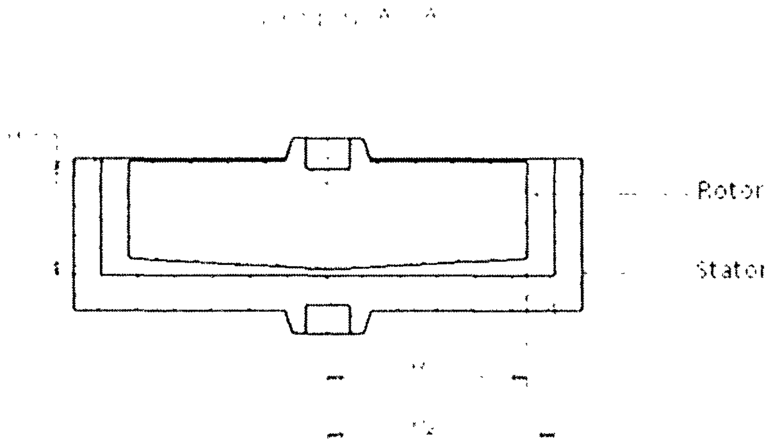


Figure 3: Cross-section of DIN Coaxial Cylinder measurement geometry The liquid is contained between the rotor and stator.

To obtain a nearly constant value of shear rate through out the liquid sample during measurement at a particular angular velocity of the rotor, the dimensions (R_2-R_1) and z in Figure 3 should be minimal. Varsani et al [8] carried out experiment with the DIN Coaxial Cylinder geometry to evaluate viscosities of liquid metals as a function of shear rates. The measurement geometry used by this group in reference to Figure 3 were that height H was 32 mm, (R2-R1) was 1 mm and the cone angle was 3°. The results indicate that the viscosity values had a large scatter for shear rates less than 400 /s and the scatter was significantly reduced for shear rates between 400 and 2400 /s. One of the critical conditions for a reliable measurement of viscosity in a rotational rheometer is that the sample liquid undergoes a laminar and stable flow (simple shear) during the experiments. Taylor vortices criteria [14] presents a evaluation of the critical angular velocity for specific measurement geometry and fluid viscosity over which vortices will develop in the sheared liquid sample thus rendering the viscosity measurements unreliable. Equation 3 presents the Taylor vortices criteria [14].

$$\frac{(\omega R_1)(R_2 - R_1)}{\left(\mu/\rho\right)}\sqrt{\frac{(1-\beta)}{\beta}} > 41.3 \qquad (3)$$

In Equation 3, ω is the angular velocity of the sheared liquid, μ is the shear viscosity, ρ is the density of the fluid R is the rotor radius, and (R_2-R_1) is the annular gap as shown in Figure 3. The quantities (ωR_1) and (μ/ρ) represent the peripheral velocity at the rotor/liquid interface and the kinematic viscosity of the sheared liquid, respectively. The evaluated values of viscosity for Al and Zn by Varsani et al [8] are about 2 mPa.s and 3.8 mPa s, respectively For the measurement geometry considered by them [8], the critical value over which vortices will develop in the shear liquid is 175 /s and 125 /s for Al and Zn respectively. Varsani et al [8] only considered shear rates between 400 and 2600 /s in evaluating viscosities of the liquid metals. This shear rate regime will present vortices in the sheared liquid thus rendering the evaluated viscosity values unreliable This is evident by the increase in viscosity with increasing shear rates between 700 and 2100 /s [8] due to loss of flow energy in vortices in the sheared liquid. Hence, the measurement regime in the Din Coaxial Cylinder geometry is constrained by the dimensions and the liquid properties. Specific geometries have to be designed for specific measurement regimes and liquid types This is another disadvantage over the cone and plate measurement geometry due to the existence of an annular region.

Double Concentric Cylinder (DCC) Measurement Geometry

The DCC measurement geometry overcame many of the problems faced in the cone and plate and the DIN Coaxial Cylinder geometries. Figure 4 shows a typical cross-section of the DCC measurement geometry. The liquid sample is sheared in the two annular regions between the rotor and the stator in Figure 4. Among the three measurement geometries discussed in this work, the DCC geometry can measure both high and low viscosity liquids at a broader shear rate regime spanning from very low shear rates to relatively high values. The dimensions of the geometry in Figure 6 are designed based on the physical properties of the sheared liquid, the desired shear rate regime and the desired level of accuracy in the consistency of the shear rate distribution in the sheared liquid. One of the design criteria for the DCC geometry is that the ratio of the radii bounding the two annular regions should be nearly constant. Thus in Figure 4, the value (R_3/R_4) and (R_1/R_2) should nearly be constant and this constant is termed β Further, as β tends to unity, the shear rate distribution in the two annular regions will be nearly constant. Typically, values of β ranging between 0.85 and 0.98 are used and this depends on the desired experiment conditions and liquid sample properties.

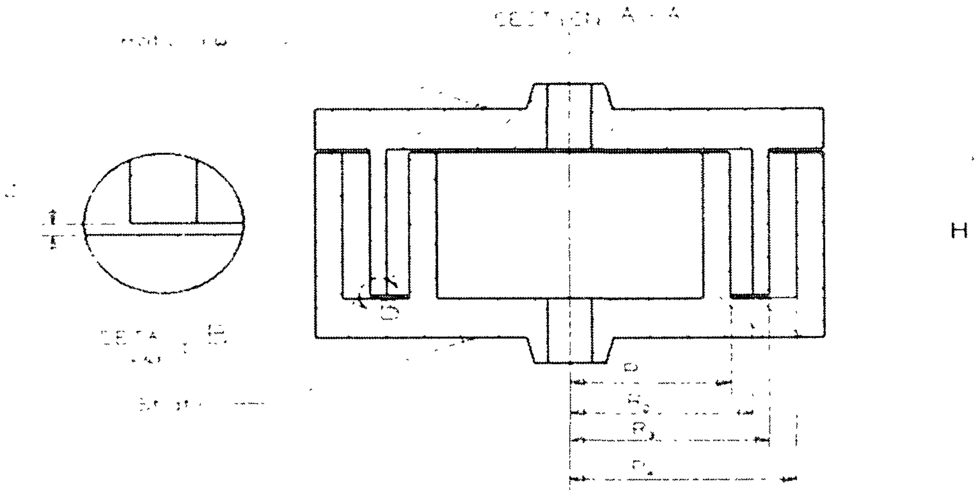


Figure 4: Cross-section of Double Concentric Cylinder (DCC) measurement geometry used in the present experiment study R_1 = 14 5 mm, R_2 = 16.5 mm, R_3 = 18 mm, R_4 = 20 .5 mm, H = 15 mm and z = 0.30 mm.

There are three equations to evaluate shear rates from the geometry dimensions in Figure 4 and the angular velocity experienced by the sheared liquid These three equations presented as Equations 4 to 6 are merely approximations by three groups of researchers, respectively. Barnes et al [15] presented equation 4, Robert L. Powell [16] presented Equation 5 and Dontula et al [17] presented Equation 6.

$$\dot{\gamma} = \frac{\omega}{(1-\beta)} \tag{4}$$

$$\dot{\gamma} \approx \frac{\omega\beta}{(1-\beta)} \tag{5}$$

$$\dot{\gamma} \approx \frac{2\omega}{(1-\beta^2)} \tag{6}$$

However, an analytical exact solution could be derived for the DCC measurement geometry This solution is presented in the subsequent section.

Analytical Solution to Evaluate Shear Rate in DCC

Figure 4 is a schematic of the DCC measurement geometry with the two annular regions containing the sheared liquid. Consider one of the annular regions with inner rotor radius R_i and outer stator radius R_o. The velocity V_θ in the annular region is defined by Equation (7)

$$V_\theta = \frac{\omega}{(1-\beta^2)}\left(\frac{R_i^2}{r} - r\beta^2\right) \tag{7}$$

In Equation (7) r is the radius variable of the annular region. The shear rate $\dot{\gamma}$ is defined as the gradient of velocity, V_θ and is given by Equation (8).

$$\gamma = r\frac{\partial\left(V_\theta/r\right)}{\partial r} + \frac{1}{r}\frac{\partial V_r}{\partial\theta} \tag{8}$$

Since $\frac{\partial V_r}{\partial\theta} = 0$, the shear rate is simplified in Equation (9).

$$\dot{\gamma} = r\left\{\frac{\omega\left(-\frac{R_i^2}{r^2} - \beta^2\right)}{r\left(1-\beta^2\right)} - \frac{\omega\left(\frac{R_i^2}{r} - r\beta^2\right)}{r^2\left(1-\beta^2\right)}\right\} \tag{9}$$

The magnitude of shear rate is obtained by further simplification of Equation (9) and presented in Equation (10)

$$\dot{\gamma} = \frac{2\omega R_i^2}{r^2\left(1-\beta^2\right)} \tag{10}$$

In Equation (10) the shear rate varies between $\left(\frac{2\omega}{(1-\beta^2)}\right)$ at r = R_i, and $\left(\frac{2\omega\beta^2}{(1-\beta^2)}\right)$ at r = R_o. The spread in shear rate in the annular region is 2ω. Hence to obtain minimum variation in shear rate between the inner and outer annular radii the value of ω for the given shear rate should be minimum. As given by Equation (10), as β^2 tends to unity the value of ω required for a given shear rate is minimum. The average shear rate in the annular region is evaluated by Equation (11).

$$\frac{\int_{R_1}^{R_2}\dot{\gamma}\cdot dr}{\Delta r} = \frac{2\omega R_i^2}{\left(1-\beta^2\right)}\int_{R_1}^{R_2}\frac{1}{r^2}\cdot dr \quad ; \quad \therefore \dot{\gamma}_{average} = \frac{2\omega\beta}{\left(1-\beta^2\right)} \tag{11}$$

The magnitude of the shear stress, τ in the annular region is given by Equation (12).

$$\tau = \frac{\left(R_i^2 + R_o^2\right)T}{4\pi H R^2 R_o^2} \tag{12}$$

In Equation (12) T is the torque measured at the rotor-liquid interface and H is the height of the sheared liquid. The shear viscosity is given as the ratio of shear stress over shear rate in the annular region. The average shear viscosity is given by Equation (13)

$$\eta_{shear} = \left(\frac{T}{\omega}\right)\left(\frac{1-\beta^4}{8\pi H R_i^2\beta}\right) \tag{13}$$

For the DCC measurement geometry shown in Figure 4, the shear stress experienced at the rotor-liquid interface is given by Equation (14). The shear viscosity for the DCC geometry is given by Equation (15)

$$\tau = \frac{\left(R_1^2 + R_2^2\right)T}{4\pi H R_2^2\left(R_1^2 + R_3^2\right)} = \frac{\left(1+\beta^2\right)T}{4\pi H\left(R_1^2 + R_3^2\right)} \tag{14}$$

$$\left(\eta_{shear}\right) = \left(\frac{T}{\omega}\right)\left(\frac{1-\beta^4}{8\pi H\beta\left(R_1^2 + R_3^2\right)}\right) \tag{15}$$

MATERIAL APPARATUS AND PROCEDURE

In this section the materials, apparatus and procedure used for evaluating the viscosity of liquid metal systems with DCC measuring geometry in a rotational rheometer is presented.

Materials

The rheometer and the measurement geometry were verified for repeatability and accuracy using a standard viscosity calibration liquid: S2000. Three liquid metal systems were used in evaluation of viscosity: pure Al, pure Zn and $Sn_{95.8}Ag_{3.28}Cu_{0.92}$ solder alloy. The pure Al was 99.99 % pure and the Zn was 99.999% pure. The liquid metal was melt and cast as hollow cylinders. The wall thickness of the cylinders was similar to the dimension of the annular gaps in DCC measurement geometry shown in Figure 4.

Apparatus

An AR-2000[2]- rheometer was used to evaluate the flow properties of the liquids. Figure 5 shows a schematic of the instrument fitted with cone and plate measurement geometry. An environmentally sealed furnace chamber (maximum temperature = 800 °C) was outfitted on the rheometer and ultra high purity Ar gas (< 2ppm oxygen) was continuously purged in the furnace chamber at a flow rate of about 5 l/min. The rheometer lends itself to fitting the cone/plate, DIN Coaxial Cylinder and Double Concentric Cylinder measurement geometries. The rheometer has a torque measurement resolution of 0.1 nN.m with a maximum measurable torque of 200 mN.m. The displacement measurement resolution is 25 nrad with a maximum measurable angular velocity of 300 rad/s.

The DCC measurement geometry was precision machined from the Cotronics 902[3] machinable ceramic rods of 50 mm diameter. This material can withstand a maximum operating temperature of 1100 °C and is chemically inert to most liquid metals. The dimensions of the DCC geometry (refer to Figure 4) were: R_1=*14.5 mm*, R_2=*16.5 mm*, R_3=*18 mm*, R_4=*20.5 mm and* H=*15 mm*.

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[2] Advanced Rheometer, TA Instruments, New Castle, DE, USA. http://www.tainstruments.com.

[3] Cotronics Corporation, Brooklyn, NY, USA. http://www.cotronics.com.

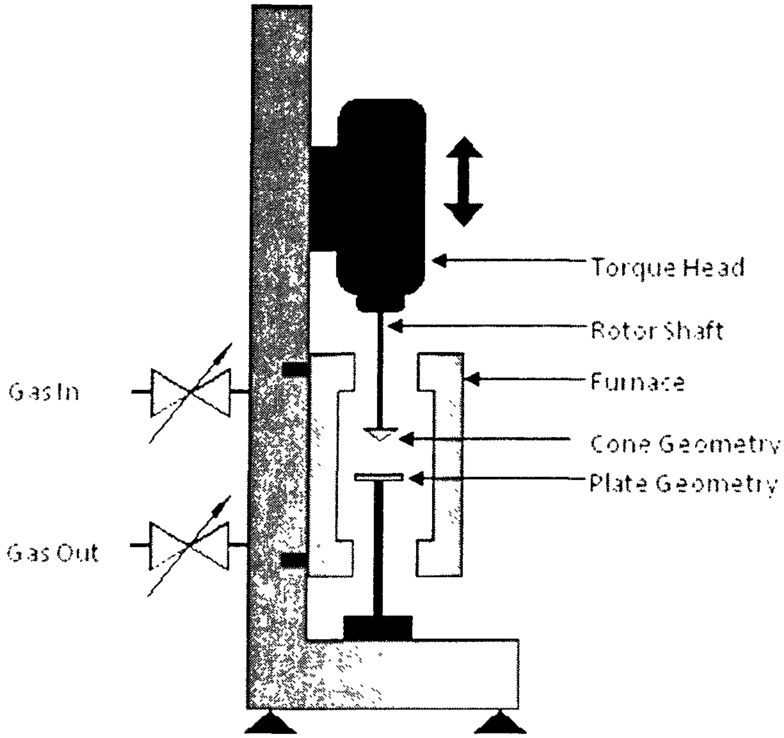


Figure 5: Schematic of the rotational rheometer (AR2000) outfitted with a cone and plate measurement geometry

Procedure

The two annular regions of the DCC geometry (shown in Figure 4) are loaded with the solid hollow metal cylinders of required height. The metal is melt under Ar gas flow. The liquid metal temperature is stabilized at the desired measurement temperature and the rotor is lowered into the molten metal to create a gap of 0.3 mm at the bottom between the rotor and the stator surfaces. The rotor is then controlled to rotate at a specific angular velocity, ω while the torque experience by the rotor is continuously measured and recorded. The measured values of T and ω were used to evaluate the shear viscosity by Equation (15). A new solid sample was loaded for each measurement temperature. The temperature of the metal was continuously monitored with a K-type thermocouple attached to the bottom of the stator It was evaluated that the variation in temperature between any two locations inside the furnace chamber is less than 1°C Table I presents the experiment parameters such as temperatures and applied angular velocities for the various liquid systems used

Table I: Experiment Parameters for rheometry of the liquid systems.

Material	**Solidification Temperature (K)**	**Experiment Temperature (K)**	**Angular Velocity (rad.s^{-1})**
Cannon S2000	N/A	323	0.01 to 5
Pure Al	933	940, 948, 960 and 973	0.01 to 12.85
Pure Zn	693	773 and 823	1 to 25
$Sn_{95.8}Ag_{3.28}Cu_{0.92}$ solder alloy	493	523 and 573	5 to 15

RESULTS AND DISCUSSIONS

Results and Discussion will be carried out on the following topics:

- Taylor Vortex Criteria
- Calibration of Rheometer
- Flow Curves for Liquid Metal Systems
- Viscosity of Al, Zn and Solder Alloy

Taylor Vortex Criteria

Equation (3) presents the mathematical inequality commonly referred to as the Taylor Vortex Criteria [14]. For a given annular gap, liquid density, liquid viscosity and applied angular velocity, vortices will be developed in the sheared liquid if the inequality in Equation (3) is satisfied. To ensure reliable viscosity evaluation in rotational rheometry, the inequality in Equation (3) should not be satisfied. Figure 6 presents a graph showing critical angular velocity for a specific viscosity value in various systems used in this study. For reliable viscosity measurements in each of these liquid systems, the graph between angular velocity and measured viscosity should lie beneath the critical angular velocity domain of the respective liquid systems. Table II shows the material property used in Equation (3) for the various systems.

