Rheological Modification of Liquid Metal Alloys (LMA) for Non-Contact Dispensing

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ABSTRACT

As previously studied, the deposition of liquid metals through needle dispensing is driven by a shearing mechanism rather than a volumetric or pressure displacement mechanism typical for viscoelastic liquids[1,2]. Parameters like print height and applied extruding pressure are crucial for quality and reliable patterning. Galinstan naturally forms a nanometer thin oxide layer when in contact with air, and the hydrophilic nature of this oxide contacting the surface allows for adhesion of the liquid metal to many substrates during deposition.

In the case of non-contact deposition of fluid, the low viscosity of the pure LMA (η = 2.4 mPas) can be problematic, as well as the high surface tension. In order to alleviate these issues, increasing the viscosity of the fluid to a certain degree by some mechanism could be an alternative.

Results concerning the increase in viscosity and effect on the viscoelastic properties of the fluid will be presented together with initial jet dispensing tests. Issues with the flow in contractions related to the increased amount of oxide will be discussed.

BACKGROUND

The contact or non-contact dispensing of functional materials is common in many fields, such as the production of electronics, or the the aeronautical and automotive industries. Commonly used methodologies for printing contact dispensing, such as capillary needle dispensing, and non-contact dispensing, such as piezo-driven inkjet printing[3], piezo-based jet printing[4], electrohydrodynamic printing[5] or laser-induced forward transfer[6]. Materials that are of interest for these deposition technologies include, structural and conductive adhesives, solder pastes, structural underfills, and sealing materials.

An area of increased interest is the deposition of conductive interconnect lines for soft, stretchable devices in the area of physiological monitoring. Characteristics of high electrical conductivity, high strain tolerance and resistance to fatigue are vital for electronic circuits of on-skin wearable systems. Gallium-based liquid metals offer a unique combination of these characteristics making them excellent alternatives to conventional conductive stretchable inks. In order to obtain a better wearing experience, it is advantageous to fabricate devices using soft elastomeric materials. However, effective automation solutions for the production of high-resolution digitally patterned circuits for soft and stretchable devices remain a challenge. Previously presented manufacturing strategies involve adopting a needle dispensing technique for the precise patterning of liquid metal conductors. An alternative to contact dispensing is to utilise a non-contact printing methodology where the formation of deposits on a substrate are formed through the rapid introduction of a volumetric change that accelerates fluid through a nozzle and the break-off of the fluid and subsequent formation of a droplet is imposed by the momentum of the fluid.

The combination of low dynamic viscosity, high surface tension and the rapid formation of an oxide layer make liquid metals a challenging material to work with. This work studies the alternative of affecting the rheology of the liquid metal by introducing oxide into the fluid through vigorous mixing in order to facilitate material handling while non-contact printing.

METHODS

Preparation of LMA sample

The liquid metal alloy used in the current study was the Galinstan (Geratherm, Germany) alloy which consists of approximately 68% gallium, 22% indium, and 10% tin, with smaller amounts of Bi and/or Sb. The modification of the viscosity of the liquid metal alloy was achieved through the vigorous mixing of the fluid with a Dremel 4300 Rotary Tool with an abrasive wheel brush for a specific time in order to introduce increasing amounts of oxide to the fluid, see Figure 1. 30 g of Galinstan was weighed into a 50 ml glass beaker. The beaker was placed so that the abrasive wheel brush was partially immersed in the fluid. During mixing, the beaker was slowly stirred and at the same time, the brush was dipped repeatedly to ensure that the entire volume of fluid was processed. The mixing rate used for the introduction of oxide as $\Omega = 5000$ rpm. Four mixing times were used, namely 45 s, 2 min, 5 min and 8 min.

Rheological characterisation

The rheology of the resulting LMA rheology was studied using standard measurement modes in order to probe dependency on shear, long-term stability and recovery from imposed shear. The measurements were performed on a Malvern Kinexus Pro (Erik Netzsch GmbH, Selb, Germany).

