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PAPER

Millifluidic production of metallic microparticles

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We use infrared thermography to monitor the cooling kinetics of a millifluidic diphasic flow comprising a fusible alloy and silicone oil; the flow is generated at high temperature and then reaches a cooler environment. Above the solidification point of the alloy, the flow pattern is analogous to that of immiscible fluids with a transition from drops to jets depending on the flow conditions. Below the solidification temperature of the alloy, the flow may become unstable and clog depending on the amount of metal drops present in the diphasic flow. At low concentration of drops in the flow, the production of solidified monodisperse particles becomes continuous and we identify some parameters that permit us to tune their geometry, either spheres, ellipsoids, or rods.

1 Introduction

Microfluidics has proven to be extremely useful for the synthesis of tailored-particles in the $10-100 \ \mu m$ size range.¹⁻³ The particles are not only monodisperse by design but they may also have non-conventional and sophisticated shapes. The main synthesis routes include (photo-)polymerization and sol–gel chemistry, and often take advantage of spontaneous formation of drops in multiphasic flows of immiscible fluids⁴ to generate delicate structures such as polymersomes, multiple emulsions, janus particles, *etc.* Going toward new materials such as metallic structures that expand the range of possible applications requires the setup and study of dedicated synthesis routes.

Here, we investigate the millifluidic genesis of submillimetric solid particles made of metal. Our primary goal concerns the fabrication of inclusions for sonic materials working in the ultrasound regime. The inclusions must be quite monodisperse, in the size range of hundreds of micrometers, and with a high density in order to confer absorption gaps to a matrix, with a narrow bandwidth and at a wavelength mainly designed by the size of the inclusions.⁵

A millifluidic device permits us to set up a standard axial coflow where the inner fluid is a metallic alloy fusible at low temperature (≈ 50 °C). The outer fluid is a silicone oil which is meant to be polymerized in a subsequent stage, not described here. Instead, we focus on the main technological bottleneck we overcame: the management of the cooling procedure until the

^aUniv. Bordeaux, LOF, UMR 5258, F-33600 Pessac, France. E-mail: jacques.leng-exterieur@eu.rhodia.com ^bCNRS, LOF, UMR 5258, F-33600 Pessac, France

^cRHODIA, LOF, UMR 5258, F-33600 Pessac, France ^dCNRS, CRPP, UPR 8641, F-33600 Pessac, France ^eUniv. Bordeaux, LOMA, UMR 5798, F-33400 Talence, France ^fCNRS, LOMA, UMR 5798, F-33400 Talence, France complete solidification of a metal in order to collect *solid particles* with a well-defined geometry at the outlet of the flow device.

We demonstrate that above the solidification temperature of the alloy, the flow resembles standard flows of immiscible fluids: depending on the flow conditions, we obtain a transition between drops and jets. Below the solidification temperature of the alloy, the flow often becomes unstable with frequent clogging. Infrared thermography permits us to assess the occurrence of the phase transition (solidification) and we correlate it qualitatively to the flow instability. Eventually, a coupling between flow diagram and thermal control permits us to propose a robust route for the fabrication of solid metallic particles with varying shapes: spheres, ellipsoids, rods, and tears of metal, whose selection originates from an interplay between flow conditions, cooling, and surface oxidation. While spherical metallic particles in the same size range have already been produced using inkjet printing,⁶ we show below that once the cooling procedure is mastered, several geometries of particles can be manufactured on demand and their size is mainly controlled by that of the flow device. Besides, the micro- or millifluidic approach may offer more versatility regarding multiple encapsulation.

2 Infrared or optical imaging of the flow

The flow setup is realized using commercial small-size tubings and junctions, is *pressure-controlled*, and is held vertically. The injection stage is controlled at a given temperature T_i , whereas the flow stage in which the axial co-flow is generated can be set at another controlled temperature T_p . In this so-called isoperibolic configuration (*i.e.*, near isothermal), the temperature scene is monitored using a high-resolution sensitive infrared camera⁷ or with a fast optical camera in order to better monitor the flow patterns.

2.1 Millifluidic flow setup

The flow setup consists of two stages, injection and flow, that can be independently controlled at different temperatures, T_i and T_p respectively, see Fig. 1.