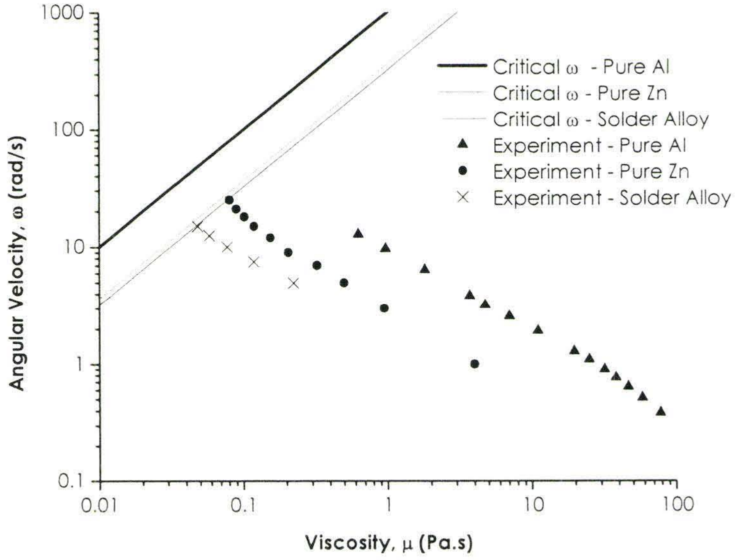


Figure 6: Representation of Taylor Vortex Criteria for three liquid metal systems. The solid lines is the plot of the critical angular velocity as a function of shear rate above which vortices will form in the respective sheared liquids during rotational rheometry with the DCC geometry shown in Figure 4. The data points are the actual experiments carried out in this study showing that Taylor vortices may not form in the sheared liquids during the experiments.

Table II: Material and Geometry Data used in Equation (3) to Evaluate Taylor Vortex Criteria

Material	Density (kg.m^{-3})	Radius of Rotor (m)	Annular Gap (m)
Pure Al	2400	0.019	0.0025
Pure Zn	6580	0.019	0.0025
$Sn_{95.83}Ag_{3.25}Cu_{0.92}$ solder alloy	7414	0.019	0.0025

The liquid viscosity and density of the standard calibration liquid (Cannon S2000) are 0.7658 Pa s and 860 kg.m^{-3}, respectively. The critical angular velocity above which Taylor vortices will develop in the sheared liquid is about 2134 rad.s^{-1}. The applied angular velocity for calibration was between 0.01 and 25 rad. s^{-1} thus ensuring no vortices formation in the sheared liquid. Figure 6 shows that for all the liquid metal systems evaluated, the applied angular velocities are well within the Taylor Vortex criteria thus ensuring that no vortices form in the sheared liquid metal

Verification of Rheometer

Figure 7 shows the flow curves (Shear Stress vs. Shear Rate) obtained for the Cannon S2000 standard liquid at 50 °C using the DCC geometry. Three experiments were carried out at various times and Figure 7 shows that the flow curves obtained are repeatable and match the standard flow curve for the liquid. The measured viscosity calculated from the slope of the experiment flow curve in Figure 7 was 0.7927 Pa.s and the viscosity of the standard liquid is 0.7658 Pa.s. This is an acceptable deviation of 3.51 %. This deviation maybe due to the viscous heating of the liquid caused by shear. This explains the increase in the observed deviation with increasing shear rate in Figure 7.

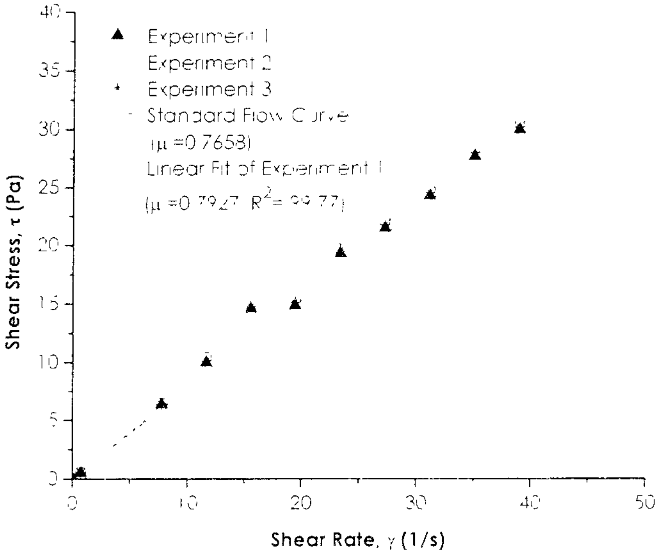


Figure 7: Flow Curve (shear stress versus shear rate) for Cannon S2000 standard liquid showing repeatability and accuracy of the rheometer.

Flow Curves of Liquid Metal Systems

Prior to evaluating the flow curves of the systems the time dependency curve (shear stress vs. tie) at a particular angular velocity and temperature will have to be analyzed. Figure 8 shows a typical time dependency curve for Al Zn and $Sn_{95.83}Ag_{3.25}Cu_{0.92}$ solder alloy. Figure 8 shows that the variation of shear stress is minimal with time thus ensuring that the sheared liquid is devoid of any discernable solid particles or solidified phases.

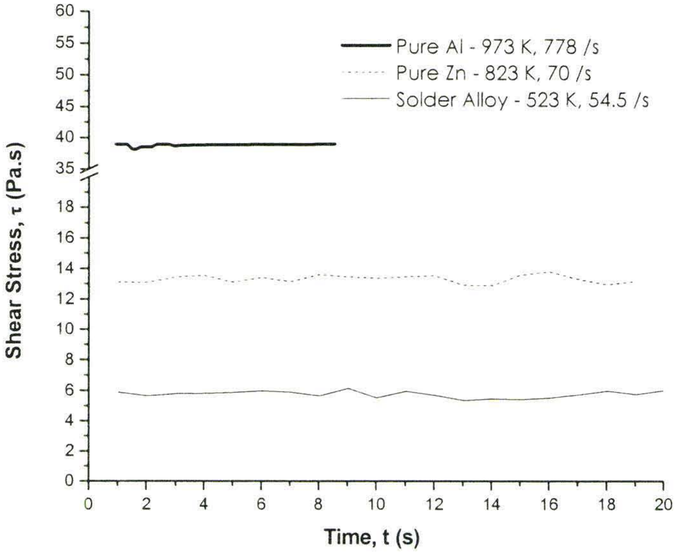


Figure 8: Time dependency Curve (shear stress versus time) for liquid metal systems at specific melt temperature and shear rate.

Figure 9 shows the flow curve (shear stress vs. shear rate) for pure Al, pure Zn and $Sn_{95.8}Ag_{3.28}Cu_{0.92}$ solder alloy. It can be observed that in Figure 9 there is a region at the low shear rate regime for all these systems, wherein the shear stress decreases with increasing shear rate. This is a unique behavior observed in metallic systems has been recently reported recently by others as well [8,18]. The shear stress initially decreases with increasing shear rate and subsequently reverses its trend and continues to increase with increasing shear rates. This is not typically observed in non-metallic systems. A hypothesis to explain this phenomenon is presented herein. The nature of atom arrangements and bonds in metallic systems are unique unlike the molecular nature of non-metallic systems. Metal systems are typically mono-atomic in nature and there are no valid models describing the behavior of atoms in liquids metal systems [1]. There are specific short-range orders existing in liquid metal systems. When liquid metals are sheared with an applied stress, there is a resistance to flow by the macro-scale layers of liquid and added to this is the resistance presented by the micro-scale atomic bond energies in the short-range order. The short-range atomic bonds which tend to deform plastically under shear present the latter resistance. To achieve a specific angular velocity in the liquid the sum of both these resistance will be recorded as the torque required. The resistance from the bond energy will reduce with increasing values of required angular velocity and the resistance from the sheared macro-scale layers of the liquid will increase steadily and proportionally. Hence, at low shear rate regime, the shear stress required to maintain an angular velocity decreases with increase in desired angular velocity. This trend is continuous until the resistance from the bond energies in short range order is overcome and the dominant resistance will only be the one from the layers of sheared liquid. If a shear stress is applied to metallic solid, the resistance from the bond energies in the long-range atomic order is so high and dominant that the resistance from the macro-scale layers of the solid will be overshadowed and hence an immeasurable and unattainable high level of torque would be required to maintain any kind of angular velocity. Upon continuously increasing the shear stress, a metallic solid will deform elastically initially, followed by plastic deformation and a stage is finally reached where in the solid will tend to flow for a very short duration (necking) [19] before the solid continuum is broken and the applied shear stress disappears. Eastgate et al [20] have shown in amorphous solids that the phenomenological constants in the constitutive law that explains the plastic flow in solids during neckings is akin to bulk and shear viscosities in liquids. They also state that the rate of flow of solids during necking increases with increasing strain rates. The behavior of liquid metals in low shear rate regime is akin to the phenomenon of 'necking' in deformed solids wherein the shear stress decreases with increasing strain rate for a very short duration in time. In Figure 9, it can be noticed that the point of inflection where in the applied shear stress reverses its trend and continues to increase with increasing shear rate occurs at lower shear rate values for liquids exhibiting lower viscosity values. This is congruent with the proposed hypothesis because for liquids with higher viscosities the atomic bond energies in the short-range order will be higher due and this will enhance the resistance to flow in the atomic scale and higher applied shear stress is needed to overcome this micro-scale resistance from the atoms.

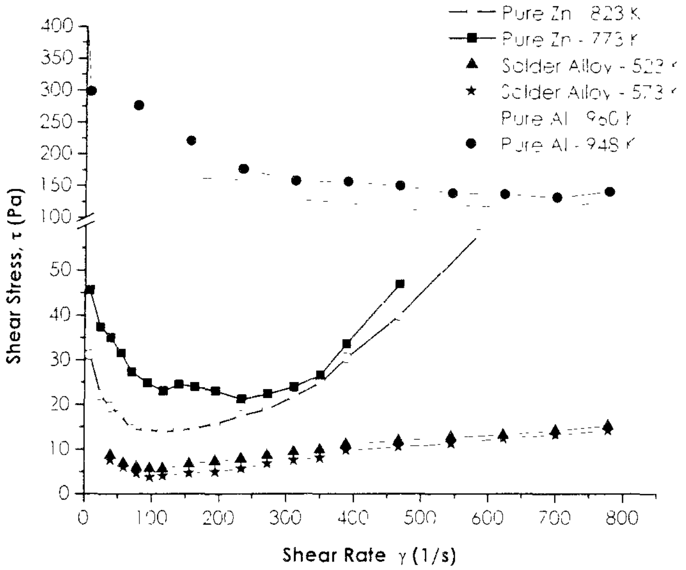
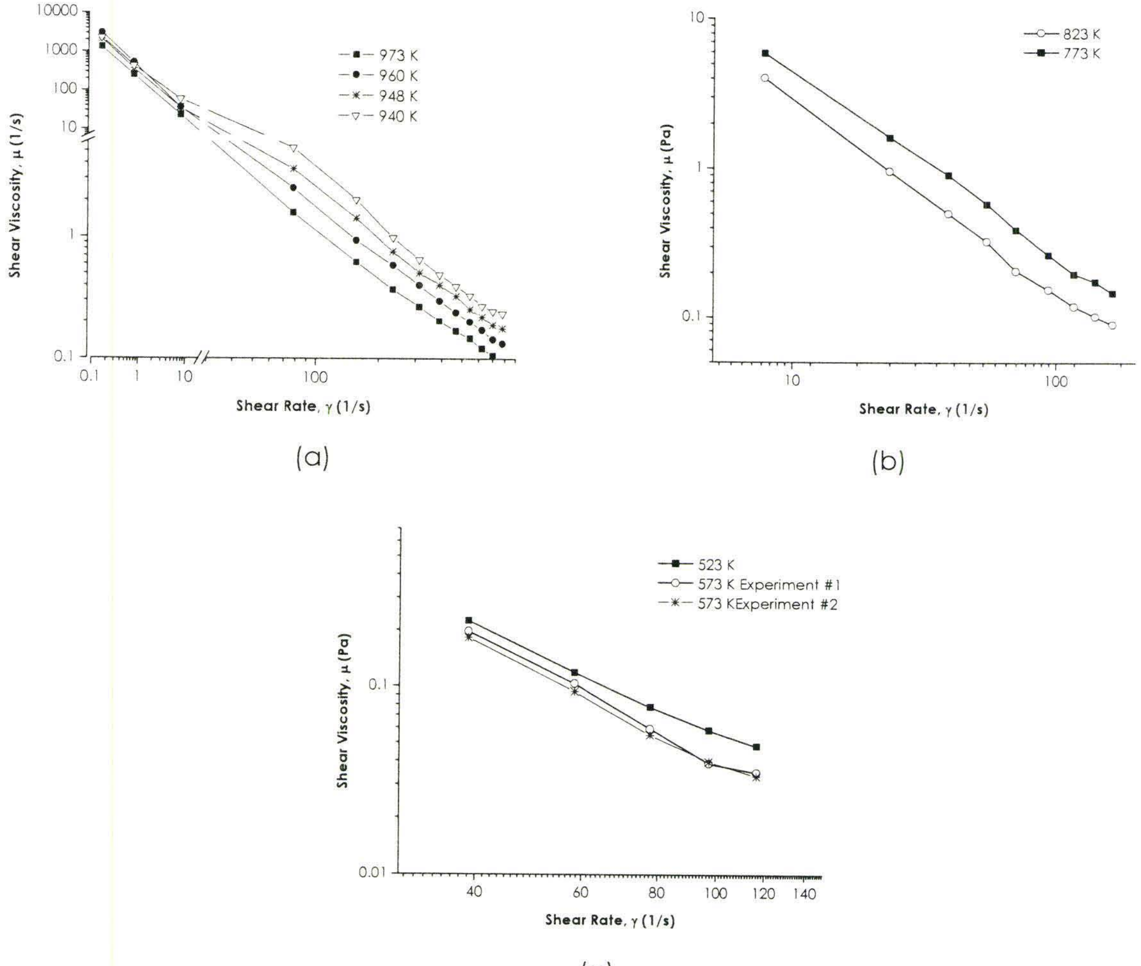


Figure 9: Flow Curves (shear stress versus shear rate) for liquid metal systems at various melt temperatures.

Viscosity of Al, Zn and Solder Alloy

Figure 10 shows the viscosity as a function of shear rate for the liquid metallic systems in this study. Figures 10 (a), (b) and (c) are the viscosity curves for Al, Zn and $Sn_{95.5}Ag_{3.28}Cu_{1.22}$ solder alloy for various experiment temperatures.

Figure 10 shows that the liquid metal systems evaluated in this study are all Non-Newtonian fluids where in the shear viscosity varied with applied shear rate. Further, all the liquid metals are shear thinning in behavior where in the shear viscosity decreases with increasing shear rate. In Figure 10, it can also be observed that the viscosity at any given shear rate is lower for lower temperatures of melt superheat.



(a)

(b)

(c)

Figure 10: Viscosity curves of liquid metal systems as a function of shear rate at various melt temperatures. (a) pure Al, (b) pure Zn and (c) $Sn_{95.8}Ag_{3.28}Cu_{0.92}$ solder alloy.

Figure 11 shows the variation of shear viscosity of liquid Al with experiment temperature. In congruence with popular belief, the variation of viscosity with temperature in Figure 11 follows the Andarde's equation [1] as presented in Equation (16).

$$\mu = A \cdot e^{B/T} \qquad (16)$$

In Equation (16), A and B are constants, and T is the temperature. In Figure 11, the curve fit of the data points by Andrade's equation is also shown. Table III shows the values of A and B for each shear rate shown in Figure 11.