A one-directional *shear sweep* was performed to study the dependency on shear. A plate-plate configuration was used with smooth, stainless steel plates with a gap of 1 mm. The measurements were performed at a temperature of $T = 29$ °C. The measurement is initiated with a 60 second interval of low shear at $\dot{\gamma} = 0.1$ s^{-1}. Thereafter, a shear sweep is performed from $\dot{\gamma} = 0.1 - 300$ s^{-1}.

When manipulating a fluid for dispensing applications, the recovery time for a fluid, when it rebuilds an inner structure that in turn affects the viscosity, is important. This sequence is referred to as *3ITT*. In order to characterise this a shear step profile is studied. In this sequence, a preshear period is initiated first, with a shear rate $\dot{\gamma} = 0.1$ s^{-1} for 60 s. A three-stage shear process follows, starting at a low shear of $\dot{\gamma} = 0.1$ s^{-1} for 30 s, followed by a high shear stage of $\dot{\gamma} = 100$ s^{-1} for 3 s, and finally a low shear period of $\dot{\gamma} = 0.1$ s^{-1} for 120 s. The gap size for this test was $h = 1$ mm. The measurements were performed at a temperature of $T = 29$ °C.

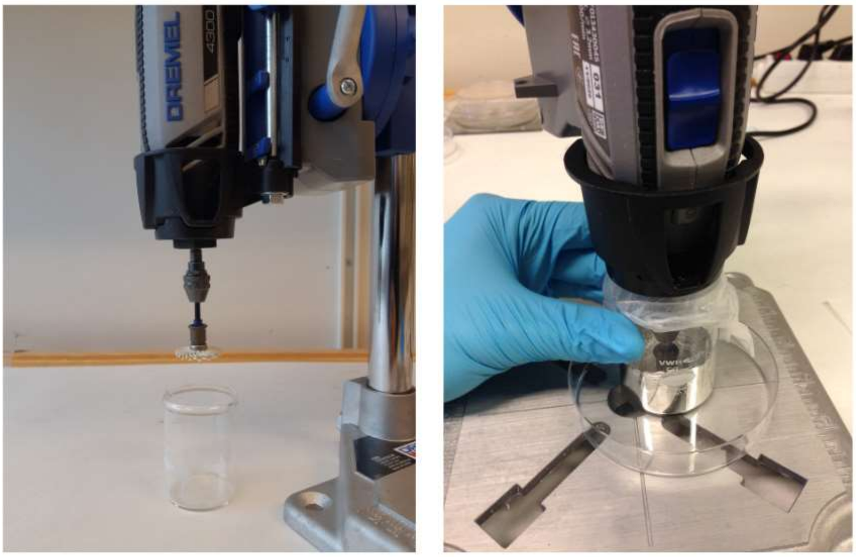

Figure 1: Photographs of the mixing setup

In order to study the long-term behaviour of the fluid in a sort of accelerated life length test, the fluid is exposed to a high shear rate for an extended time. This test is referred to as a Constant Shear Test (*CST*). In this constant shear sequence, a preshear is introduced at $\dot{\gamma} = 0.1$ s^{-1} for 60 s. Thereafter, a high shear of $\dot{\gamma} = 100$ s^{-1} is imposed for 120 s. The gap size for this test was $h = 1$ mm. The measurements were performed at a temperature of $T = 29$ °C.

A non-contact dispensing tool was used to test the printing quality of the manufactured LMA fluid samples. A MY700 Jetprinter (Mycronic AB, Täby, Sweden) was used together with an Advanjet HV-2000 Jet (Graco, Minneapolis, MN, USA). A nozzle with a diameter of $d = 150$ μm was used together with a tube pressure of $p_{\text{tube}} = 100$ Pa for the fluid reservoir. The actuation pulse had a pressure $p_{\text{pulse}} = 210$ Pa for $t_{\text{pulse}} = 3$ ms.

RESULTS AND DISCUSSION

The results from the rheological and dispensing tests are presented below.