The injection stage consists of two storage cartridges (200 mL from Nordson EFD) which contain the oil and the metal, and tubing of a large section (1/8") in order to minimize the pressure drop between the cartridges and the injection nozzle. The latter is made of a home-made aluminum T-junction which permits us to convert the 1/8" tubing for the alloy into a 1/32" PEEK tubing, to nest it inside a 1/16" tubing which becomes the flow stage where we generate a sheath-flow with the metal inside and the oil outside. Every single part of this stage is wrapped with a flexible silicone heater from Minco connected to a temperature-probe (PT100 from Minco) and a temperature controller (CT325 from Minco), which altogether permit us to choose and regulate a temperature within 0.5 °C. Our current working temperature was $T_i = 80$ °C.

The flow stage is the place where the coflow takes place, and consists of a 1/16" PFE tubing (we used an inner diameter of $2r_i = 508 \,\mu\text{m}$ for all studies except for IR thermography where we chose $2r_i = 750 \,\mu\text{m}$ for a better visualization: thermal conductivity of PFE $k_t = 0.25 \,\text{W} \,\text{m}^{-1} \,\text{K}^{-1}$) inserted in a 1 mm deep groove carved in a brass plate (10 cm long, 3 mm thick); the metal plate is temperature-controlled with a flat silicone heater (plus temperature probe and controller, Minco) glued on its backside which ensures a very constant and homogeneous temperature T_p on the outer surface of the tubing.

2.2 Chemicals

The silicone oil (PDMS) was purchased either from Sigma-Aldrich ($\eta_o = 50$ and 500 mPa s at 25 °C) or from Dow Corning ($\eta_o \approx 4000$ mPa s at 25 °C). The density is $\rho_o = 920$ kg m⁻³, the specific heat $C_p = 1370$ J kg⁻¹ K⁻¹, and the thermal conductivity $k_o = 0.1$ W m⁻¹ K⁻¹.



Fig. 1 (a) Schematic millifluidic setup used for the controlled genesis of metallic drops. The liquids are kept and injected at high temperature, typically 80 °C, and the temperature of the flow stage is controlled by inserting the tubing where the co-flow takes place inside the groove of a metal plate (kept at T_p). (b) Infrared imaging of the segmented co-flow. (c–e) Optical imaging with a fast camera of the three flow patterns obtained depending on the flow conditions: drops, plugs, and jets.

The metal is a fusible eutectic alloy which undergoes liquefaction at ≈ 47 °C, supplied by Indium Corp. (Indalloy F117, contains 44.7% Bi, 22.6% Pb, 19.1% In, 8.3% Sn, 5.3% Cd). Its density is $\rho_m = 9160 \text{ kg m}^{-3}$, specific heat $C_p = 197 \text{ J kg}^{-1} \text{ K}^{-1}$ in the liquid state, and we assume its thermal conductivity to be similar to that of bismuth $k_m \approx 8 \text{ W m}^{-1} \text{ K}^{-1}$. The viscosity of the alloy has been measured in a home-made capillary viscosimeter which yields η_m that diminishes linearly with temperature from 10 to 2 mPa s when *T* varies in the range 50–80 °C.

2.3 Infrared and fast optical imaging

We monitor the flow in the tubing with either an infrared (IR) camera or a fast camera, but not simultaneously.

The IR camera (Cedip Jade MWIR J550, edevis GmbH) works in the near-IR range ($\lambda \approx 2-5.6 \,\mu\text{m}$) and is equipped with a 25 mm lens which yields a pixel resolution of about 200 µm when imaging the 10 cm tubing embedded in the brass plate; its acquisition frequency was set to 50 Hz. We used two calibration procedures which permit us to convert the digital level provided by the camera into either a temperature or a heat flux. Temperature calibration-which permits us to account for the specific emissivities of the various materials we used—is done as follows: the tubing was fully filled either with oil or with metal and the temperature of the metal plate in which the tubing was held was then increased step by step; the corresponding digital level delivered by the IR camera was then recorded. It thus provided two temperature calibration curves for the two systems (oil + tubing) and (metal + tubing). In the dilute regime of diphasic flows of the metal in oil we studied next (few drops flowing in oil), only the (oil + tubing) calibration curve was used to convert the digital level into temperature. This approach yields an indetermination of the metal temperature while that of oil remains adequate. We also developed a proper code to extract the two temperature fields which shall be used in a future work for a refined analysis.

