APPLICATION OF ULTRASONIC ATOMIZATION IN THE THREE DIMENSIONAL PRINTING AND SPRAY PYOLYSIS

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ABSTRACT: Control of droplet size and distribution, jettability of fluid with high viscosity and surface tension, microfeeding to solid particles are important problems in the three dimensional printing. Meanwhile, spray pyrolysis technique has been used to produce film or nanoparticle synthesis. In this paper, the application of ultrasonic atomization in these new fields has been reviewed. The principle of atomization was introduced, and the current performance in comparison to conventional approaches was summarized. Overall, ultrasonic atomization could generate small droplets with a narrow distribution at a low power, liquid with high viscosity and surface tension can also be ejected under ultrasound excitation. Nozzle design should be optimized for higher efficiency.

INTRODUCTION

In recent years, three dimensional printing (3DP) has become a very competitive process in terms of cost and speed with a significantly increased sales of related equipment. Generally speaking 3DP is an up runner of the ink-jet printing technology, which was originally developed 30 years ago. Because of more materials available today as well as the wide variety of procedures, the scope of this technology grows far beyond the original idea of generating inexpensive parts from a CAD file in design iterations. Major applications of 3DP include concept modelling, rapid prototype manufacture, bone implant, tissue engineering, organ printing, visualization of architectural design, etc. Much of the bioprinting work has focused on 2D patterning for basic biological studies and is a logical antecedent to 3D printing. In the mask-less printing, drops of paste are injected on a glass substrate by electrostatic force to form electrode patterns for the micro rapid-prototyping and manufacturing of a micro-mold for casting.

The phenomenon of ultrasonic atomization was found in the late 19th century by Lord Kelvin. When a liquid film is placed on a smooth surface with vibration perpendicular to it, the liquid absorbs some of the vibration energy and a spray of tiny drops is ejected from the surface. One feature that distinguishes ultrasonic atomizing nozzles from the other pressure-based ones is their soft, low-speed fine mist spray. Ultrasonic atomization has already been used widely in industry and healthcare, such as painting, coatings in the manufacture of float glass, precision semiconductor, solar cell, fuel cell, blood collection tubes, implantable drug eluting stents and balloon/catheters, anti-microbial coatings onto food, spraying flux onto printed circuit boards, and nebulizer for the treatment of asthma.

Ultrasonic spray pyrolysis is utilized in the formation of a variety of materials, such as nanoparticle formation of aqueous silver nitrate, synthesis of zirconia particles, and fabrication of solid oxide fuel cell cathodes. An atomized spray produced from an ultrasonic nozzle is subjected to a heated substrate typically ranging from 300-500 °C.

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ATOMIZATION MECHANISM

Liquid can be atomized into a fine mist using high frequency sound vibrations. Piezoelectric transducers convert electrical energy into mechanical vibrations, which create capillary waves in the liquid when introduced into the nozzle. Capillary waves form a rectangular grid pattern in the liquid on the surface with regularly alternating crests and troughs extending in both directions. When the amplitude of the capillary waves exceeds the threshold of maintaining stability, the waves collapse and tiny drops of liquid are ejected from the surface. The wavelength of the capillary waves, λ, can be described by the Kelvin equation.

$$\lambda = \sqrt[3]{8\pi\sigma / \rho f^2} \qquad (1)$$

where ρ is the fluid density, σ is the surface tension, f is the frequency. The drop diameter is proportional to the capillary wavelength with a proportionality constant of 0.34. Since the Taylor mode (different from the Rayleigh mode in ink-jet printing) is involved in the atomization, the drop diameter is much smaller than the channel (orifice) diameter. The motion of waves on the liquid jet surface is given by the Taylor equation derived from the equations of continuity and motion with the assumptions of zero tangential stress at the air-water interface and temporal instability (Tsai et al. 1996).

$$\left(\zeta + 2\upsilon k^2\right)^2 + \frac{\sigma k^3}{\rho} - 4\upsilon^2 k^3 \sqrt{k^2 + \zeta / \upsilon} - \frac{\rho_A}{\rho} V_A^2 k^2 = 0 \qquad (2)$$

where υ is the kinematic viscosity, ζ is the growth rate. Atomization by high-velocity air occurs similar to ultrasonic atomization, Taylor-mode break-up of capillary waves in particular. In addition, uniform drops in diameter determined by the ultrasonic frequency can be obtained by adjusting the air velocity. When in resonance, the ultrasound generated liquid capillary waves are further magnified in amplitude by the air blowing around the nozzle tip. Since part of the atomization energy comes from the air, atomization occurs at a much lower ultrasonic power level impossible for ultrasonic atomization.