Shear sweep

The results of the one-directional shear sweep study are represented in Figure 2. The data shows a clear increase in viscosity with mixing time, i.e., the amount of introduced oxide. For comparison, a standard SAC305 Type 5 solder paste (shown in green) is included. It is observed that the shear-thinning behaviour is stronger in the LMA samples than in the solder paste.

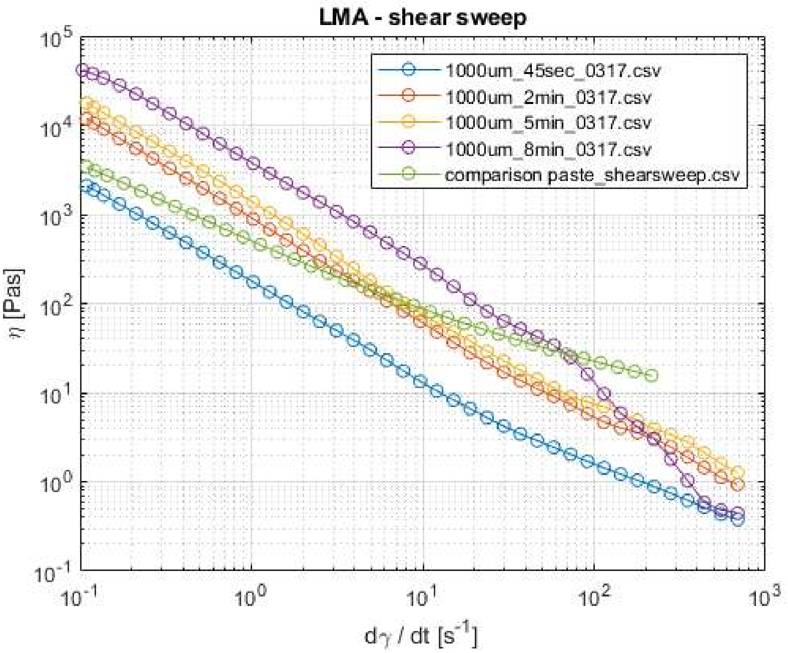

Figure 2: Viscosity of modified LMA samples at for a shear sweep for $\dot{\gamma} = 0.1 - 300$ s^{-1}.

3ITT

The recovery behaviour of the LMA samples as studied by the step shear sequence is shown in Figure 3. The trend of increasing viscosity with increased oxide content is also observed here, but little difference in the speed of the recovery is seen between the various samples. There is a slight difference in the level of the viscosity when the sample has recovered from the high shear stage in that for samples with higher levels of oxide content, the recovered viscosity is lower compared to the viscosity before the high shear stage. The recovery time is very fast when compared the comparison paste.

Constant shear behaviour

In Figure 4, the behaviour of the LMA samples during an extended high-shear sequence is presented. The smooth, relatively constant behaviour of the comparison paste is not observed for the LMA samples. Instead, an increasingly erratic behaviour is noticed for the samples with increasing levels of oxide. This behaviour is also mirrored in the normal force, N. The observed jumps in viscosity for the samples during the constant shear sequence indicate that aggregation of oxide is occurring.

Dispensing behaviour

A preliminary non-contact jetting test was performed and the results are presented in Figure 5 for the sample mixed for t = 5min. The six horizontal rows were all jetted using identical jetting parameters as described in the Methods section. The jetting pattern is a simple interconnect line with a length of 5 cm. The jetting results are promising in that the line is straight, collected and does not exhibit any spraying or swelling. The line resistance was measured and was measured to bef $R = 0.4\ \Omega$. A point of concern is