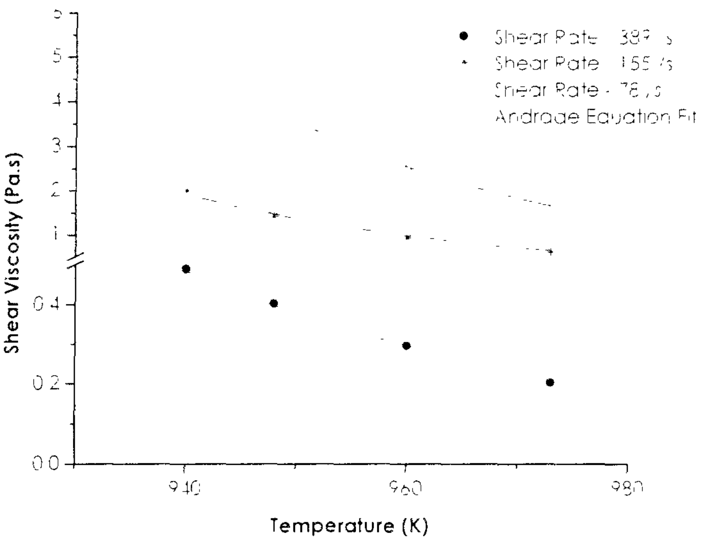
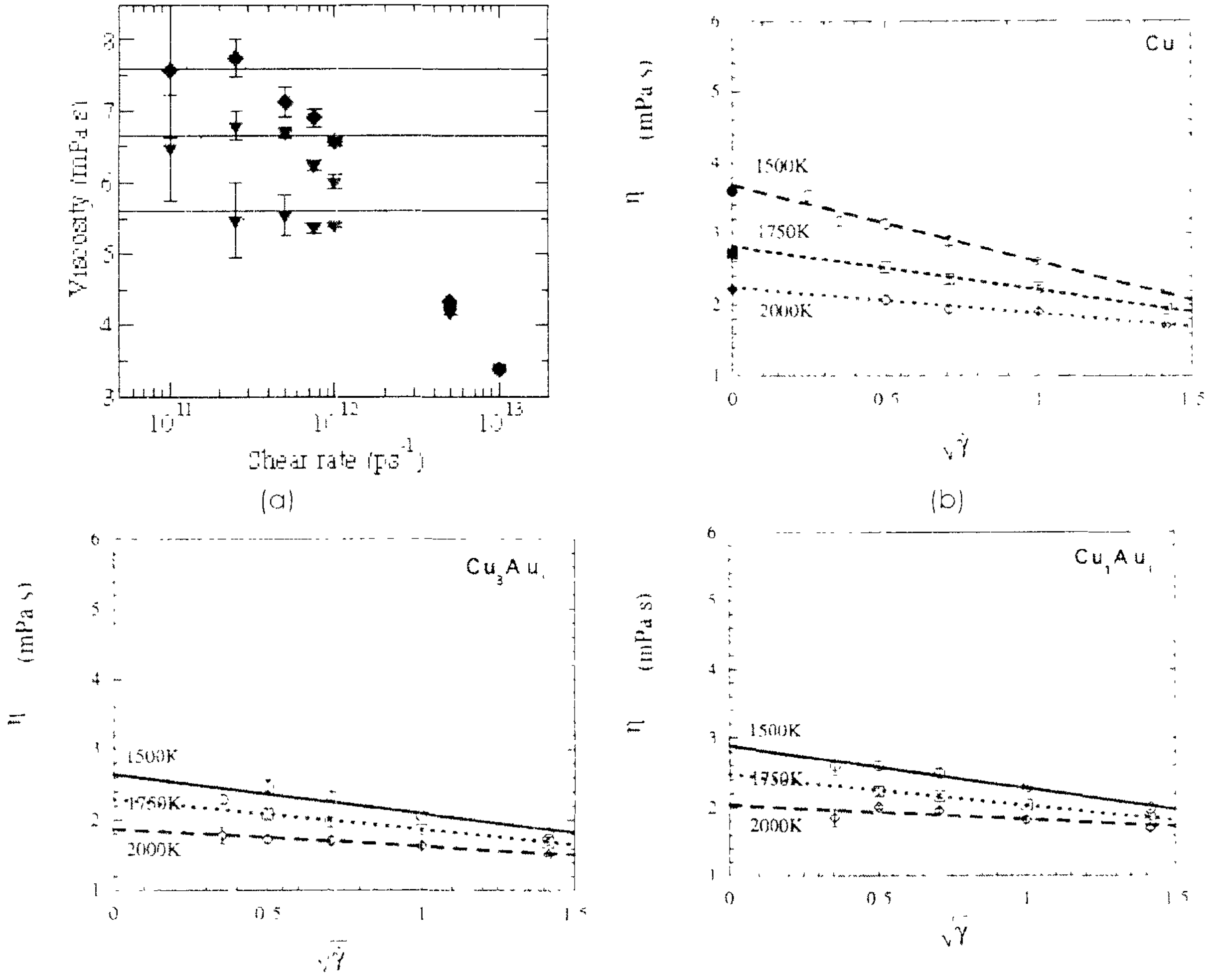


Figure 11: Viscosity at various shear rates as a function of melt temperature for liquid pure Al. Also shown is the curve fit to the data points for each shear rate with Andrade's equation shown in Equation (16)

Table III: Values of constants for curve fit of data points in Figure 11 Andrade's equation.

Shear Rate (s^{-1})	A (Pa.s)	B (K)	R^2 value of the fit
389	2.62×10^{-11}	22224.19	0.9915
155	2.27×10^{-14}	30143.92	0.9833
78	3.51×10^{-14}	30638.79	0.9704

The hypothesis presented in the previous section can be used to explain the non-Newtonian behavior of liquid metals. The added resistance from the micro-scale atomic bond energies in the short-range order will continuously decrease with increasing shear rate but will not disappear. Although, the resistance from the macro-scale layers of liquid could increase proportionally with increasing shear rate, the overall resistance to flow (measured as shear stress) will not vary proportionally with increasing shear rate. Hence, shear viscosity, which is a ratio of applied shear stress and measured shear rate will continuously decrease with increasing shear rates showing a shear thinning behavior for all metal systems. Moreover the rate of decrease in shear viscosity with increasing shear rate vastly varies among metallic systems. For systems exhibiting a strong resistance from the atomic level the rate of decrease in viscosity will be slower than for systems exhibiting a weak resistance in the atomic level. An example of the former is Al and latter is the $Sn_{95.8}Ag_{3.5}Cu_{0.7}$ solder alloy, as shown in Figures 10 (a) and 10 (c) respectively

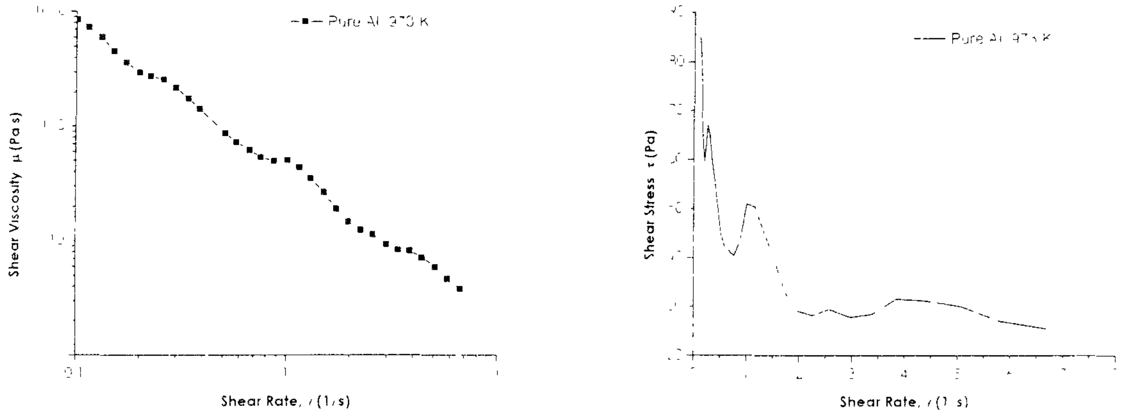


(a) (b)

(c) (d)

Figure 12: Viscosity as a function of shear rate for various liquid metal systems obtained by Non-Equilibrium Molecular Dynamics simulation. (a) pure Fe [20], (b) pure Cu [9] (c) Cu$_3$Au$_1$ [9] and (d) Cu$_1$Au$_3$ [9].

Desgranges et al [21] showed with Non-equilibrium Molecular Dynamics (NEMD) simulation studies that liquid Fe exhibits a non-Newtonian and shear thinning flow behavior. Figure 12 (a) shows the shear thinning behavior of liquid Fe by NEMD at three temperatures. Qi et al [9], in a similar NEMD simulation study to evaluate the shear viscosity for the binary Au-Cu and pure Cu liquid alloy systems have shown that both pure Cu and any alloy of Au-Cu liquid system also has a non-Newtonian shear thinning behavior. Figures 12 (b) (c) and (d) shows graph of pure Cu and Au-Cu alloys. Figure 13 (a) is a graph from one of the posters developed by Paroline et al [18] showing that pure Al exhibits a shear thinning behavior at 973 K When the graph in Figure 13 (a) was converted to a flow curve, as shown in Figure 13 (b), it was evident that the unique behavior of the flow curve in the low shear rate regime where in the applied shear stress decreases with increasing shear rate is valid and reproducible. This can be ascertained by comparing Figure 13 (b) and Figure 9.



(a) (b)

Figure 13: Rheology curves for pure Al at 700 °C (a) viscosity versus shear rate and (b) flow curve.

CONCLUSION

The significant conclusions from this study can be summarized as below:

- The results of this study indicate that liquid metal systems are non-Newtonian fluids which exhibit a shear thinning behaviour This understanding has been clearly substantiated by the current study coupled with a few recent researches from around the world [8 9,18,21].
- The flow curve for liquid metals have repeatedly shown a unique behaviour in the low shear rate regime where in the applied shear stress decreases with increasing shear rate A plausible hypothesis has been presented in this study to explain this unique phenomenon. The point of inflection where in the applied shear stress begins to continuously increase with shear rate moves to higher shear rates for liquid metals with higher viscosity values.
- Rotational rheometry is the one of the few techniques that will yield reliable data for viscosity of liquid metals and alloys as a function of shear rate Techniques where in the shear rate is uniform in the sheared liquid for a particular value of applied shear stress can be used to evaluate viscosities of liquid metal systems. The Oscillation Vessel Viscometer (OVV) is unsuitable for this purpose.
- In evaluating viscosity of liquid metal systems the Double Concentric Cylinder (DCC) measurement geometry shall prove to be one of the most effective in that it is less complicated to manufacture and utilize, and yields results with tolerable deviations and errors. An analytical solution has been presented in this study to evaluate the shear viscosity in DCC measurement geometry

ACKNOWLEDGEMENTS

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Rheology of liquid Al and Hypoeutectic Al-Si alloys

Mohammad Minhajuddin Malik , Manickaraj Jeyakumar[1], Mohammed S Hamed[1] Michael J Walker Sumanth Shankar[1]

Centre for Solidification & Thermal Processing (CSTP), McMaster University Hamilton ON
Canada L9H 2E8
[2]General Motors, Michigan, USA.

ABSTRACT

Viscosity of the liquid metals and alloys is one of the key transport properties affecting solidification and quality of a casting. In the present work viscosity of liquid Al and Al-Si alloys is evaluated as function of shear rate, temperature and shear history for rheological characterization of the alloys in liquid phase. Using Double concentric cylinder measuring geometry in the rotational rheometer the flow behavior was observed to be non-Newtonian for liquid Al and Al-Si alloy systems.

INTRODUCTION

Aluminum-Silicon hypoeutectic alloys are extensively used in the automotive and aerospace industry [1]. Their wide spread application can be attributed to their property of better strength to weight ratio and ability to be recycled with high recovery rate [2]. Understanding the rheological properties (flow behavior) of these alloys in the liquid state is critical to predict the product quality and performance of the cast components. The important rheological property that affects the solidification characteristics of these alloys is the viscosity at various superheats of the melt during solidification. Further, the Al-Si hypoeutectic alloys solidify through a semi-solid mushy zone where in both the primary aluminum phase and the liquid coexist until complete solidification of the alloy. Understanding Viscosity as a function of Si content and melt superheat temperature, will enable to predict and model the behavior of the liquid flowing around the solid Al phase in the semi-solid regime during solidification.

In recent years much research has been devoted to the understanding and control of the microstructure of the solidified cast part to enhance mechanical and performance properties. Evolution of the solidified structure during solidification of these alloys influences the fluid flow during the final stages of solidification and hence controls the efficiency of liquid metal feeding in the semi-solid mushy zone [3] Feeding efficiency in turn affects the formation of shrinkage porosity and chemical segregation in cast parts. Understanding how the liquid metal feeds the interdendritic regions in the final stages of solidification is key to the prediction and control of the structure of the cast part

In this study, the viscosity of pure Al and Al-Si hypoeutectic alloys has been evaluated by rotational rheometry. The measurement geometry was selected to ensure that the shear rate experienced by the sheared liquid metal during rotation is nearly uniform

BACKGROUND

Significant research has been carried out to experimentally determine viscosity of Al and Al-Si alloys during the past 60 years [4,5 6,7] However, there is about 400 % spread in the reported values of viscosity for liquid Al and Al-Si alloys [4,8]. Figures 1(a) and 1(b) presents the viscosity data reported for Al and Al-Si alloys during the past 60 years, respectively. All the data sets shown in Figures 1(a) and 1(b) except one in Figure 1(a) was obtained using the Oscillating Vessel Viscometer (OVV). Although, past researchers shown in Figure 1 have used various different mathematical formulations in addition to the possible experimental errors in evaluating viscosity by OVV, the large variation in reported values may not be fully attributed to these factors [4,8] The shear rate experienced by liquid metal in the OVV is not uniform both in spatial and temporal regimes Figure 2(a) shows a schematic of an OVV device with the typical spatial and temporal variation in Figures 2(b) and 2(c). In an OVV device, the cylindrical container with the liquid metal is given a twist (torque) and the time required to completely dampen the oscillations of the cylinder is correlated to the viscosity of the liquid. The viscosity is measured over a range of shear rates and reported as one value over the entire spatial and temporal regimes for the experiments. This reported value of melt viscosity is meaningful if and only if the liquid exhibits a Newtonian flow behavior where in the shear viscosity of the liquid does not vary with the shear rate experienced [9]. Non-Newtonian fluids are those in which the viscosity varies with the shear rate experienced by the liquid. There are two types of non-Newtonian fluids shear thinning behavior is characterized by decrease in shear viscosity with increasing shear rates and shear thickening behavior is characterized by increase in shear viscosity with increasing shear rates. The inherent assumption in using an OVV is that liquid metal systems are Newtonian. However, lately it has been reported that metal system may not be Newtonian fluids.

Malik et al [8] and Paoline et al [10] have recently shown that liquid Al exhibits a non-Newtonian and shear thinning flow behavior. Varsani et al [11] also suggested that all the liquid metals are non-Newtonian but exhibits a shear thickening behavior. The Equilibrium Molecular Dynamics (EMD) and Non equilibrium molecular dynamic (NEMD) simulation of viscosity of Iron by Desgranges et al [12] shows non-Newtonian and shear thinning flow behavior Qi et al [13] carried out NEMD simulations to claim that liquid Cu and Cu-Au liquid metal alloy system exhibit a non-Newtonian and shear thinning behavior. Figure 3 presents typical examples of liquid metal systems exhibiting non-Newtonian and shear thinning behavior.

Al-Si alloys being commercially important and subjected to various research studies on the solidification behavior of the alloy has been chosen for this study to characterize the rheology by experimentation. Rotational Rheometry is a popular technique that can be used for such a characterization. In rotational rheometry, there are no assumptions regarding the Newtonian or non-Newtonian flow behavior of the liquid. A Measurement geometry selected in this study has been designed to carry out experiments with Al and Al-Si alloys where in the shear rate experience by the liquid metal is nearly uniform.

In rotational rheometry the liquid is contained between a rotor and a stator. The rotor is made to rotate at a fixed angular velocity, ω and the torque, T necessary to maintain the angular velocity is measured The measured T and ω are then converted to applied shear stress and shear rate experienced by the liquid respectively Figure 4(a) shows a photograph of the AR2000* rotational rheometer outfitted with the Double Concentric Cylinder (DCC) measurement geometry used in this study Figure 4(b) shows a schematic of the DCC measurement geometry with the dimension variables.