The heat flux calibration consists of inserting a tin wire inside the tubing to inject a known electrical power which produces heat *via* the Joule effect; the digital level given by the camera is then converted into heat flux.

We are aware that IR-based thermography must be performed with care due to specific emissivities of the bodies under study along with, when relevant, some absorption of the IR radiation by the bodies. For instance, PFE is semi-transparent in the relevant range of IR (transmits $\approx 60\%$ per mm) while silicone is nearly transparent (transmits $\approx 90\%$ per mm). Therefore, when imaging a diphasic flow in a tubing, we argue that the temperature we measure represents a mean temperature averaged across the diameter of the tubing, including the thickness of the tubing itself.

The fast camera (Phantom V5, Vision Research) is equipped with a 50 mm lens which yields a pixel resolution of about 20 μ m and a typical frame rate of 1000 Hz in the conditions we were working in. Images are then processed in order to extract the size of the drops, their distance, velocity, *etc*.

3 Results

The temperature control of the flow stage permits us to ensure flow conditions in which the alloy remains liquid. It permits us to study an all-liquid system for which we expect to recover the common drop-to-jet⁴ transition depending on the flow conditions, which we indeed demonstrate by producing the flow diagrams for several silicone oils. We then turn to the cooling kinetics, as probed by IR imaging, which turns out to be especially highlighting. We understand why the flow often becomes unstable: the drops that undergo solidification alter so strongly the local flow that they interact and clog. This is obvious from the thermal scene which permits not only the characterization of the cooling kinetics of the mixture of oil-metal, but also evidences the phase transition upon cooling, and especially its impact on the local flux of the metal. Eventually, we identify the conditions in which we can produce metallic objects that are already solidified *at the outlet* of the flow device.

3.1 Flow diagrams

The flow diagrams are plotted in Fig. 2 for several conditions of oil viscosity and flow stage temperature *above the solidification* point of the alloy. Pressures are given relative to the atmospheric pressure. In all cases, we observed three flow patterns: drops (Fig. 1c), plugs (Fig. 1d), and oscillating jets (Fig. 1e). As the flow is well resolved by the fast optical camera, we discriminate drops and plugs on a geometrical basis, for example plugs are segmented flows where the spatial extent of the dispersed phase is longer than the diameter of the capillary. The flow diagrams of Fig. 2 encode this automatically processed geometrical criterion.

We recover a transition between drops, plugs, and jets, the latter being always oscillating. Both the temperature and the viscosity of the continuous phase have a significant impact on the transitions between the different flow patterns; for instance, increasing the temperature of the flow stage from 55 to 80 °C slightly enlarges the domain of drops and significantly shrinks the domain of plugs, see Fig. 2a and b. Increasing the oil viscosity also impacts the location of the domain boundaries, making the drop zone fairly fine in this range of pressures.

The quantitative analysis of these diagrams is not within the scope of the present paper; they look fairly similar to the ones produced at a controlled flow rate with however no re-entrant drop-to-jet transition at high metal pressure.⁴ It might be due to the fact that flow is pressure-controlled⁸ and or simply because of the limited range of pressure we explored here (P < 5 bar), or also because of the specific properties of the fluids we used. Indeed, the

metal–liquid interface is known to have an especially high surface tension ($\approx 0.3-1$ N m⁻¹) which makes drops more favorable than jets. It might be the reason why the jets we observe at high oil pressure are always oscillating, *i.e.* never stable (Fig. 1e).

3.2 IR observations

We now question the impact on the flow patterns of the cooling kinetics below the solidification of the metal. With our setup, we can tune precisely the temperature of the flow stage and, when trying to reproduce the diagrams of Fig. 2, we very often observe a massive jamming of the metal drops that of clog downstream, especially below some critical temperature and IR imaging permits us to evidence the occurrence of the metal solidification. We focus first on the cooling kinetics in the high-temperature range of the flow stage ($T_p > 50$ °C) when the amount of metal in the flow is increased and we then turn to the cooling kinetics against temperature ($30 < T_p < 50$ °C) at a constant amount of metal.