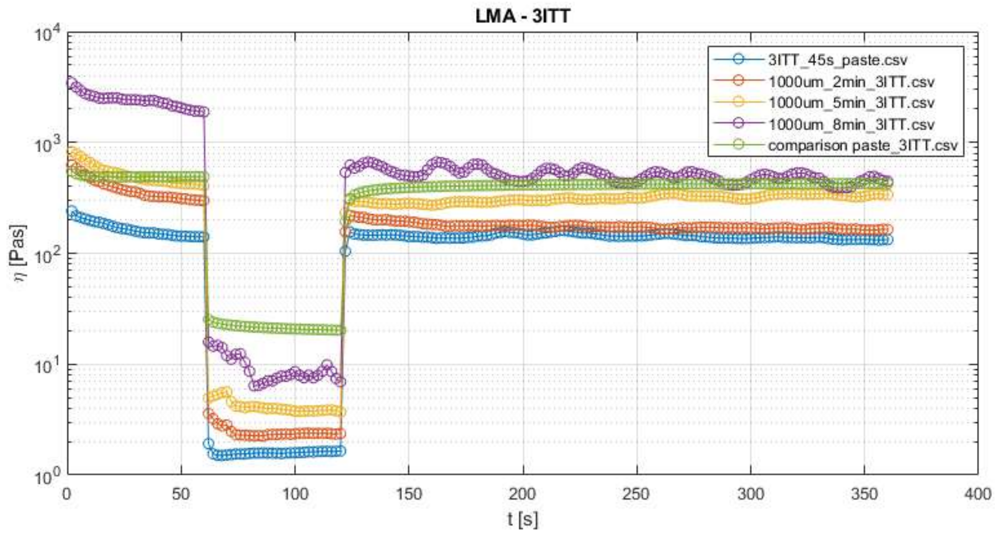

Figure 3: Viscosity of modified LMA samples and a comparison paste during a step shear profile going from low, $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$, to high, $\dot{\gamma} = 100\ \mathrm{s}^{-1}$, to low, $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$, shear.

the gradual decrease in the width of the interconnect line that is observed over this small jetting pattern. This decrease could indicate that the oxide content is being filtered out in the nozzle and actually creating a filter in the jetting device.

SUMMARY

In order to facilitate material handling and dispensing behaviour during non-contact jetting of liquid metals, a procedure to affect the rheology of the fluid using vigorous mixing to introduce varying amounts of oxide into the fluid was studied. A characteristic shear-thinning behaviour was achieved for the four samples that were prepared. The liquid metal samples all exhibited a very rapid recovery after having been exposed to a period of high shear which should be advantageous when trying to maintain a constant behaviour of the fluid during printing in spite of periods of rest while for example translating the printing head across the substrate. An extended constant shear test showed that the material has a varying viscosity that may be due to the building of large-scale oxide aggregates.

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REFERENCES

1. Cook, A. et al., Shear-Driven Direct-Write Printing of Room-Temperature Gallium-Based Liquid Metal Alloys. *Adv. Eng. Mater.*, **21**, 1900400, 2019

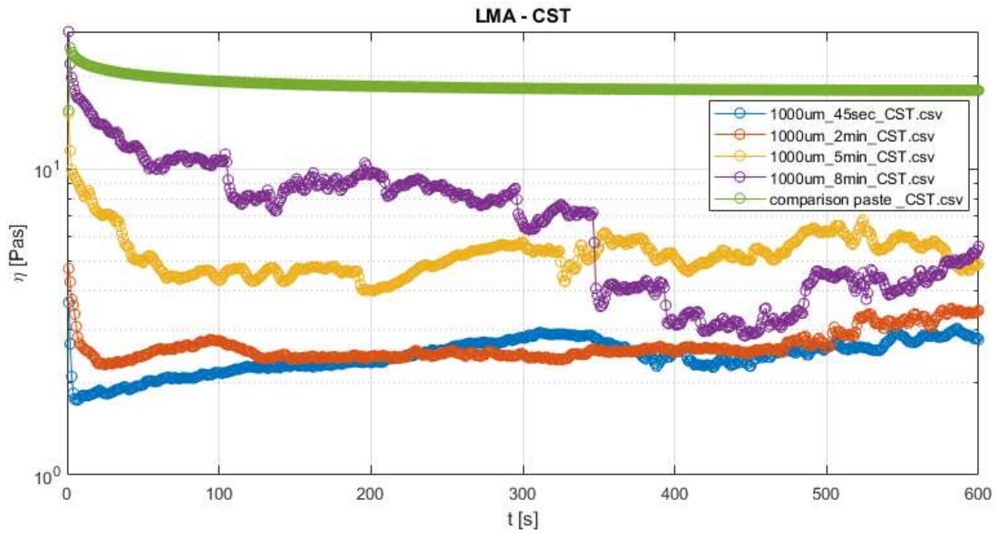

Figure 4: Viscosity of modified LMA samples at constant shear $\dot{\gamma} = 100\ \mathrm{s}^{-1}$ for 600 s.