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* Advanced Rheometer, TA Instruments, New Castle, DE, USA. http //www tainstruments com

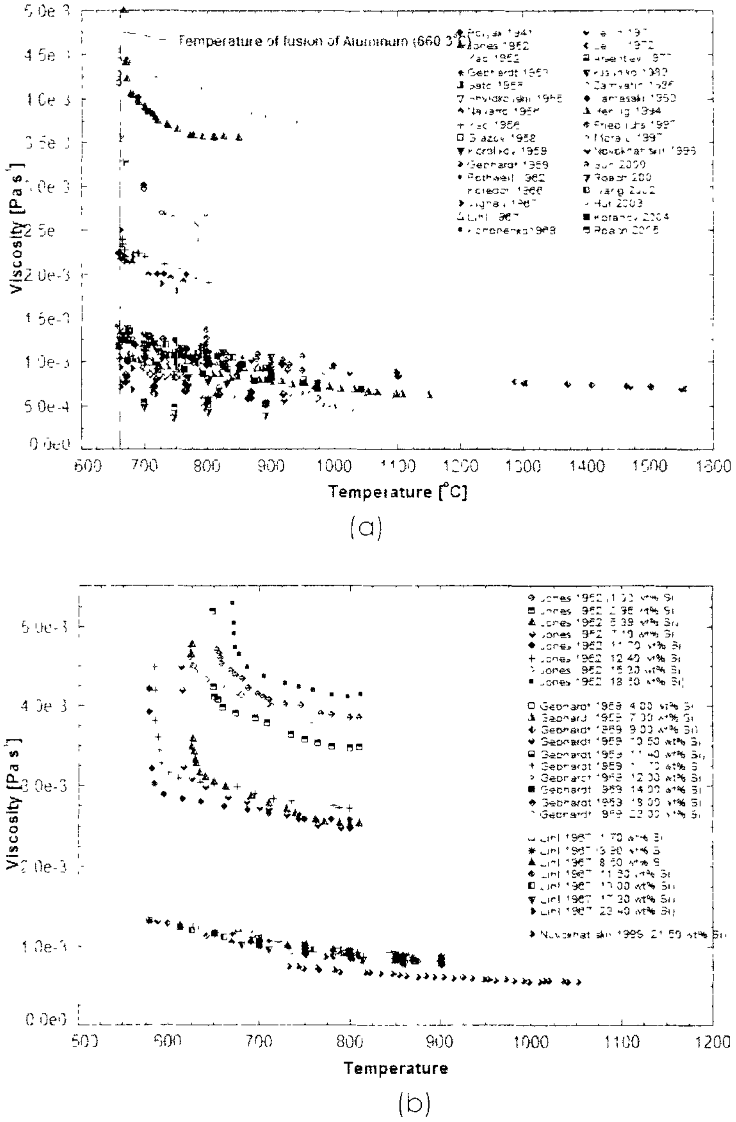


Figure 1: Viscosity as a function of temperature for (a) pure Al and (b) Al-Si alloys. The spread in data is about 400 %. All data were evaluated by Oscillation Vessel Viscometer (OVV) except Jones et al

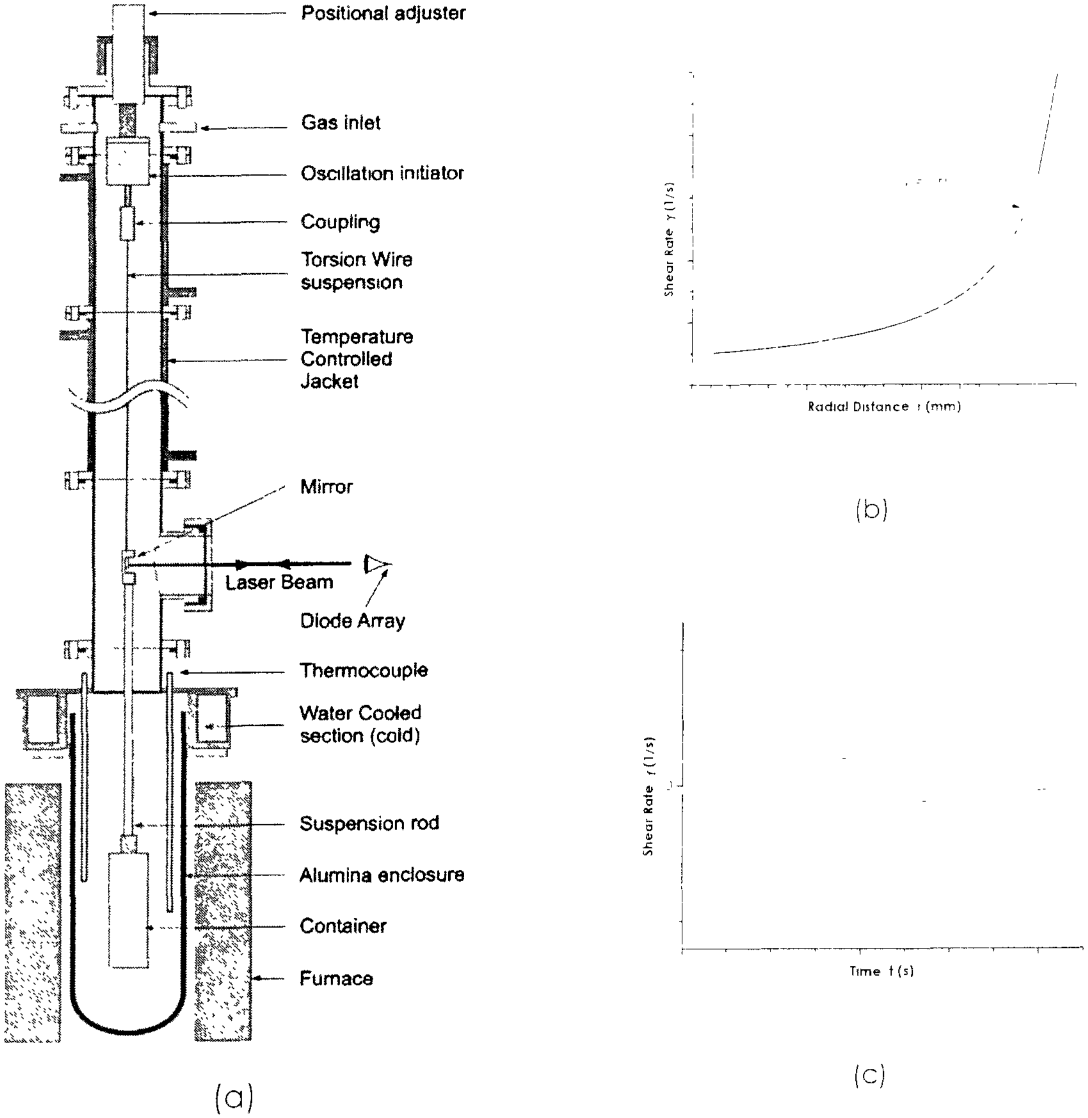
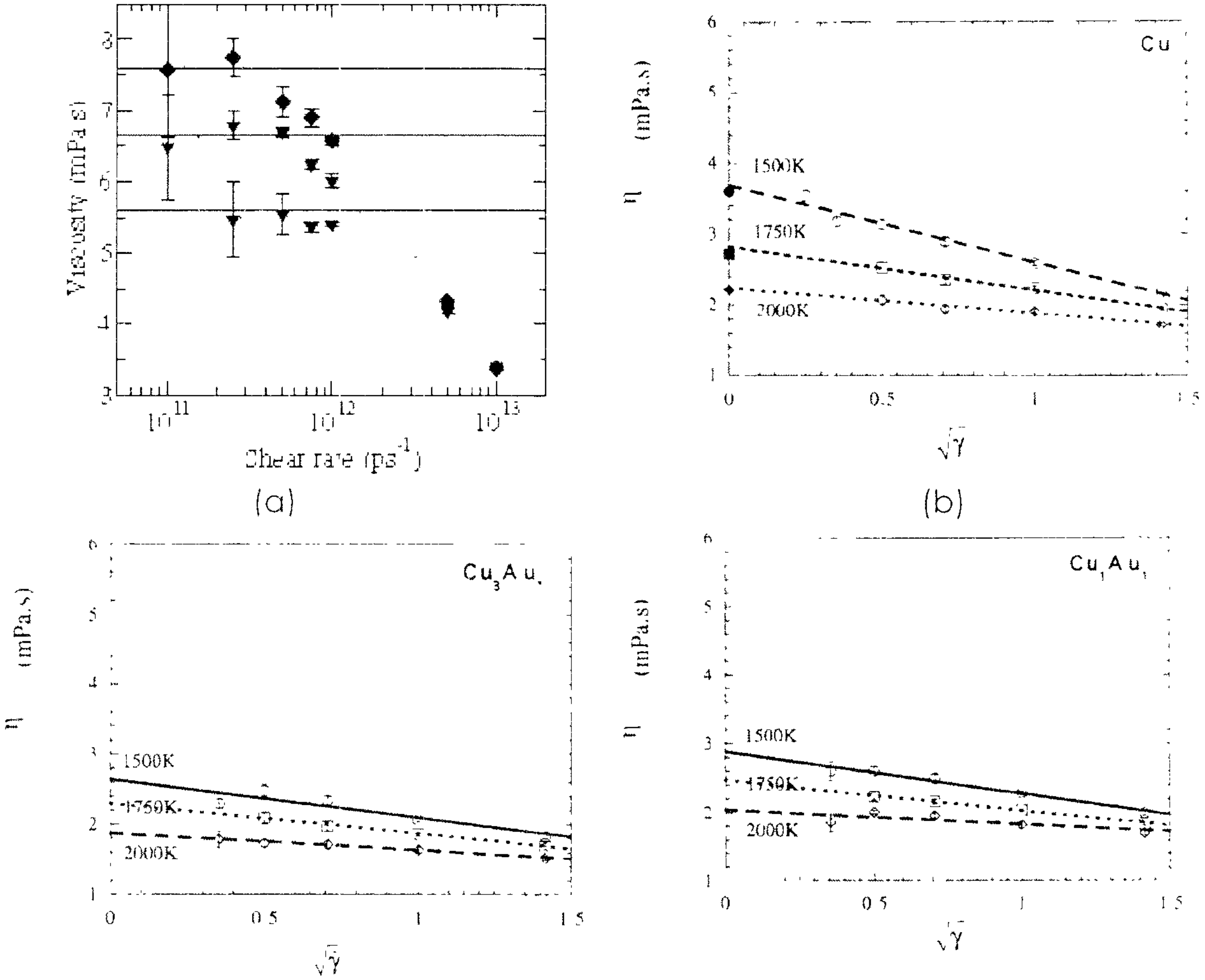


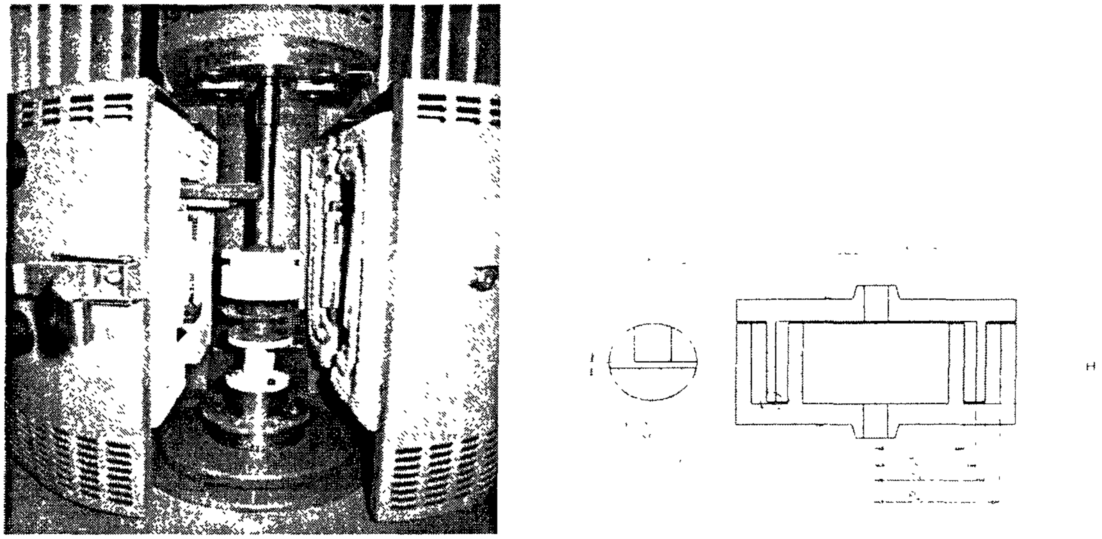
Figure 2: Schematic of a typical (a) Oscillating Vessel Viscometer (OVV), (b) the spatial variation of shear rate and (c) the temporal variation in shear rate.



(a) (b)

(c) (d)

Figure 3: Viscosity as a function of shear rate for various liquid metal systems obtained by Non-Equilibrium Molecular Dynamics simulation. (a) Pure Fe [12], (b) pure Cu (c) Cu$_3$Au and (d) CuAu$_3$ [13].



(a) (b)

Figure 4: Rotational Rheometry Experiment setup (a) Photograph of the AR2000 rheometer (b) Cross-section of Double Concentric Cylinder (DCC) measurement geometry used in the present experiment study. R1 = 14.5 mm, R2 = 16.5 mm, R3 = 18 mm, R4 = 20 .5 mm, H = 15 mm and z = 0.30 mm.

In Figure 4(a) the torque head applied a torque to maintain a specific angular velocity in the liquid contained in the DCC geometry Equations (1) and (2) present the evaluation of shear stress, τ and shear rate, $\dot{\gamma}$, respectively.

$$\tau = \frac{\left(1+\beta^2\right)}{4\pi H\left(R_1^2+R_3^2\right)} \cdot T \tag{1}$$

$$\dot{\gamma} = \frac{2\beta}{\left(1-\beta^2\right)} \cdot \omega \tag{2}$$

The shear viscosity, μ_{shear} is the ratio between the applied shear stress and the shear rate and is presented in Equation (3).

$$\mu_{shear} = \left(\frac{T}{\omega}\right)\left(\frac{1-\beta^4}{8\pi H\beta\left(R_1^2+R_3^2\right)}\right) \tag{3}$$

In Equations (1) to (3), $\beta = \frac{R_1}{R_2} = \frac{R_3}{R_4}$. The design of the DCC geometry (Figure 4(b)) should be such that the radius ratios in the inner and outer annular regions containing the liquid should be constant. Further, as β tends to unity the shear rate experienced by the sheared liquid is uniform throughout. In this study the value of β is 0 878 and this results in a variation of less than 10% in the shear rate between the rotor and the stator shown in Figure 4(b). Equations (1) to (3) were derived for the DCC geometry and presented in one of our recent publications [14]

MATERIALS AND PROCEDURE

Figure 5 shows a typical phase diagram of Al-Si hypoeutectic binary system. Also shown in Figure 5 are the temperatures and Si composition of the alloys used in this study (shown in Table I). The aim was to include alloys encompassing the range of Si content between 0 wt% and 12.5 wt%

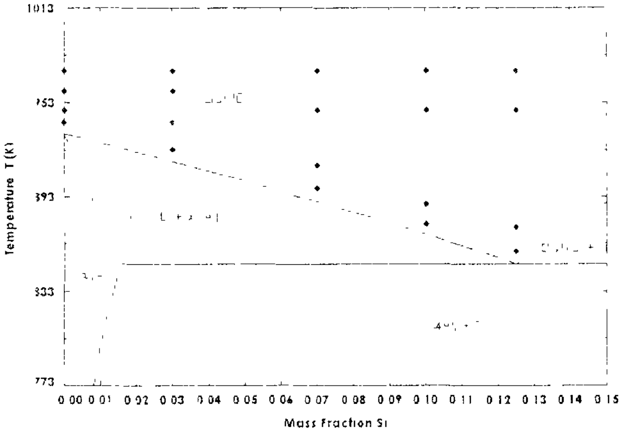


Figure 5: Alloy phase diagram for Al-Si system showing the eutectic composition at about 12.5 wt% Si. The spots in the figure represent the Si level and melt temperatures at which the experiments were carried out as shown in Table I.

Materials

The alloys used in this study are presented in Table I. The chemical composition of the alloys was verified by Inductively Coupled Plasma (ICP) spectroscopy. The alloys were all made from high purity materials and cast into hollow cylinders to fit the annular regions of the DCC measurement geometry shown in Figure 4(b). The DCC measurement geometry was precision machined from the Cotronics 902† machinable ceramic rods of 50 mm diameter. This material can withstand a maximum operating temperature of 1100 °C and is chemically inert to most liquid metals.

Table I: Alloy compositions, melt superheat temperatures and shear rates used in the study

Name	Si (wt%)	Fe (wt%)	Others (wt%)	Liquidus Temperature (K)	Experiment Temperatures (K)	Angular Velocity (rad.s^{-1})	Shear Rate (s^{-1})
Al	0	0.093	0.015	933	973, 960, 948, 940	0 to 60	0.16 to 467
Al-3Si	3.60	0.087	0.020	928	973, 960, 948, 933		
Al-7Si	7.29	0.063	0.014	883	973, 948, 913, 888		
Al-10Si	5.68	0.074	0.018	868	973, 948, 888, 873		
Eutectic	12.25	0.065	0.015	853	973, 948, 878, 858		

Procedure

Thermal analysis was carried out on the alloy samples at a slow cooling rate to evaluate their respective liquidus temperatures. Figure 6 shows the graphical results of the thermal analysis of the alloys. Table I shows the liquidus temperature for each alloy along with the melt temperature and the shear rates at which the experiments were carried out. Each of the hollow cylinder cast alloy sample was sectioned to the required length and loaded into the stator of the DCC geometry (Figure 4). The rotor and the stator were heated inside an environment

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† Cotronics Corporation, Brooklyn, NY, USA. http://www.cotronics.com

furnace under constant purge of ultra high purity Ar (<2 ppm oxygen) gas at 5 l/min. At the required melt temperature (monitored by a K-type thermocouple) the rotor was inserted into the melt and the height of the rotor from the base of the stator was maintained at 0.3 mm. A new alloy sample was loaded for each experiment melt temperature The melt was then subjected to a ramp-down shear rate from 467 s^{-1} to 0.16 s^{-1}. The residence time in each shear rate was 5 s. The measure torque data was obtained between 2 and 5 s at each shear rate. Between 0 and 2 s the applied torque stabilized to maintain a constant angular velocity (shear rate). This is shown in the subsequent section (Figure 7). About 25 data points were recorded between 2 and 5 s of experiment at every shear rate. The measured Torque was used to evaluate the shear stress using Equation (1). The melt temperatures for each alloy was so chosen to include the temperature at 5 K melt superheat from liquidus temperature and 973 K. The temperature distribution in the sheared liquid was observed to be less than 1 K. The torque measurement resolution for the rheometer was 0.1 nN.m and the angular displacement resolution was 25 nrad.