3.2.1 Cooling kinetics. The imaging of the thermal scene permits us to extract the temperature profile during the cooling kinetics of the fluids injected at high temperature in a flow stage kept at lower temperature. As we film the scene, we extract the temperature profiles against space and time and reconstruct a spatio-temporal diagram such as in Fig. 3, top. The latter clearly shows the averaged cooling effect along the spatial direction, but also evidences the presence of flowing droplets. The apparent difference of the temperature of drops and oil actually comes here from the simplified calibration procedure we used (only the oil temperature is believed to be accurate) but it is clear that even though the two liquids are injected at the same temperature, they can and do evolve differently in space.

The bottom part of Fig. 3 shows both the instantaneous temperature profile (black line) and the same data averaged over time (red line) for several flow conditions. The local oscillations of the temperature profile permit us to evidence and locate the drops of metal from which we may obtain their spatial periodicity and local velocity; these oscillations are smeared out by time averaging. The three curves displayed in the figure are given for an increasing amount of metal in the flow, obtained by increasing the pressure of metal $P_{\rm m}$ while keeping the pressure



Fig. 2 Flow diagrams of the silicone oil/liquid alloy pressure-controlled co-flow showing the flow pattern as a function of the oil and metal pressures (P_o and P_m respectively). Different symbols are for the drops (red), the plugs (gray), and the jets (white) whereas the black dots show the absence of metal flow; see Fig. 1(c)–(e). Conditions are: (a) $\eta_o = 290$ mPa s, $T_p = 55$ °C, (b) $\eta_o = 200$ mPa s, $T_p = 80$ °C, (c) $\eta_o = 1400$ mPa s, $T_p = 80$ °C.



Fig. 3 IR imaging of the cooling kinetics. Top: temperature cartography giving the temperature profiles as a function and space and time for one given set of flow conditions: each horizontal line of the cartography corresponds to a temperature profile and the map also evidences the drops and their trajectories. Bottom: instantaneous temperature profile (black line) and temperature profile averaged over time (red line) for several flow conditions (from top to bottom: pure oil flow and progressive addition of metal with $P_o = 0.5$ bar and $P_m = 0.14$, 0.26, 0.38 bar from top to bottom; corresponding volume fraction of drops: $\phi = 0$, 0.3, 0.52). Inset: thermalization length against volume fraction of metal for several temperatures of the flow stage (red 35 °C, blue 40 °C, black 50 °C).

of oil $P_{\rm o}$ constant; it corresponds to a horizontal line of the flow diagram of Fig. 2b. We obtain the counter-intuitive result that the thermalization becomes more and more effective as the amount of metal is increased, which is not expected for a fluid that gets more capacitive (increasing the averaged $\rho C_{\rm p}$) and flows faster.

The averaged *T*-profile is well described by an exponential drop: $T(x) = T_p + \Delta T_0 \exp(-x/l_T)$ where *x* is the spatial direction downstream, and ΔT_0 and l_T are fitting parameters. The fitting (see Fig. 4a) is quite convincing and we obtain that $\Delta T_0 \approx T_i - T_p$ and we measure l_T , the typical distance needed for the liquid to cool down to T_p . The precise modeling of the cooling process is not in the scope of the present paper and we have no model yet to explain why a single exponential is a reasonable, first order description of the cooling kinetics of the diphasic flow.

We nevertheless extract the thermalization length $l_{\rm T}$ as a function of the flow conditions which is shown in the inset of Fig. 3, bottom, as a function of the volume fraction ϕ of the metal in the flow. The latter is calculated based on the droplets' spatial periodicity $d_{\rm D}$ (distance between centers of mass) extracted from IR-image analysis and their approximated diameter is assumed to be that of the tubing of inner diameter $2r_i$: $\phi = 4r_i/3d_{\rm D}$. We obtain that $l_{\rm T}$ decreases with ϕ by a factor of about two when ϕ reaches 0.5, regardless of the actual flow stage temperature $T_{\rm p}$. To put it simply, when producing the flow diagrams of Fig. 2 at a given temperature $T_{\rm p}$, the more metal in the flow the quicker the fluid reaches $T_{\rm p}$.