2. J. Maslik et al., Soft, Stretchable and Wireless Sensor Patch with Digitally Printed Liquid Metal Alloy Interconnects, *2022 IMAPS Nordic Conference on Microelectronics Packaging (NordPac), Gothenburg, Sweden*, 2022, 1-6.

3. Du, X., Wankhede, S. P., Prasad, S., Shehri, A., Morse, J., Lakal, N. (2022). A review of inkjet printing technology for personalized-healthcare wearable devices. *Journal of Materials Chemistry. C, Materials for Optical and Electronic Devices*, **1**, 1491–14115. https://doi.org/10.1039/d2tc02511f

4. Mårtensson, G. E., Göhl, J., Mark, A. (2021). Simulation of jet printing of solder paste for surface mounted technology. *Soldering & Surface Mount Technology*, **33**, 266–273. https://doi.org/10.1108/SSMT-10-2020-0048

5. Cong, C., Li, X., Xiao, W., Li, J., Jin, M., Kim, S. H., Zhang, P. (2022). Electrohydrodynamic printing for demanding devices: A review of processing and applications. *Nanotechnology Reviews (Berlin)*, **11**, 3305–3334. https://doi.org/10.1515/ntrev-2022-0498

6. Serra, P., Piqué, A. (2019). Laser-Induced Forward Transfer: Fundamentals and Applications. *Advanced Materials Technologies*, **4**, 1800099–n/a. https://doi.org/10.1002/admt.201800099

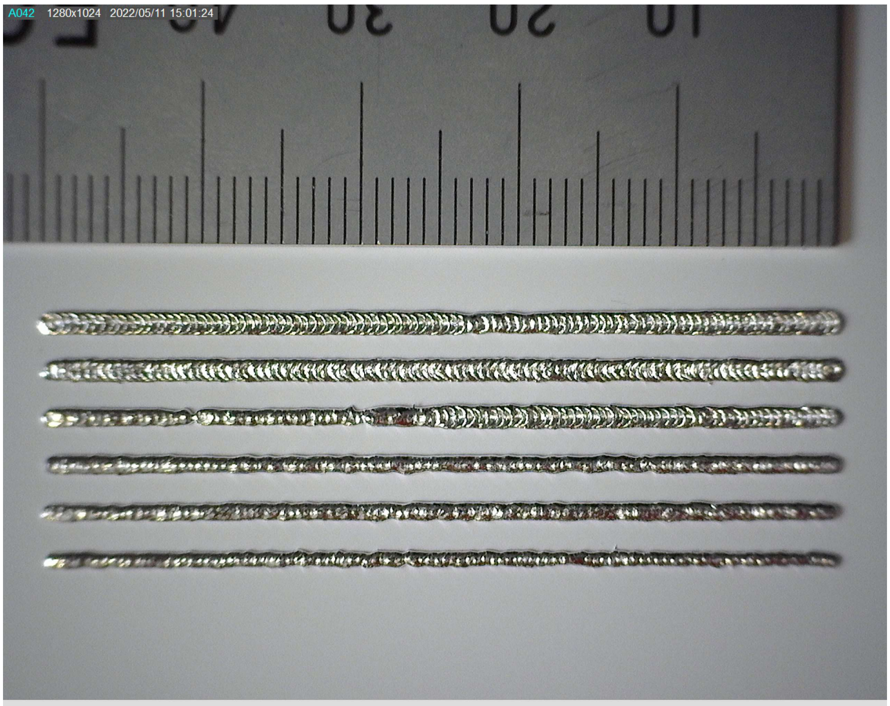

Figure 5: Example of non-contact jetting of the modified LMA sample mixed for $t = 5$ min.