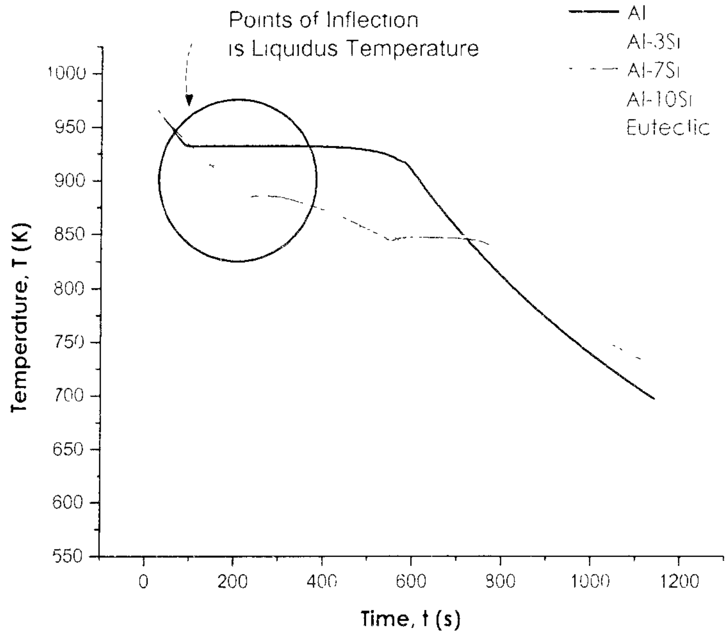


Figure 6: Thermal data during solidification of the alloys presented in Table I.

RESULTS AND DISCUSSIONS

The results and discussion are presented for the following topics:

- Taylor Vortex Formation Criteria
- Time Dependency Curve (Shear Stress versus Time)
- Viscosity of Al and Al-Si alloys

Taylor Vortex Criteria

Experiments in rotational rheometry of liquid should ensure that the sheared liquid undergoes a laminar and steady flow behavior without the formation of vortices in the liquid

$$\frac{(\omega R_1)(R_2 - R_1)}{\left(\frac{\mu}{\rho}\right)} \sqrt{\frac{(1-\beta)}{\beta}} > 41.3 \qquad (4)$$

In Equation 4 ω is the angular velocity of the sheared liquid, μ is the shear viscosity, ρ is the density of the fluid, R_1 is the rotor radius, and (R_2-R_1) is the annular gap as shown in Figure 2(b). The quantities (ωR_1) and (μ/ρ) represent the peripheral velocity at the rotor/liquid interface and the kinematic viscosity of the sheared liquid respectively. The critical angular velocity is obtain when Equation (4) is an equality.

Figure 7 shows the value of critical angular velocity of eutectic alloys below which experiments should be carried out with the DCC geometry in this study (Figure 2(b)). Eutectic alloys will have the least density among the alloys studied and hence have the least critical angular velocity. Figure 7 also shows that the typical experiment data points for all the alloys lie well below their respective Taylor vortex criteria thus vouching for the reliability in the measured viscosity values.

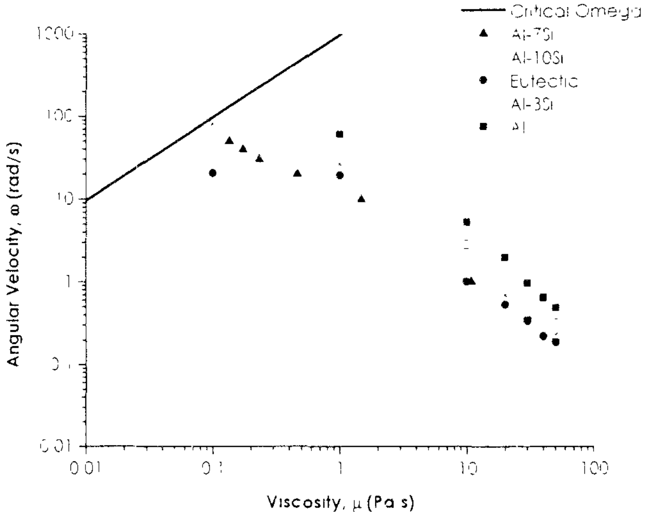


Figure 7: Representation of Taylor Vortex criteria for Al alloy system. The solid line is the plot of critical angular velocity for Eutectic as a function of shear rate above which the vortices will form in the sheared liquid.

The inequality presented in Equation (4) is known as the Taylor vortex criteria. If the inequality is satisfied, vortices will form in the sheared liquid. To obtain reliable results in rotational rheometry the inequality in Equation (4) should not be satisfied.

Varsani et al [11] have recently carried out rotational rheometry experiments on pure Al. They have shown non-Newtonian shear thickening behavior for the metal between shear rates of 400 and 2600 s^{-1}. However, the Taylor vortex criteria (Equation (4)) for the measurement geometry used by them and properties of pure Al dictates that vortices will form if the shear rate in their experiments exceed a value of 175 s^{-1}. Above the critical shear rate, the vortices will absorb the energy of the sheared liquid and hence more energy is required to over come the vortices to maintain a constant shear rate. This translates to measurement of higher torque values by the instrument thus reporting a higher viscosity and shear thickening behavior. Hence controlling the shear rate regime used in the experiment with the Taylor vortex criteria shown in Equation (4) is critical.

Time Dependency Curves

Time dependency curves represent the graph of applied shear stress versus time for a constant angular velocity (shear rate) applied to the liquid Figure 8 shows typical time dependency curve for various alloys at a melt temperature of 973 K and a shear rate of 467 s^{-1}.

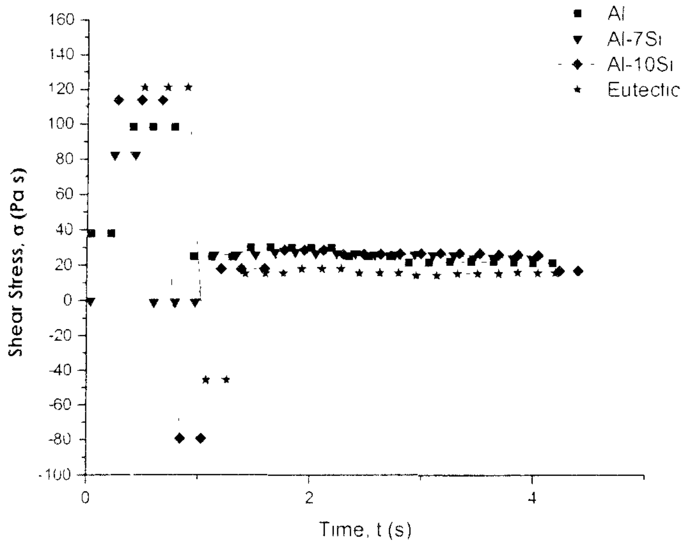
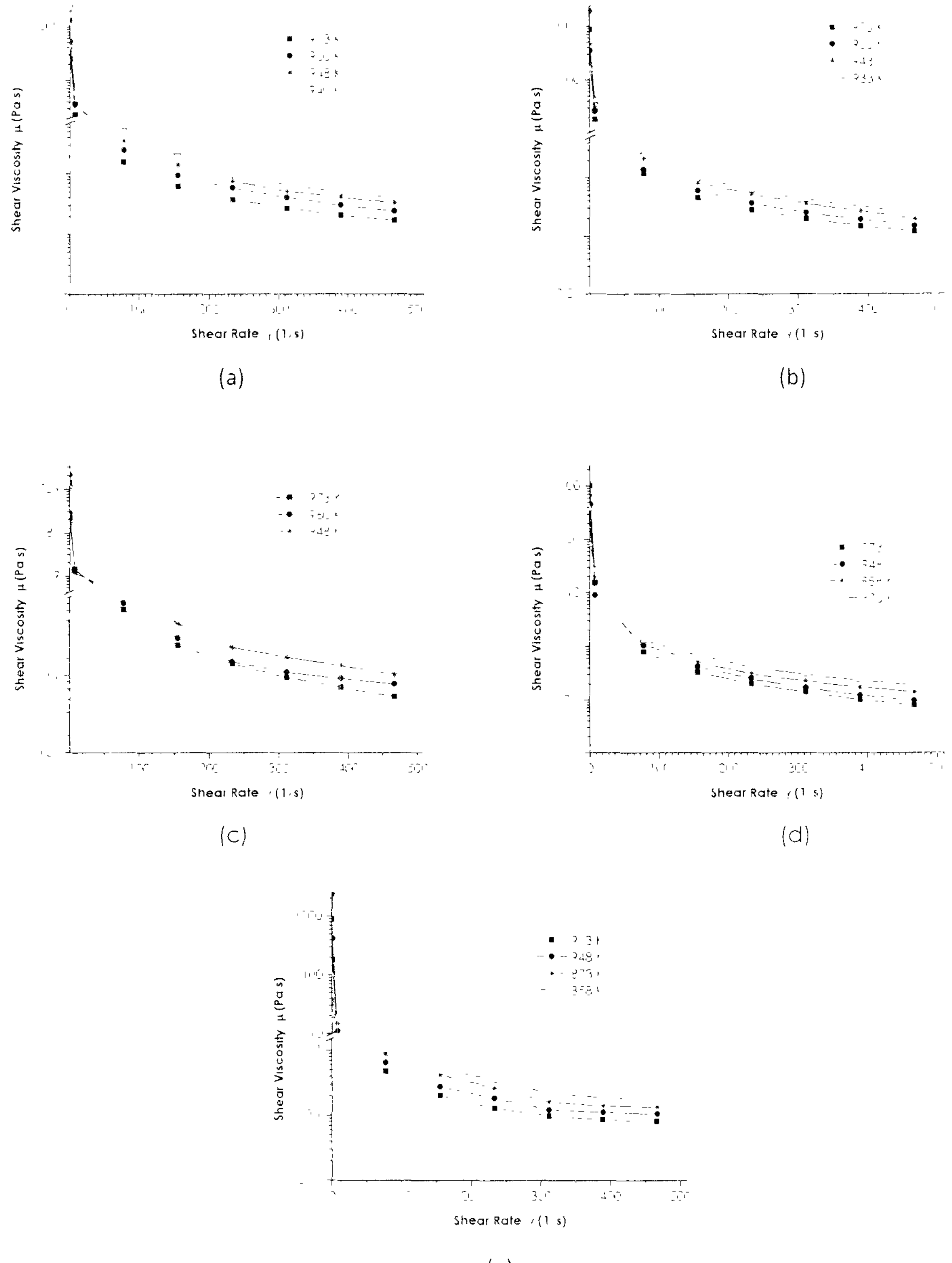


Figure 8: Time dependency curve (Shear stress versus time) for liquid Al-Si alloy system at specific melt temperature and shear rate

The time dependency curve shows that the shear stress does not vary with time at the constant temperature and shear rate. The time dependency curve obtained for the other temperatures and shear rates were similar to that shown in Figure 8. The constant time dependency for the alloys shows that the alloy system is completely liquid and devoid of any solid particles such as solidified phases or extraneous impurities.

Viscosity of Al and Al-Si alloys

The viscosity of the alloys was evaluated using Equation (3). Figures 9(a) to 9(e) shows the variation of viscosity with shear rate at various temperatures for each of the alloys in Table I. All the alloys in Figure 9 show non-Newtonian and shear thinning behavior. In accordance to our understanding, In Figures 9(a) to 9(e), the viscosity decreases with increasing temperature for all the alloy compositions. The rate of decrease of viscosity with shear rate is decreases with increasing shear rates.

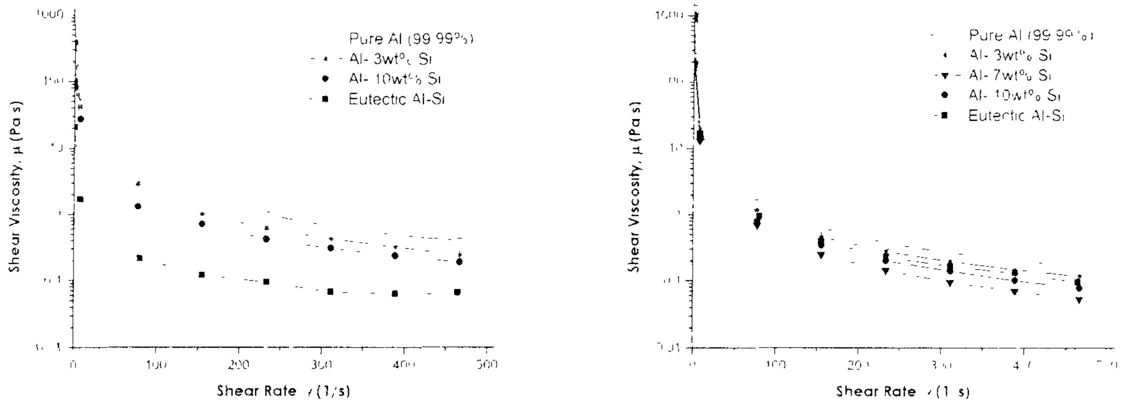


(a) (b)

(c) (d)

(e)

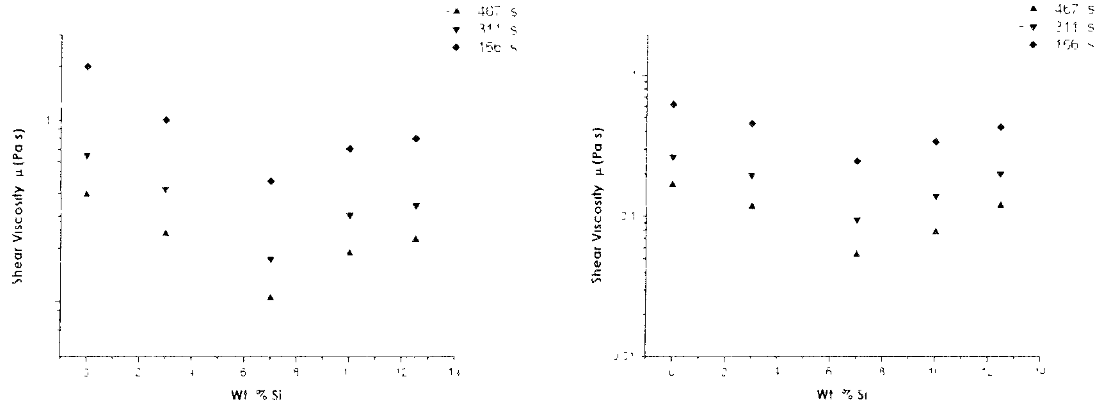
Figure 9: Viscosity curve of the Al-Si alloy system as a function of shear rate for four melt superheat temperatures. The curves show that Al-Si alloys are non-Newtonian and shear thinning fluids. (a) Al, (b) Al-3Si (c) Al-7Si, (d) Al-10Si and (e) Eutectic



(a) (b)

Figure 10: Comparison of viscosity versus shear rate for the various alloys. (a) 5 K melt superheat temperature, and (b) 973K melt temperature

In Figures 10(b) it can be observed that the viscosity of Al-7Si is lowest among the hypoeutectic Al-Si alloys. Al-7Si is one of the most commonly used alloys for sand and permanent mold casting processes. The Al-Si 356 and 357 alloy families typically have around 7 wt% Si content. These alloys are more prevalently used to cast high integrity structural components compared to other Al-Si hypoeutectic alloys compositions.