Fig. 4 (a) Time-averaged temperature profiles measured by IR thermography when the temperature $T_{\rm p}$ of the flow stage is diminished progressively (color-coded) below the solidification point of the alloy, while keeping the flow conditions constant. The two solid black lines illustrate the phenomenal exponential fitting. (b) Difference between temperature profiles and exponential relaxation. (c) Temperature at which heat starts to be released against the cooling rate of the drops.

3.2.2 Evidence of metal solidification. We decreased systematically the temperature of the flow stage while keeping the pressures $P_{\rm o}$ and $P_{\rm m}$ of oil and metal constant. $T_{\rm p}$ is varied from 50 to 30 °C and we display in the top part of Fig. 4a the corresponding *time-averaged profiles* color-coded with $T_{\rm p}$.

We observe that the temperature decreases in space to reach roughly exponentially the temperature of the flow stage at T_p down to a critical temperature ($T_p \approx 35$ °C) where the temperature profile becomes *non-monotonous*: below this temperature, a temperature bump develops in the late stage of the cooling kinetics. The fluid is therefore heated by an internal source of heat, which has to be *latent heat* released during the solidification of the metal.

This local increase of temperature is better seen in the bottom part of Fig. 4b where we compare the actual profiles to an exponential fitting (shown as a solid line for the two extreme profiles) performed on the first stage of the cooling (x < 0.04 m). The temperature difference ΔT between a simple exponential cooling and the actual temperature clearly shows up with a temperature that starts to raise again when the liquid reaches a temperature of ~35 °C, which *does not* correspond to the liquidus temperature (T = 47 °C), and with a maximum increase up to 4 °C. We also notice that the thermalization length l_T obtained from the fit does not depend on the flow stage temperature (within 10%, data not shown).

The phase transition itself has a kinetics which may be complex. Inset (c) of Fig. 4 shows the temperature at which the heat starts to be released depending on the temperature quench. We see that the phase transition does not initiate at liquidus, but rather around 35 °C over a range that spans about 5 °C. More precisely, we plot this temperature as a function of the temperature quench (cooling rate) the drops undergo defined by $\dot{T} = (v/l_T)(T_p - T_i)$ where v $(\approx 15 \text{ mm s}^{-1})$ is the velocity of drops obtained by image analysis and $l_{\rm T}$ (≈ 15 mm) the thermalization length measured by the exponential fit of the temperature profile. The order of magnitude of the cooling rate is fairly high ($\approx 50 \text{ °C s}^{-1}$) and the deeper the temperature quench, the lower the temperature at which the phase transition starts. It is a conventional result illustrating the undercooling of the alloy: nucleation may start as soon as the temperature is diminished below liquidus, although supercooling occurs and requires the nucleation of a germ. The induction time is then related to the volume of the drop; the smaller the volume the less likely is nucleation to occur, and that is why microfluidics offers an interesting way to analyze the type of nucleation kinetics (homogeneous versus heterogeneous) via the control of the volume of the drops.^{9,10} The duration of the transition is then limited by the rate at which latent heat is extracted from the drop.

This experiment could be turned into microcalorimetry¹¹ for the measurement of the latent heat of solidification. It requires first to calibrate the camera in flux which permits us to convert the signal collected into a heat flux Φ_W (in watts, integrated over the emitting surface by calibration); actually, the heat flux looks quite similar to the ΔT curve of Fig. 4 (bottom part). Then, upon integration of the total heat flux released during the solidification kinetics, we can estimate the latent heat. Instead of time, we use the positions x_1 and x_2 of the beginning and end of phase transition in the tubing and, thanks to the time–space equivalence ($t \equiv x/v$), we extract directly the latent heat: $L = (mv)^{-1} \int_{x_1}^{x_2} \Phi_W(x) dx$ where *m* is the mass responsible for the heat released.¹¹ This mass is calculated using the volume fraction ϕ of metal in the flow in between x_1 and x_2 : $m = \pi r_i^2(x_2 - x_1)\rho_m\phi$ with ρ_m the density of metal. Both *v* and ϕ were