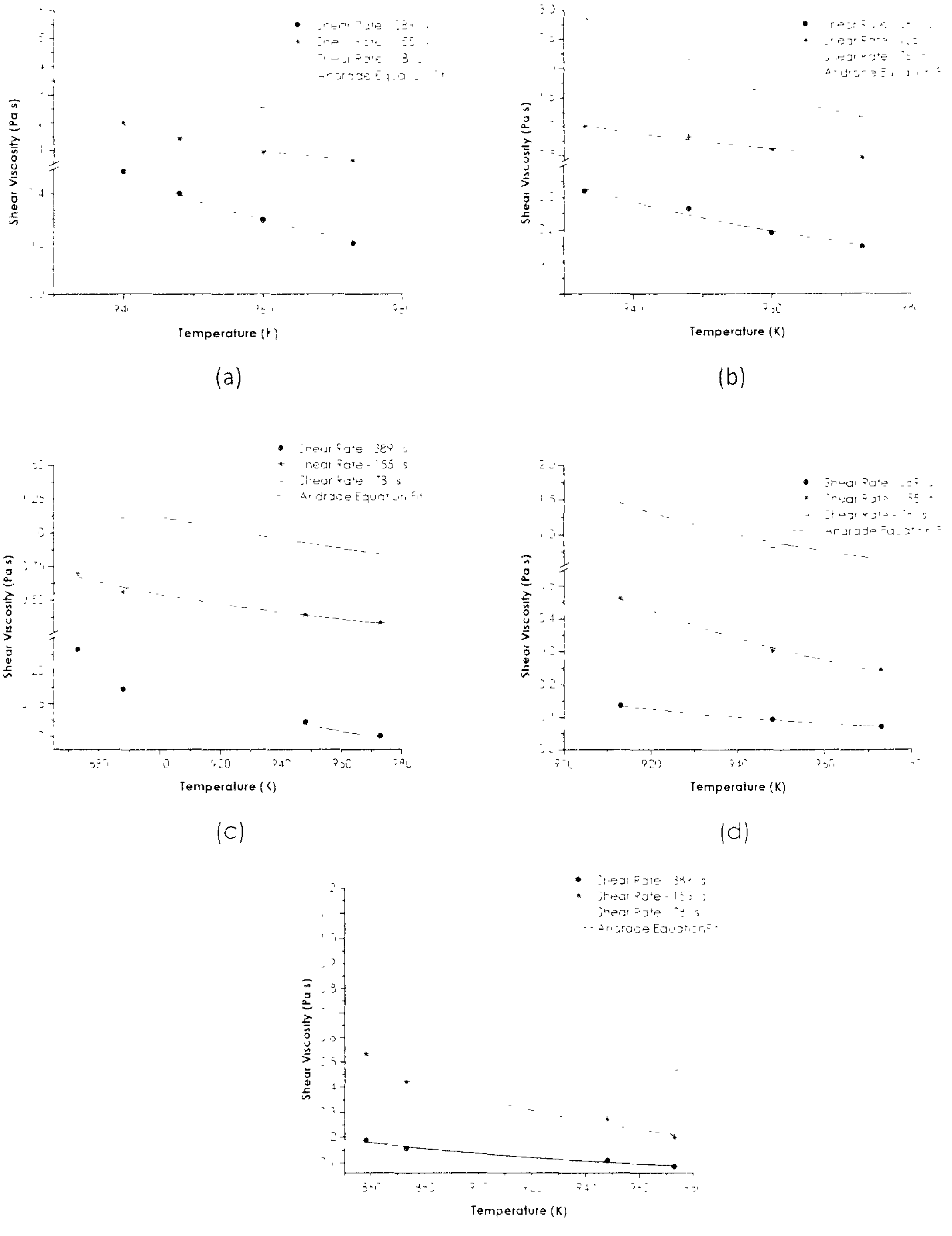


(a) (b)

Figure 11: Viscosity as a function of Si content for three different shear rates (a) 5K melt superheat temperature and (b) 973K

Figures 11(a) and 11(b) show the variation of viscosity with Si content for the alloys at various shear rates for 5 K melt superheat temperature and 973 K melt temperature, respectively. Figure 11(a) demonstrates that the lowest viscosity is shown by Al-7Si. Figure 11(b) shows a similar trend in variation of viscosity as in Figure 11(a). Further, experiments will have to be carried out to better resolve the viscosity data with respect to Si content between Al-3Si and Al-10Si. Marisa di

Sabatino [15] has also shown that the casting fluidity of Al and Al-Si hypoeutectic alloys have a unique behavior where a minima in the fluidity value is reached between 3 wt% and 7 wt% Si



(a)

(b)

(c)

(d)

(e)

Figure 12: Viscosity as a function of temperature. (a) Al, (b) Al-3Si (c) Al-7Si (d) Al 10Si (e) Eutectic

Figures 12(a) to 12(e) show the variation of viscosity with temperature for four specific shear rates each for all the alloys. The data points in Figure 12 are the experiment results and the solid lines represent the curve fit with Andrade's equation [16] which is presented in Equation (5)

$$\mu_{sh,al} = A \cdot e^{\frac{B}{T}} \tag{5}$$

In Equation (5), A and B are constants, and T is the temperature. Table II presents the values of A and B for the curve fits shown in Figures 12(a) to 12(e). As expected the viscosity decreases with increasing temperature.

Table II: Values of constants in Andrade Equation shown in Equation (5)

Material	Shear Rate	A	B	R^2
Al	389	2.62E-11	22224.189	0.99149
	155	2.27E-14	30143.921	0.98329
	78	3.51E-14	30638.792	0.97044
Al-3wt%Si	389	3.87E-09	17028.839	0.9581
	155	1.08E-08	17137.129	0.96407
	78	7.82E-10	20549.581	0.95382
Al-7wt%Si	389	3.32E-06	9695.650	0.99975
	155	1.11E-05	9709.911	0.99006
	78	2.76E-06	12033.003	0.96281
Al-10wt%Si	389	9.10E-05	6796.850	0.91204
	155	7.00E-04	5996.627	0.95945
	78	0.02579	3398.403	0.84121
Eutectic	389	4.30E-04	5195.038	9.64E-01
	155	2.89E-04	6424.690	9.55E-01
	78	3.89E-03	4761.866	0.95186

CONCLUSION

The results from this study can be summarized as follows:

- Pure Al and Al-Si hypoeutectic alloys exhibit a non-Newtonian and shear thinning behavior.
- Al – 7wt% Si shows the least viscosity among the alloys in the study.
- Viscosity for all the alloys decreases with increasing temperature and the trend in decrease follows the Andrade's equation [16].
- In future, solidification studies in the semi-solid mushy zone of Al-Si alloys should not assume Newtonian flow behavior
- Most metal systems seem to exhibit non-Newtonian shear thinning behavior [14].

ACKNOWLEDGEMENTS

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PUBLICATIION D

Effect of Sr addition on the Rheology of Liquid Al-Si Hypoeutectic Alloys

Mohammad Minhajuddin Malik[1], Manickaraj Jeyakumar[1], Mohammed S Hamed[1], Michael J Walker[2], Sumanth Shankar[1]

[1]Centre for Solidification & Thermal Processing (CSTP), McMaster University, Hamilton ON Canada L9H 2E8
[2]General Motors, Michigan, USA.

ABSTRACT

Addition of about 0.02 wt.% Sr to the Al-Si hypoeutectic alloy melt changes the morphology of the eutectic Si and Al phases in the solidified structure. Innumerable attempts are continuously being carried out globally to understand the mechanism of this technologically important transformation. One popular theory is that Sr addition changes the rheological characteristics of the molten alloy and influences the interface energies between the primary Al and inter-dendritic liquid phases thus affecting the nucleation of the eutectic phases resulting in a drastic refinement of their morphologies during solidification. This study attempts to understand the effect of Sr addition on the rheological properties of these alloys by experimentation with rotational rheometry. It was found that Sr significantly increases the shear viscosity of the Al-Si hypoeutectic alloy melt at low superheat temperatures.

INTRODUCTION

Understanding the mechanism of the modification of the morphologies of the eutectic phases with trace level additions of Na and Sr has been an intense research topic for several researchers during the past 50 years [1]. Al-Si alloys without the Sr or Na additions are termed *unmodified alloys* the ones with Sr or Na are termed *modified alloys*. The phase diagram for Al-Si alloy is a simple binary eutectic system [2]. There are three main schools of thought for the theory of such a modification. One [1] proposes that the Sr atoms influence the growth of the eutectic Si phase by attaching themselves to the growth ledges and arresting the growth. Si is believed to grow by the Twin Plane Re-entrant Edge (TPRE) mechanism [1] where in the phase twins on preferred planes and continues to grow. Sr is believed to poison these growth planes in the TPRE mechanism. This theory fails to explain many observed events that occur along during solidification of the eutectic phases [1 2 3]. The second theory was proposed recently by Cho et al [4] and states that the AlP phase particle inherently present in Al-Si hypoeutectic alloys act as nucleating sites for the eutectic Si phase and that Sr addition creates the Al_2Si_2Sr intermetallic phase in the melt which ties up the AlP phase and rendering them ineffective to act as inoculants for the eutectic Si phase. This is merely a hypothesis and not substantiated by sufficient experiment evidence such as crystallographic relationships between the AlP particles and the eutectic Si in an unmodified alloy. The third theory [2, 5] proposes that the Sr changes the rheological properties of the inter-dendritic liquid during solidification of the semi-solid mushy zone of the alloy and alters the interfacial energies between the inter-dendritic liquid and the primary Al phase. This change in interfacial energy delays the nucleation of the eutectic Si phase creating a super-saturation of Si in the inter-dendritic liquid which results in copious nucleation event of the eutectic phases at sufficient undercooling and hence restricts growth to render the eutectic phases with a refined morphology. There are sufficient experimental evidences to support this theory. The theory also states that contrary to popular belief, addition of Sr or Na not only refines the morphology of the eutectic Si phase but also refines the grain size of the eutectic Al grains [5] One of the critical features of this theory is that the Sr addition to liquid Al-Si alloys alters the rheological properties and the atom arrangement in the liquid state.

All the past research [1] in this topic has concentrated on understanding the effect of Sr addition in the solidified structure There is a lack of research studies to evaluate the structure of liquid Al-Si alloys. Such a study will throw more light into the fundamental properties and characteristics of the liquid prior to nucleation events of solidifying phases. There are no experimental evidences to understand the effect of Sr on the liquid structure of these alloys There are two research projects that are being carried out at our casting laboratory. One is to evaluate the structure of liquid Al-Si alloys and the effect of Sr addition to this structure. The liquid structure is being evaluated by diffraction experiments on bulk liquid alloys with neutron and high energy X-Ray (Synchrotron) beams. The complimentary research study presented in this publication evaluates the rheological properties, especially the viscosity of the liquid alloys by rotational rheometry experiments. This publication quantifies the viscosity of Al-Si hypoeutectic alloy with addition of 0.024 wt% Sr by rotational rheometry experiments. The results of this study not only brings us closer to concluding the half a decade search for the theory of modification of Al-Si alloys but can also be utilized effectively in developing constitutive models to predict the microstructure, gas porosity and shrinkage porosity formations in Al-Si alloys during solidification of the binary alloys

BACKGROUND

Experiments to evaluate viscosity of Al and Al-Si alloys have been carried for the past 60 years. Figures 1(a) and 1(b) represent the tabulation of these experiment results. In Figure 1, there is nearly a 400 % variation in the observed viscosity data for these alloys. The Oscillation Vessel Viscometer (OVV) [6,7] has been used to obtain viscosity in all the experiments shown in Figure 1 The main assumption in using the OVV is that the liquid metal system behaves like a Newtonian fluid where in the viscosity value does not change with the shear rate experienced by the liquid. This assumption has not been verified until recently [7,8,9 10,11,12,13] and it has come to light that liquid metal systems tend to behave as non-Newtonian and shear thinning fluids where in the viscosity values decrease with increasing shear rates in the liquid. The present experiments on rotational rheometry using the AR2000[1] rotational rheometer, involves rotating a specific volume of liquid at high temperature to evaluate the torque, T required to maintain a specific constant angular velocity, ω.

The applied shear stress, τ and the shear rate, $\dot{\gamma}$ can be evaluated from the measured values of T and ω. The viscosity, μ is the ratio of τ and $\dot{\gamma}$. Equations (1) to (3) present the expressions to evaluate τ $\dot{\gamma}$ and μ respectively.

$$\tau = \frac{\left(1+\beta^2\right)}{4\pi H\left(R_1^2+R_3^2\right)} \cdot T \qquad (1)$$

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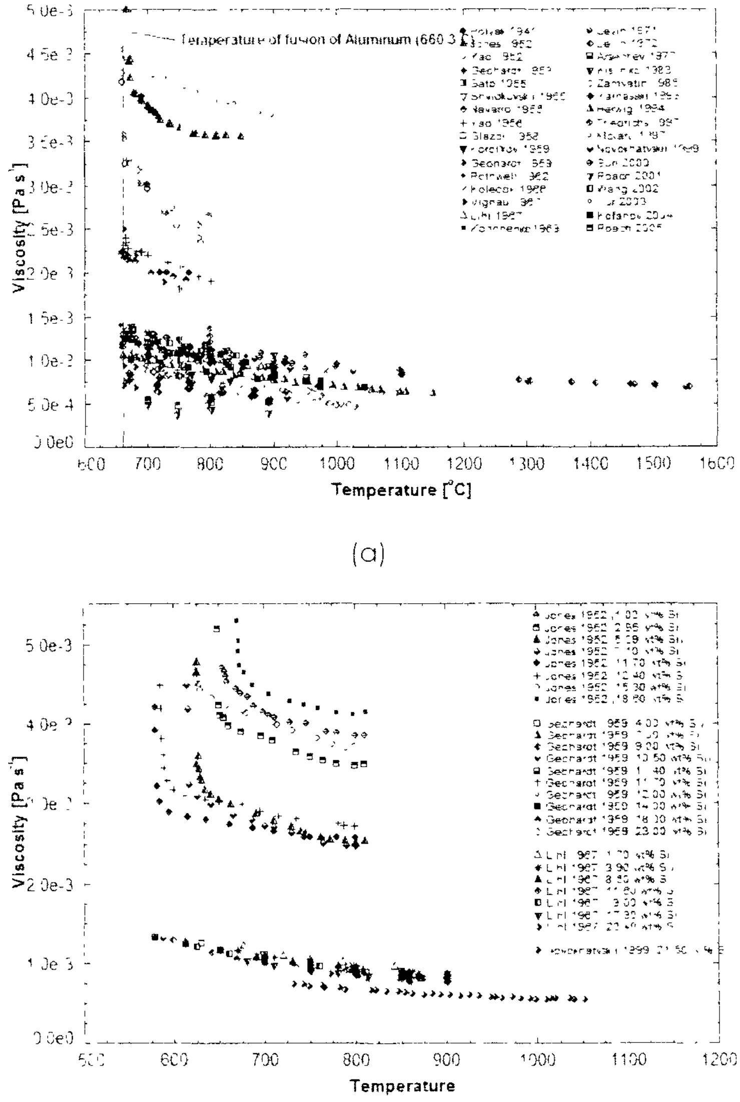
[1] Advanced Rheometer, TA Instruments, New Castle, DE, USA http //www tainstruments com

$$\gamma = \frac{2\beta}{\left(1-\beta^2\right)} \cdot \omega \tag{2}$$

$$\mu_{shear} = \left(\frac{T}{\omega}\right)\left(\frac{1-\beta^4}{8\pi H\beta\left(R_1^2+R_2^2\right)}\right) \tag{3}$$



(a)

(b)

Figure 1: Viscosity as a function of temperature for (a) pure Al and (b) Al-Si alloys. The spread in data is about 400 %. All data were evaluated by Oscillation Vessel Viscometer (OVV) except Jones et al.

The measurement geometry inside the rheometry was the Double Concentric Cylinder (DCC) and shown in Figure 2. The design of the DCC geometry should be such that the radius ratios in the inner and outer annular regions containing the liquid should be constant. In Equations (1) to (3) $\beta = \frac{R_1}{R_2} = \frac{R_3}{R_4}$. Further, as β tends to unity the shear rate experienced by the sheared liquid is uniform throughout. In this study the value of β is 0.878 and this results in a variation of less than 10% in the shear rate between the rotor and the stator shown in Figure 2. Equations (1) to (3) were specifically derived for the DCC geometry and presented in one of our recent publications [8]

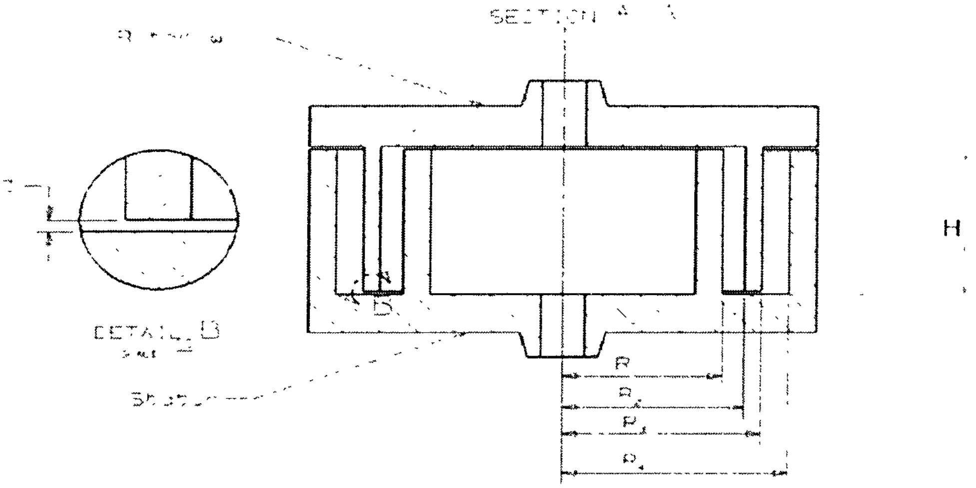


Figure 2: Cross-section of Double Concentric Cylinder (DCC) measurement geometry used in the present experiment study. R1 = 14.5 mm, R2 = 16.5 mm R3 = 18 mm R4 = 20 .5 mm, H = 15 mm and z = 0.30 mm.

MATERIALS AND PROCEDURE

The DCC measurement geometry used in the rheometer was precision machined from the Cotronics 902[2] machinable ceramic rods of 50 mm diameter. This material can withstand a maximum operating temperature of 1100 °C and is chemically inert to most liquid metals.

Figure 3 shows the alloy phase diagram for a typical Al-Si hypoeutectic system. The data shown superimposed in Figure 3 are the Si content and melt temperature of the alloys used in this study. Table I shows the name of the alloys in this study, their chemical composition, the liquid temperature melt temperatures during experiment and the range of shear rate used in the experiments.

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[2] Cotronics Corporation, Brooklyn, NY USA http //www cotronics com

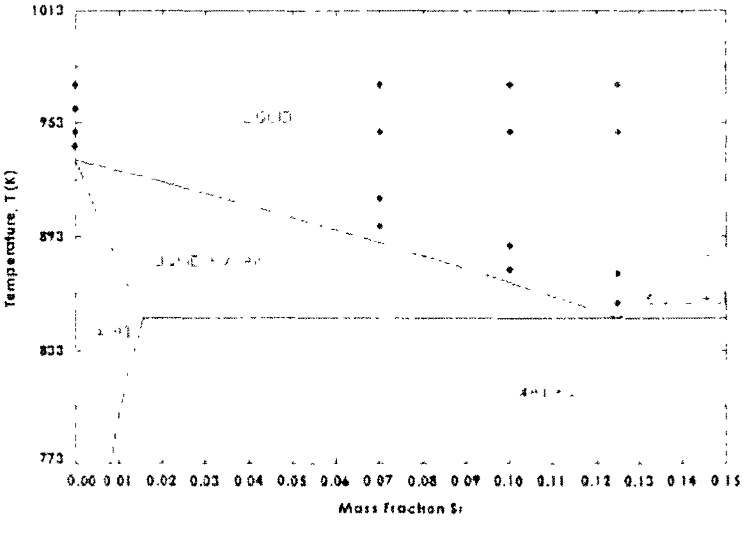


Figure 3: Alloy phase diagram for Al-Si system showing the eutectic composition at about 12.5 wt% Si. The spots in the figure represent the Si level and melt temperatures at which the experiments were carried out as shown in Table I.

Table I: Alloy compositions experimental parameters used in this used in the study.

Name	Si (wt%)	Fe (wt%)	Sr (wt%)	Liquidus Temperature (K)	Experiment Temperatures (K)	Angular Velocity (rad.s^{-1})	Shear Rate (s^{-1})
Al	0	0.093	0.022 to 0.024	933	973, 960, 948, 940	0 to 60	0.16 to 467
Al-7Si	7.29	0.063		883	973, 948, 913, 888		
Al-10Si	5.68	0.074		868	973, 948, 888, 873		
Eutectic	12.25	0.065		853	973, 948, 878, 858		

The Al, Si and Sr used in preparing the alloys listed in Table 1 were from 99.99 %, 99.9999 % and 99 % purity raw materials, respectively. The chemical composition of the alloys was verified by Inductively Coupled Plasma (ICP) spectroscopy The alloys were prepared in fresh ceramic crucibles and cast into hollow cylindrical rods with diameters to match the annular regions of the DCC geometry shown in Figure 2. The hollow rods were then sectioned and inserted in the annular region of the stator. The rotor and the stator were then raised to the experiment temperature inside an environment furnace purged with high purity Ar (<2 ppm oxygen) at 5 l/min. The system was equilibrated at the experiment temperature and the temperature difference between any two points in the liquid metal was measured to be less than 1 K The rotor is then lowered down to reach a distance of 0 3 mm from the base of the stator The rotor was then rotated with specific angular velocities and the torque required to maintain the angular velocity was recorded. The system was rotated at every angular velocity for a period of 5 s The torque values for the first 2 s were discarded as the system reached steady state flow. The torque data measured between 2 and 5 s were averaged to evaluate the applied shear stress using Equation (1) There are about 25 torque values measured between 2 and 5 s. Figure 4 shows a typical time dependency curve where in the measured torque is plotted as a function of time for a specific angular velocity. Figure 5 shows that the steady state of rotation is reached between 0 and 2 s and that the torque value is constant between 2 and 5 s, thus ascertaining that the liquid sample is devoid of any solidified phases or solid discernable solid impurity particles. Each experiment was repeated to evaluate repeatability and the standard deviations in shear stress was observed to be less than 10 % of averaged value. The range of angular velocities presented in Table I was chosen to enable a laminar and stable flow of the sheared liquid at all times. Taylor Vortices Criteria [14] dictates the critical angular velocity for a particular liquid and measurement geometry dimension above which vortices will form in the sheared liquid and render the results unreliable. The Taylor Vortex Criteria for the Al-Si hypoeutectic alloys and the DCC geometry used in this study were presented in one of our recent publications [13].

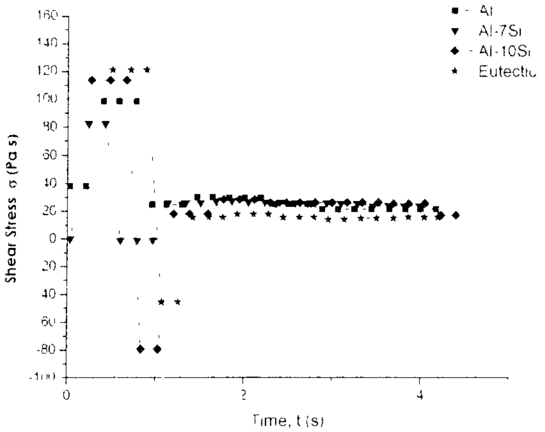
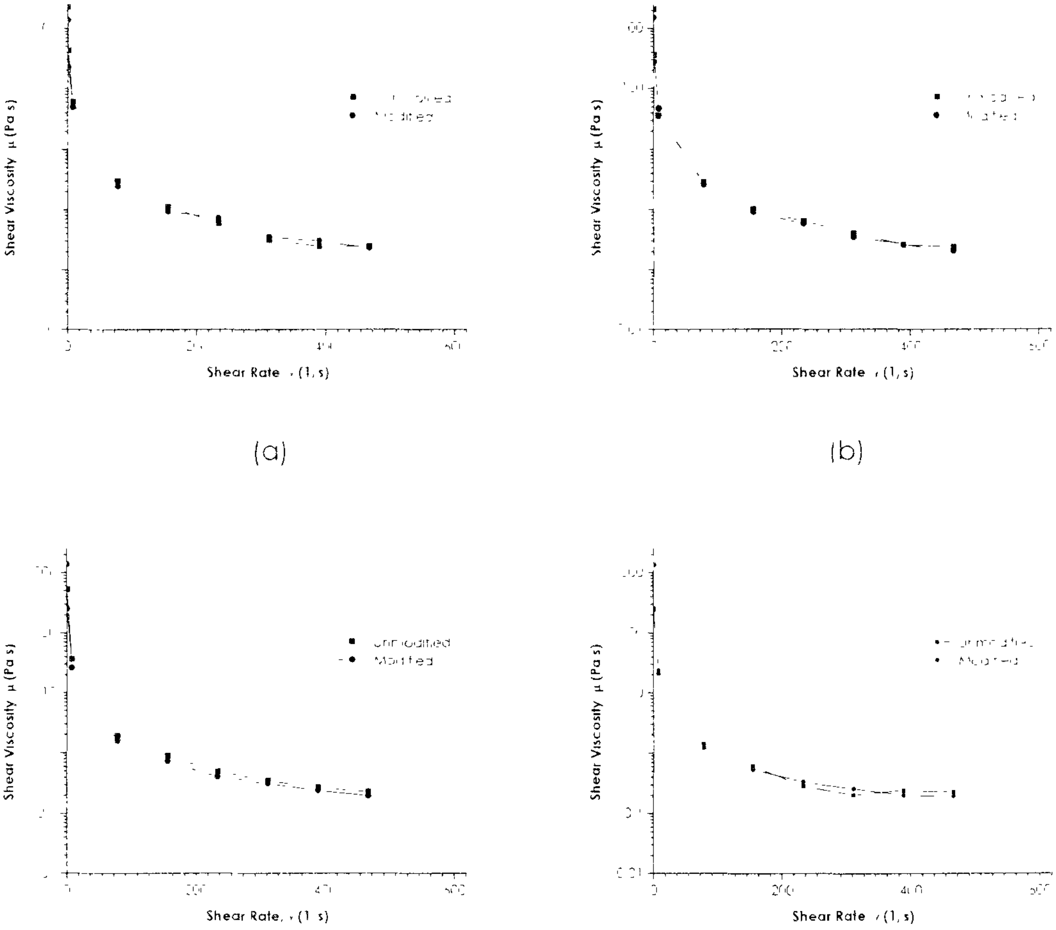


Figure 4: Time dependency curves (Shear stress versus time) for liquid Al-Si alloy modified system at specific melt temperature and shear rate

RESULTS AND DISCUSSION

The standard deviation of the measured shear stress and viscosity was less than 10% and was not included in the results presented in this section to enable better visual clarity

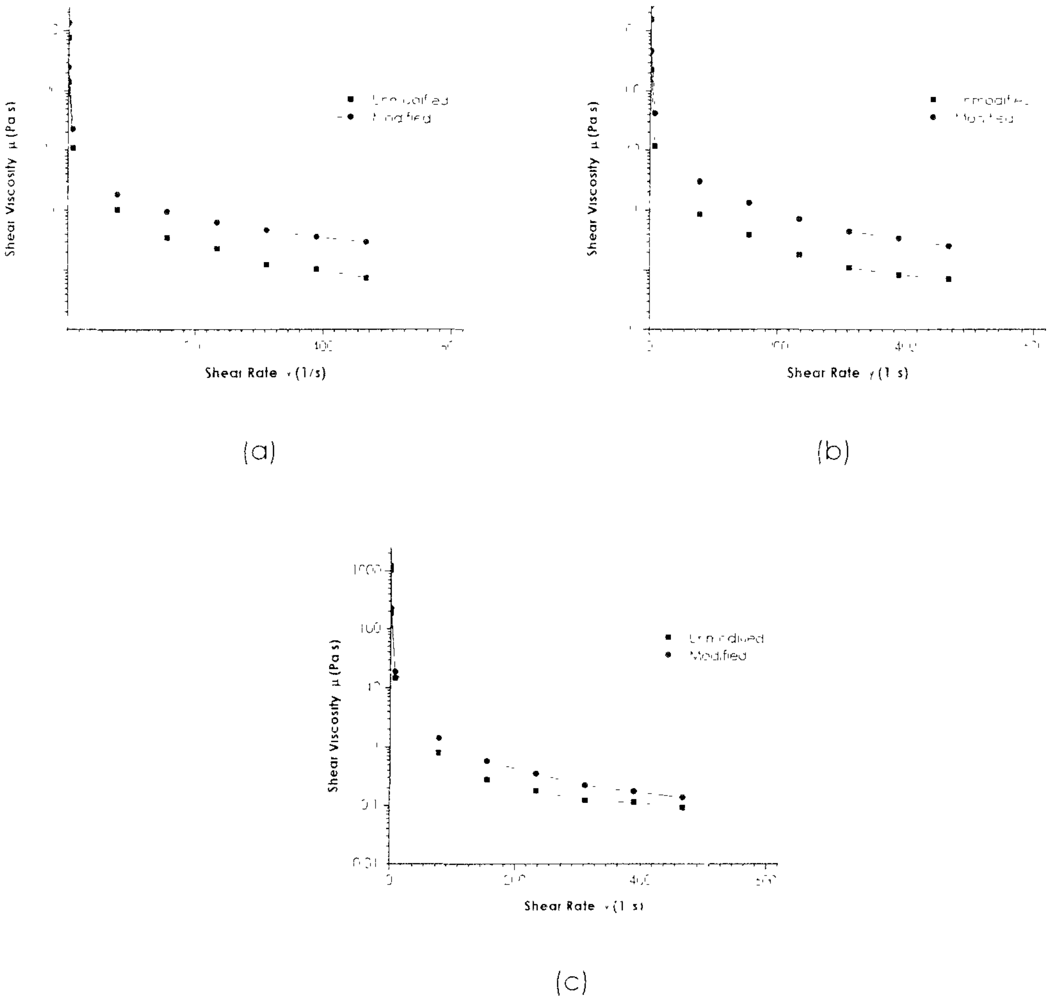
Figures 5(a) to 5(d) show the graphs of viscosity for pure Al at the four melt superheat temperatures, respectively. Figure 1 shows that trace levels of Sr addition does not affect the viscosity of pure Al. Figures 6 to 8 present the results of the viscosity as a function of shear rate for alloys with and without Sr addition to the melt at four melt superheat temperatures for Al-7Si, Al-10Si and Eutectic alloys, respectively. In Figures 6 to 8, addition of Sr significantly increases the viscosity of Al-Si alloys. The increase in viscosity is more significant for the Al-7Si alloy compared to the Al-10Si and eutectic alloys. The effect of Sr in increasing viscosity is more significant for these alloys at lower melt superheat temperatures and the effect fades as the melt superheat increases. For Al-10Si and eutectic alloys as shown in Figures 7 and 8, the effect of Sr fades at temperatures of 948 and 973 K. The effect of Sr on the viscosity of the Al-7Si alloy seem to be the most pronounced among the alloys evaluated



(a) (b)

(c) (d)

Figure 5: Comparison of viscosity versus shear rate for Al with and without Sr traces (a) 940K, (b) 948K, (c) 960K, and (d) 973K



(a)

(b)

(c)

Figure 6: Comparison of viscosity versus shear rate for modified and unmodified Al-7Si (a) 913K, (b) 948K, and (c) 960K,