have to be constant (if not, the integration must account for it). We performed this analysis on the last temperature profile of Fig. 4 (converted into heat flux). We first notice that the heat bump is well-fitted by a sum of two Gaussian curves, which is probably a signature of the cooling kinetics of the alloy; it is also convenient to make up the few missing points of our partial heat–flux profile, and to define as x_1 and x_2 the beginning and end of the heat release respectively. For this set of data $\rho_m \phi$ is roughly constant and we obtain $L \approx 26 \text{ kJ kg}^{-1}$, which is in reasonable agreement with measurements we performed on the same metal with conventional calorimetry $L = 20 \pm 0.5 \text{ kJ kg}^{-1}$.

obtained directly from image analysis and, in principle, do not

Owing all the steps required to calibrate the IR camera and the uncertainties regarding our analysis, the actual results seem interesting for continuous calorimetry as they require little time and material, but deserve more accurate and systematic studies which we defer to a future work. Most importantly, the reasonable agreement we find assesses the occurrence of the phase transition which initiates around $T \approx 35$ °C but which also depends upon the cooling rate.

3.2.3 Cooling kinetics. We now discuss briefly the parameters affecting the thermalization kinetics and address the main differences between monophasic and diphasic flows, see Fig. 5.

For a monophasic flow in the range of velocities we explore here (low to moderate Reynolds numbers $Re = 10^{-3}$ to 10^{2} depending on the fluid and mean flow rate), the distribution of velocity is given by a Poiseuille flow and the thermalization depends on two parameters: Péclet and Biot numbers. The thermal Péclet number $Pe = \bar{v}r_i/\alpha_f$, where \bar{v} is the mean velocity of the flow and $\alpha_{\rm f} = k_{\rm f} / \rho C_{\rm p}$ the thermal diffusivity of the fluid, compares the temperature transport phenomena inside the liquid where longitudinal convection competes with radial conduction over the diameter $2r_i$ of the tubing. It states whether the temperature is radially homogeneous or not inside the liquid. The Biot number compares conduction inside the fluid to conduction across the tubing $Bi = k_t/k_f$ where k_t and k_f are conductivities of the tubing and of the fluid respectively. It expresses whether or not the temperature inside the fluid varies significantly in space while the fluid is being cooled from its surface. The temperature of the fluid averaged over the section of the tubing decreases nearly exponentially with a thermalization length that scales like $l_{\rm T} \sim {\rm PeBi}^n r_{\rm i}$ where n = -1 for Bi $\gg 1$ and n = 0 for Bi $\ll 1.^{12}$

Here, we keep the conductivity of the tubing constant, however, the conductivities of oil or metal are quite different; therefore, $Bi = 0.03 \ll 1$ for the metal whereas Bi = 2.5 for the oil; the tubing is an insulator for the metal but not for the oil, which permits a better homogenization of temperature inside the flow for the metal. The Péclet numbers are also different for the two fluids in the range of velocities explored here: for the oil, Pe = 20-200 and the fluid develops radial and longitudinal gradients, whereas Pe = 0.5-5 for the metal which thus remains more homogeneous (radially). Therefore, for a monophasic flow driven at the same velocity, we expect the metal to cool down homogeneously whereas the oil develops radial and longitudinal gradients over a longer spatial extent downstream.

While it may be the basis for understanding why the thermalization length decreases with the amount of metal introduced in the flow (Fig. 3, inset), the thermalization mechanisms at work for a diphasic flow are different (Fig. 5). First, this type of flow induces recirculations inside and outside the drops^{13,14} (although the nature of recirculations has still to be clarified¹⁵) which totally alter the heat transfer mechanisms and enhance it as observed numerically for liquid–liquid diphasic flows¹⁶ and experimentally and numerically for gas–liquid flows.^{17–19} However, there is not theory yet to describe it in the general case of two liquids with



Fig. 5 Sketch of the thermal exchanges in the cases of monophasic and diphasic flows. Red arrows illustrate the heat fluxes whereas other arrows schematically depict the mass flow: the important difference between the two cases is the possible homogenisation of temperature in diphasic flow due to intra- and inter-drops recirculations, along with thermal transfer between oil and metal.

arbitrary thermal properties and inter-liquid exchanges (in the gas–liquid case, the gas is considered as thermally neutral). Then, the transfer mechanisms are also affected by the presence of the two fluids, as exemplified by the wetting film which surrounds the drops and creates a thermal resistance; the latter depends on the shape of the drops. The fine understanding of these interwoven effects deserves a dedicated work.