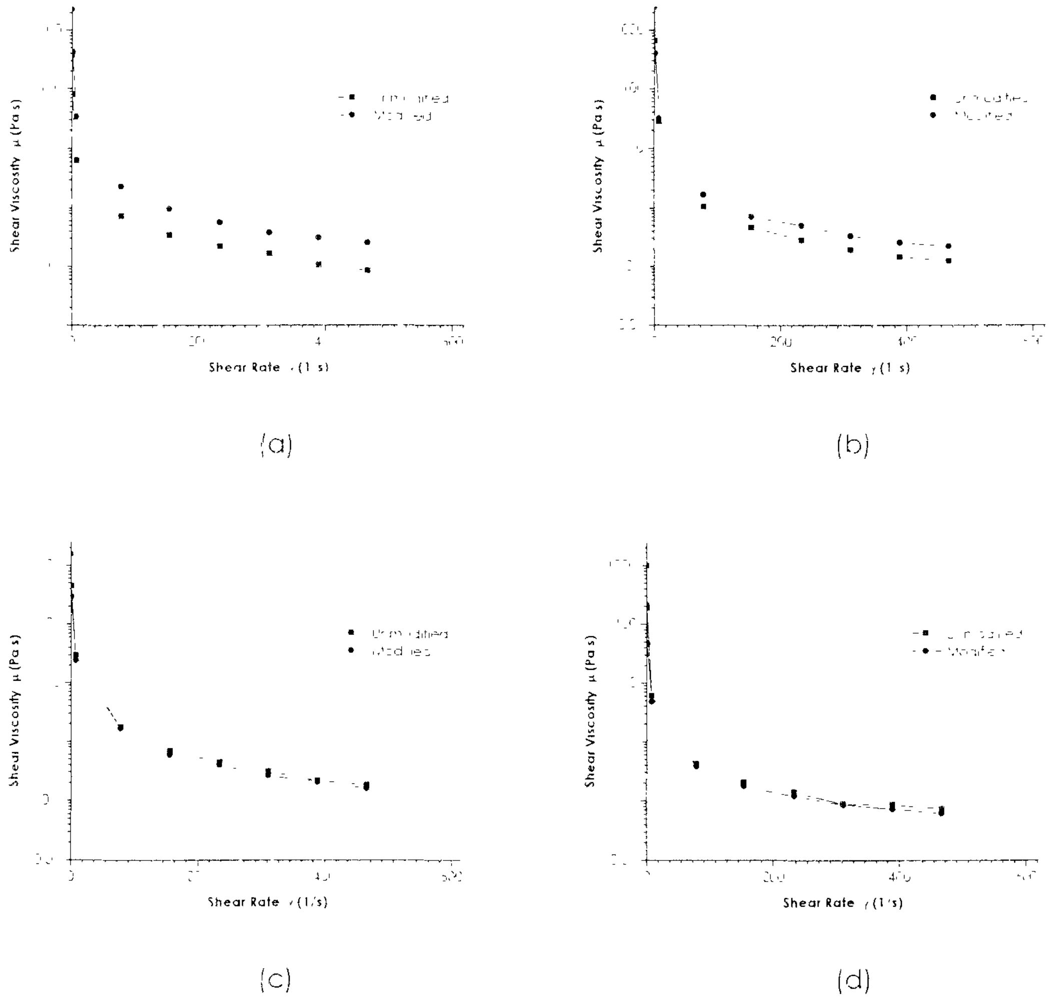
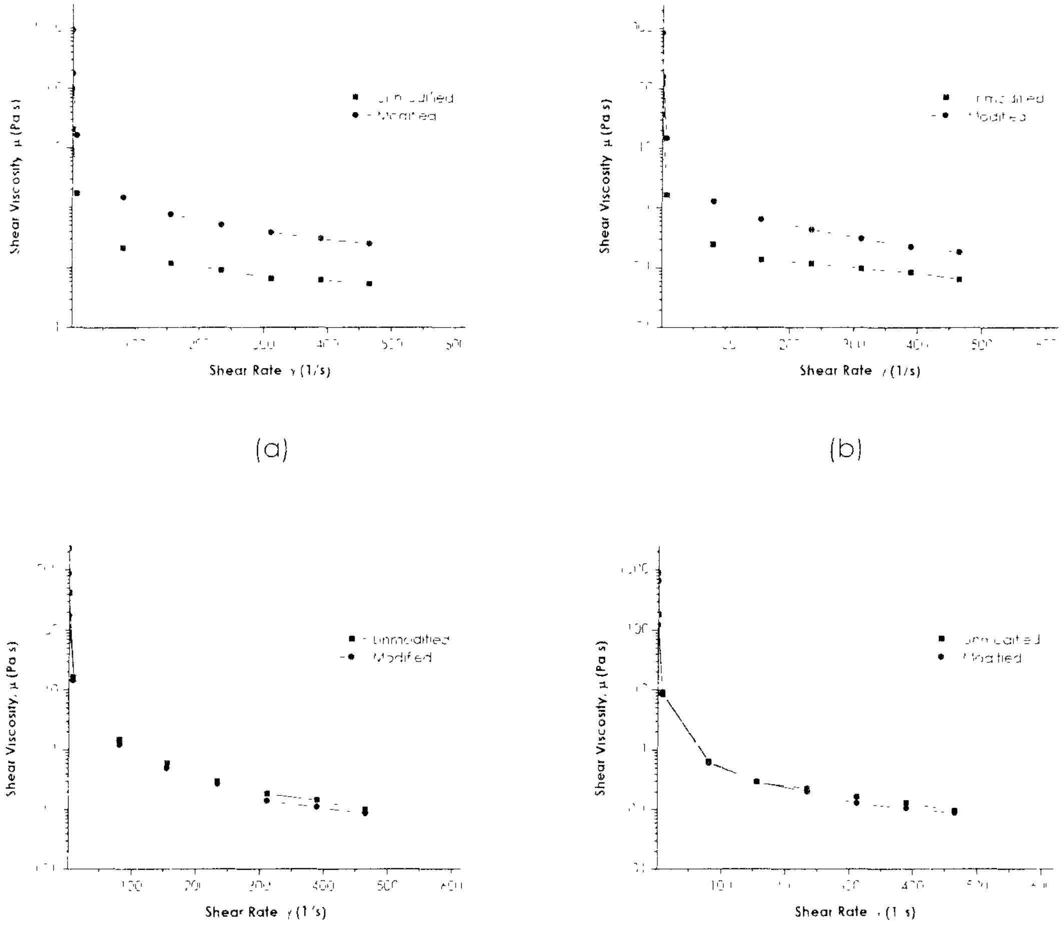


Figure 7: Comparison of viscosity versus shear rate for modified and unmodified Al-10Si (a) 873K (b) 888K (c) 948K, and (d) 973K



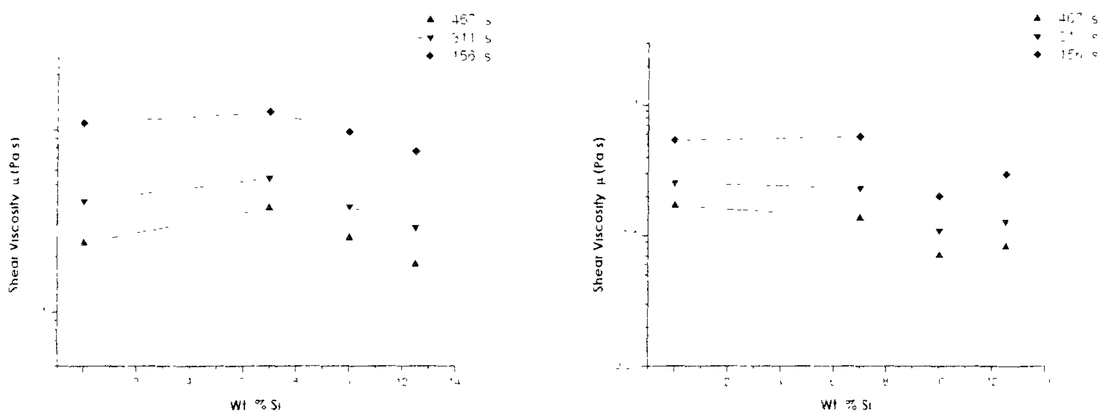
(a) (b)

(c) (d)

Figure8: Comparison of viscosity versus shear rate for modified and unmodified Eutectic (a) 858K, (b) 878K, (c) 948K, and (d) 973K

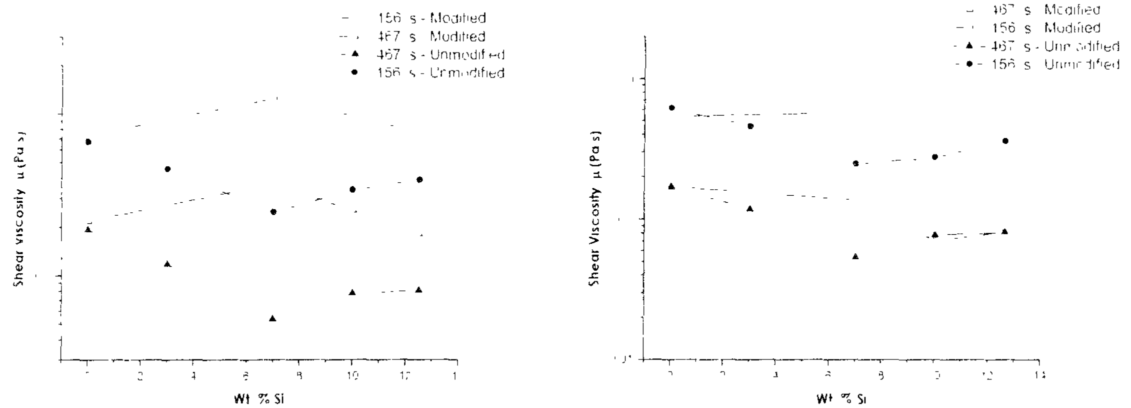
One of the critical observations from these experiments is that the entire Al-Si hypereutectic alloy system exhibits a non-Newtonian shear thinning behavior in both the unmodified and Sr modified states. The effect of Sr is only to increase the viscosity of the Al-Si alloys at all shear rates between 0 and 400 s^{-1}. This is congruent with our findings in our recent experiment with other pure metals such as Zn and low melting Sn based solder alloy [13]. Typically metal systems were believed to Newtonian in nature. However, this assumption has not been experimentally validated. Rotational rheometry offers an opportunity to validate the flow behavior of metals and recent experiments by our group [7,8,13] and others [11,12] have indicated that metal systems seem to behave as non-Newtonian and shear thinning fluids Accurate evaluation of rheological properties especially the viscosity values are imperative in developing constitutive models explaining the flow behavior of inter-dendritic liquids during the feeding and solidification of these alloys. The limited success in predicting solidification microstructure porosity formation and shrinkage cavity formation in solidified Al-Si alloys could be attributed to incorrect assumption for the flow models of these liquid alloys. The evaluated viscosities of the Al-Si hypereutectic alloy show a very high value at low shear rate regime. One of the reasons for the liquid systems to show a non-Newtonian flow behavior may be due to the nature of atomic bonds and energies that define the liquids Liquids unlike solids and gases do not have a constitutive model to define the atom arrangement and behavior [6]. Unlike non-metallic liquid systems that are molecular in nature, liquid metals are mono-atomic in nature The bond energies binding the liquid structure are vastly different from non-metallic systems. Liquids form co-ordination shells at short range orders by forming clusters of atoms that are bonded to each other [6 15] Our recent diffraction experiments on Al-Si alloys have shown that these coordination clusters are spheres of diameters between 2 and 5 A^o [16, 17]. In non-metal systems such as water [13], the molecules do not cluster into coordination shells and the molecules are not strongly bonded to each other. Hence, in metal systems, there will be resistance offered by the short-range order of atom clusters to any shear stress When liquid metal system is sheared, there is a resistance offered by the liquid to maintain a constant angular velocity. In addition to the macro-scale layers of liquid, the micro-scale bond energies of the short-range order of liquid atoms also resist the flow The latter resistance is not present in non-metal systems. The sum of these two resistances is measured as the torque and subsequently shear stress. Although, the resistance offered by the macro-scale liquid layers will increase with increasing angular velocity, the resistance from the micro-scale bond energies of the short range order may tend to decrease as increasing angular velocity overcome these bond energies atom clustering. Increasing angular velocity may change the nature of the coordination clusters in liquids and this may result in a change in the density gradient in the atomic scale. This may explain why in Figures 5 to 8 the rate of decrease in shear stress is quite high at low shear rates compared to higher shear rates. At higher shear rates the viscosity value tends to an asymptote. It may be that the viscosity may attain a nearly constant value at higher shear rates than used in this study This explanation is only a hypothesis and further experiments will have to be carried out to verify and validate the same. There are qualitative evidences to support that the addition of trace levels of Sr to the Al-Si melt significantly alters the coordination clusters of atoms [16,17,19]. This may be the reason why Sr addition causes significant change to the viscosity of the liquid Al-Si hypoeutectic alloys.

Figures 9(a) and 9(b) show the viscosity as a function of Si content for three shear rates for the Sr modified alloys at 5 K superheat and 973 K melt temperature, respectively. It can be observed that the viscosity increases between Al and Al-7Si and decreases from Al-7Si to eutectic alloys. Figure 10 (a) and 10(b) compares the viscosity of the unmodified and modified alloys as a function of Si content at two different shear rates for 5 K superheat and 973 K melt temperature, respectively. Figures 10(a) and 10(b) show that the behavior of Al-7Si alloy is unique in that it shows the lowest viscosity in the unmodified state and the highest in the modified state Moreover, the effect of Sr on viscosity is most pronounced for Al-7Si alloy Further it can be seen that there is minimal effect of Sr addition on Viscosity for 973 K temperature except in Al-7Si alloy. Diffraction experiments of liquid Al-7Si alloys along with other Al-Si hypoeutectic alloys are currently being carried out to evaluate the unique structure of the Al-7Si alloy and explain the unique behavior of viscosity. Interestingly, Al-7Si constitutes the 356 families of Al alloys that are more popular as for structural casting applications due to superior casting and performance properties compared to other Al-Si hypoeutectic alloys [20].



(a) (b)

Figure 9: Viscosity as a function of Si content at three different shear rates for Sr modified alloys (a) 5K melt superheat temperature, and (b) 973K



(b) (b)

Figure 10: Comparison of Viscosity as a function of Si content at three different shear rates for Sr modified and unmodified alloys (a) 5K melt superheat temperature, and (b) 973K

The results of this study show that theory of modification proposed by Shankar et al [5] which is based on Sr changing the interfacial energies between the inter-dendritic liquid and the primary Al phase and leading to a delay in the nucleation events of the secondary eutectic phases This study shows that Sr addition significantly changes the viscosity of the Al-Si hypoeutectic alloys, especially the Al-10Si and eutectic Al-Si alloy which in Si content are similar to the inter-dendritic liquid in contact with the primary Al phase during solidification in the semi-solid mushy zone. The results also suggest that the change in viscosity caused by Sr addition is more pronounced at temperatures closer to the eutectic temperature of the alloy

SUMMARY

The results of this paper can be summarized as follows.

- Al-Si hypoeutectic alloys are non-Newtonian and shear thinning fluids.
- Addition of 0.022 to 0.024 wt.% Sr to AL-Si hypoeutectic alloys leads to the following observations.
    - Addition to pure Al does not have a significant effect on melt viscosity between melting and 40 K melt superheat temperatures.
    - Addition to Al-Si hypoeutectic alloys significantly changes the melt viscosity at various melt superheat temperatures The change in viscosity is more pronounced at lower superheat temperatures and decreases with increasing melt superheat temperatures.
    - The effect of increase in viscosity is most pronounced in Al-7 wt % Si alloy
    - The change in viscosity between unmodified and modified Al-Si alloy is most pronounced in Al-7 wt% alloy. In unmodified alloys, the Al-7 wt.% Si exhibits the least viscosity and in Sr modified alloys the Al – 7 wt.% Si alloy exhibits the highest viscosity among the hypoeutectic alloys
- A hypothesis has been presented to explain the non-Newtonian and shear thinning behavior of liquid Al and Al-Si alloys.
- Sr addition to Al-Si hypoeutectic melts changes the atomic structure and hence the rheological properties of the melt which will lead to changes in surface tension and interface energy of the melt and primary Al phase in the semi-solid state during solidification. A hypothesis has been proposed to explain the increase in viscosity with Sr addition in these alloys.

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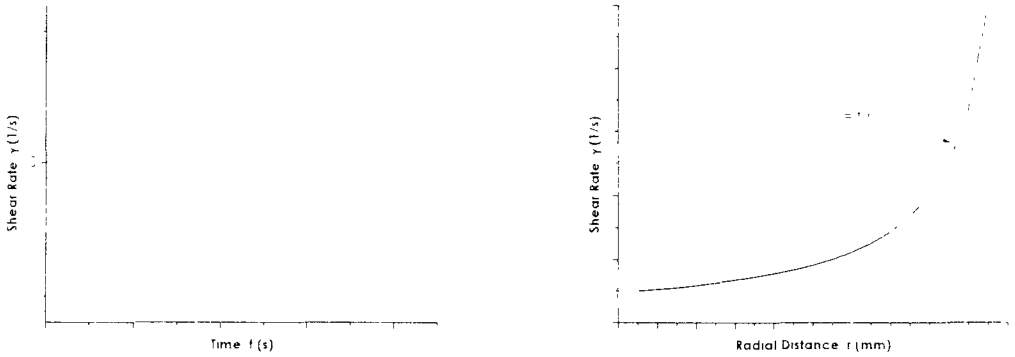
SUMMARY OF THESIS

The contents of this thesis can be summarized as follows:

- A high temperature rotational rheometer equipped with an environmental furnace capable of carrying out experiments at 1100 K melt temperature has been commissioned
- Oscillating Vessel Viscometer (OVV) cannot be utilized to evaluate rheological properties such as viscosity of liquid metals. Only rotational rheometry can be used for this task.
- The Double Concentric Cylinder (DCC) is the most practical measurement geometry for viscosity evaluation of liquid metals in rotational rheometry
- Flow curves of liquid metal systems show a unique behaviour where in the applied shear stress decreases with increasing shear rates at low shear rate regime and the trend reverses at a specific shear rate value unique to the liquid system evaluated. This unique trend may be due to the nature of atomistic bonding in liquid metals which are different form non-metallic systems.
- Liquid meta systems in general seem to exhibit a non-Newtonian and shear thinning behaviour.
- Liquid Al and Al-Si hypoeutectic alloys exhibit a non-Newtonian and shear thinning behaviour between shear rates of 0 and 467 s^{-1}. The viscosities of these alloys decreases with increase in melt superheat and the trend follows the Andrade's equation.
- The viscosity of Al-Si hypoeutectic alloys do not continuously decrease with increasing Si content. Among these alloys, Al – 7 wt.% Si exhibit the minimum viscosity value at all shear rates between 0 and 467 s^{-1} and all melt superheat temperatures.
- Sr addition to Al-Si hypoeutectic alloys between 0.022 and 0.024 wt.% significantly increases the viscosity of these alloys. At high melt superheat temperatures the effect of Sr addition on viscosity is not appreciable.
- The effect of Sr addition Sr addition to Al-Si hypoeutectic alloys between 0.022 and 0.024 wt.% is most significant in Al – 7 wt.% Si alloys at all shear rates between 0 and 467 s^{-1} and all melt superheat temperatures.

ERRATA

1. In publication A, on page 11 of this thesis, Figure 3 (a) and (b) should be read as given below:



(a) (b)

Figure 3: Schematic graphical representation of the variation of shear rate in an oscillation vessel viscometer. (a) temporal variation and (b) spatial variation

2. In publication A, on page 17 of this thesis, the caption in Figure 10 should read as below:

Figure 10: Apparent Viscosity curve for 99.999% pure Al melt showing non-Newtonian (shear thinning) behaviour [15].