3.2.4 Consequences of cooling on the flow. We observe that below some temperature, which we now identify by the solidification kinetics, the flow may jam: above some given volume fraction of drops, the flow becomes unsteady and the drops get more and more concentrated and eventually clog.

Several effects may contribute to this unexpected behavior. First, physical constants of the fluids change with temperature (viscosities, densities, etc.). More importantly, the flow pattern of a single drop flowing in oil is expected to be modified upon solidification of the metal droplet; indeed, the boundary conditions for the velocity and stress between the oil and the metal deeply depend on the state of the metal (liquid or solid) and alter significantly the flow of oil. As a matter of fact, we expect a low viscosity liquid-metal drop to flow slightly faster than the oil while a solid drop flows slower than the oil.^{15,16,20} Note also that the hydraulic resistance held by the drops is expected to depend strongly on the viscosity of the metal but also on the velocity of the drops.²¹ Then, jamming has been described before²² as being due to hydrodynamic interactions between drops:^{23,24} indeed, the flow pattern is modified by the presence of drops and the alteration may propagate in the far-field in confined geometries, leading to an added modification of the velocity of the drops: trains of concentrated liquid drops are observed to flow slower that dilute drops. However, if the distance between the drops becomes large (as compared to the size of the capillary), these interactions fade away and the fluctuations of the flow do not induce a flow instability.

The interplay of these effects makes it very difficult to predict the flow pattern but the consequences can be addressed: variations of the local flux of drops may make the flow unstable, and, importantly, this dynamics is somehow self-amplified when recalling that the thermalization length $l_{\rm T}$ is a strong function of the amount of metal (inset of Fig. 3, bottom): the more metal the quicker the temperature drops and the more likely hydrodynamic interferences between drops to occur. We thus empirically define the conditions in which the flow stays stable and does not clog: we require the distance between drops to be large enough (say, ten times larger than their diameter, *i.e.*, $\phi < 0.1$) in order for them not to interfere. We tested experimentally this criterion, which implicitly selects the pressure range for metal, and found it indeed allows the drops to solidify under flow before the outlet of the tubing even when the latter is at room temperature $(\approx 20 \ ^{\circ}\text{C}).$

3.3 Production of solid metallic particles

The IR study thus permits us to empirically determine the conditions in which we can *continuously* produce drops that are solidified at the outlet of the device: the distance between the drops must be large enough so that the cooling kinetics does not impede the flow. We now detail the main parameters that permit

us to tune the morphology of these metallic microparticles: the viscosity of the oil and the surface oxidation.

3.3.1 Effect of the oil viscosity. The particles we produce have a shape that is strongly altered by the viscosity of the oil we used, going from spheres to ellipsoids.

We produced microparticles using several oils of viscosity 50, 500, and \approx 4000 mPa s; these liquids were thoroughly degassed prior experiments. For the low viscosity oil, we collect spherical particles whereas for higher viscosities, the particles are elongated ellipsoids. In both cases, the image analysis on about 50 to 100 particles permits the characterization of their size distribution. Spherical drops have a Gaussian-like size distribution centered at $\bar{R} = 249 \ \mu m$ with standard deviation $\delta R = 16 \ \mu m$ (Fig. 6a), leading to a number-weighted polydispersity of less that $\sigma = \delta R/\bar{R} \approx 5\%$. Note that the drop diameter is very close to that of the tubing (508 µm nominally). Ellipsoids are characterized by their short and long axes, each having a peaked Gaussian-like distribution (Fig. 6b, $\bar{R}_{-} = 233 \ \mu m$ and $\delta R_{-} = 19 \ \mu m$, $\bar{R}_{+} = 284 \ \mu m$ and $\delta R_{+} = 20 \ \mu m$) yielding an ellipticity of $e = 0.57 \pm 0.23$ and an aspect ratio $\bar{R}_+/\bar{R}_- = 1.22 \pm$ 0.19. The volume is conserved between spheres and ellipsoids suggesting that the actual flow rate has a weak effect on the break-up mechanism during the drop formation.

The origin of the transition between spheres and ellipsoids may be found in the relative effects between surface and viscous forces, often described in terms of capillary number $Ca = \eta \times \bar{\nu}/\gamma$ where η is the viscosity of the external liquid, $\bar{\nu}$ the mean velocity, and γ the surface tension. With the typical velocity $\bar{\nu} \approx$ 210^{-2} m s⁻¹ and the surface tension $\gamma \approx 300$ mN m⁻¹, $Ca \approx$ $710^{-2}\eta$. Therefore, one expects an increase of viscosity of the oil to tune Ca from Ca \ll 1 to Ca \approx 1 ($\eta > 50$ mPa s), and the drops to be deformed by the high viscosity oils, as clear in Fig. 1c (with $\eta = 500$ mPa s).

40

a



Fig. 6 Metallic particles solidified online and produced with a low viscosity oil (top: $\eta_0 = 50$ mPa s) or with a high viscosity oil (bottom: $\eta_0 = 500$ mPa s; 2*R* is the length of each axis of the ellipsoid). The bar represents 250 μ m.

3.3.2 Effect of surface oxidation. Tears of metal are produced when a combination of high-viscosity and non-degassed silicone oil is used (Fig. 7, top). When the same oil is thoroughly degassed, we recover conventional elongated drops; when the viscosity is decreased significantly, again, drops are recovered. We attribute the formation of such a tail to the surface oxidation of the alloy, known to be quite sensitive to such a phenomenon.^{25–27} We believe that oxidation is due to gas dissolved in the oil (and indeed removed by degassing) which produces a thin shell that can totally alter the mechanical properties of the drops and prevent the surface relaxation toward near-spherical objects; preliminary X-ray photoelectron spectroscopy experiments indeed suggest the presence of a nanometer thick layer of oxide. Such an oxide is likely to have a much higher fusion point than the alloy and would therefore be solid in the range of temperature we studied here. The oxide layer develops while the drop is being formed, at a frequency that strongly depends on the flow rate (via the oil viscosity): the more slowly the drop forms, the longer is given for the oxide layer to develop at the level pinching zone and to block the shape relaxation.

3.3.3 Production of rods via double-encapsulation. The last example of metallic particles we give concerns the production of rods. The latter were produced with a double encapsulation (three-level) device where the oil-metal diphasic flow is engulfed into a flow of viscous fluorinated oil (≈ 1000 mPa s), not shown here (see ref. 28 and 29 for details on the design). The goal of this approach is to wrap the metallic objects into a layer of elastomer for the production of sonic inclusions. By doing so, we found that there is a regime where plugs can be significantly spaced, which is probably due to the high pressure at the outlet of the diphasic stage (because of the high viscosity of the fluid flowing in the ultimate flow-level); this regime does not exist when the outlet is left at atmospheric pressure. As a consequence, the plugs can cool down without blocking and rods are collected at the outlet of the flow device. We will describe in a future work the several encapsulation regimes along with the properties of the resulting sonic materials.

4 Conclusion

Millifluidics is a convenient plug-and-play tool for generating small-size calibrated particles. Thanks to IR thermography, we evidenced that a hot liquid alloy may undergo *in-line* solidification upon cooling. In most conditions at room temperature, the flow is impeded by the particles that become solid and clog. When the flow conditions are chosen in order to dilute the drops, it is possible to create metallic particles of various shapes: spheres, ellipsoids, rods, which are solid at the outlet of the device, a condition required for preserving their shape.

Several steps for producing these particles deserve further studies: the cooling kinetics of the diphasic fluid, the impact of solidification on the hydraulic resistance held by the drops, the effect of confinement on the alloy undercooling, *etc.* However, the present work shows that the production of metallic particles is totally in reach of microfluidics. There is in principle no obstacle to miniaturization and the versatility of the microfluidic tool should permit us to generate more complex and diversified composite particles with non-polymeric bodies.

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Fig. 7 Top: tears of metal produced with a highly viscous, non-degassed silicone oil. Bottom: metallic rods produced by double encapsulation.



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