DROPLET EJECTION

Recent developments in inkjet printing methods have not kept pace with the evolution of printed materials from inks deposited onto porous surfaces in the form of 2D text or images to complex fluids used for the free-form fabrication of 3D multilayer devices. Viscosity is typically limited to below 40 mN·s/m^2 and surface tension to 28 mN/m. Current print-heads in the market are capable of producing 30–100 μm droplet. Printing of conductive polymers and colloidal semiconductors is particularly useful for manufacturing flexible circuits, organic light emitting diodes (OLEDs), polymer photovoltaics, and transistors. Additive manufacturing via microarray deposition (AMMD) with a bulk ceramic ultrasonic transducer at frequencies between 0.5 MHz and 3 MHz makes the use of high-viscosity materials, such as biomaterial suspensions, ceramic pastes, and non-Newtonian polymers, and fast deposition of large volumes of material possible. Unique to this new printing technique are the high frequency of operation, use of fluid cavity resonances to assist ejection, and acoustic wave focusing to generate the pressure gradient required to form and eject droplets. A small number of cycles are required to establish a sufficient steady-state pressure field for ejection within the fluid reservoir. Printing indicator (p.i.) defined as the ratio of the Reynolds number to the square root of the Weber number $p.i. = \sqrt{\mathrm{Re}/We} = \sqrt{\rho r \sigma} / \mu$ can be used to predict the jettability, which should be within a range of 1–10. Drop size was found to reduce from 50 μm to less than 5 μm. Ultrasonic actuation, resonant operation, and acoustic wave focusing combine to enable efficient deposition of materials that conventional approach are unable to print. Furthermore, multi-material structures can potentially be created by utilizing different reservoirs driven by one or more piezoelectric transducers (Meacham et al. 2010).

Microencapsulation improves oxidative stability and shelf life of material, such as fish oil. The conventional approach is freeze drying under vacuum, but there is still possibility to catalyze oxidation at low temperatures and in the absence of oxygen during the microencapsulation process. The ultrasonic nozzle showed a significantly narrower and uniform particle size distribution than the other nozzles, reduction of overspray and minimal clogging. Utilization of ultrasonic nozzles eliminates the need for emulsion preparation prior to drying. However, disadvantages were lower oil encapsulating efficiency compared to pressure nozzles and freeze dried microcapsules at the same core to wall ratio (Legako and Dunford 2010).

MICROFEEDING OF SOLID NANOPARTICLES

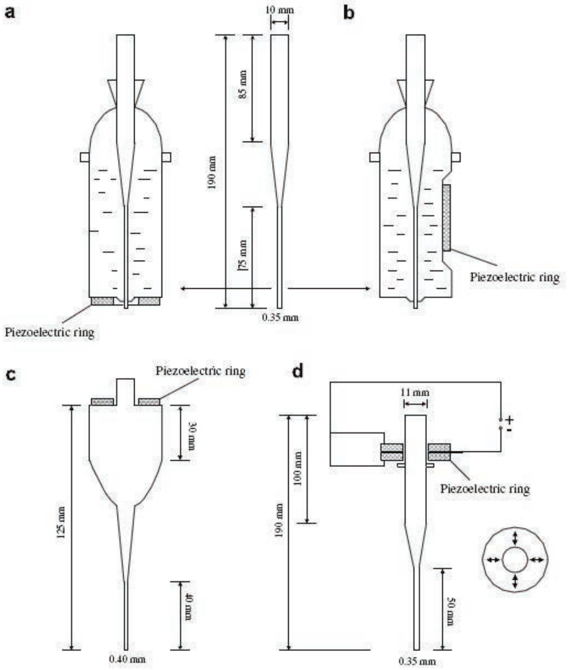

Figure 1. Nozzle designs for microfeeding.

Microfeeding of multiple powders onto a selective laser sintering platform for 3D compositional gradients, which is regarded as dry jet printing. Four designs of ultrasonic nozzle were investigated: a piezoelectric transducer ring bonded to the base of a cylindrical water-containing vessel or attached to the sidewall of the vessel or connected to the glass wall of the capillary to give nominally longitudinal vibration or connected to the glass tube but arranged to give progressive wave vibration as shown in Fig. 1. The propagation of a wave along the pipe leads to an oscillatory movement so that grains inside are pushed forward via friction. The propagation direction of flexural ultrasonic progressive waves could be changed by modulating the excitation frequency. Ultrasonic vibration has two effects on particles in the capillary tube: compaction and decrease of particle-wall friction due to transient dilation. When the gravitational force on the rod is higher than the internal cohesive force of particles in the transverse direction, the rod breaks off and falls. The water depth in the transmission vessel has a strong effect on the resonant frequency and the acoustic pressure. The relative standard deviation of powder microfeeding is about 10% and individual samples of mass down is about 50 μg (Lu et al. 2009).

SILICON ULTRASONIC NOZZLE

In comparison to conventional bulky ultrasonic nozzles, silicon-based ones have advantages of large electromechanical coupling, high sound speed, and easy mass production of any resonator profile by micro electro mechanical system (MEMS) technology. Ultrasound-modulated twin-fluid (UMTF) atomization, that uses air to assist ultrasonic atomization, has been demonstrated to produce much smaller and more uniform drops than the conventional ultrasonic atomization at the same fundamental frequency. The peak drop diameter obtained by UMTF atomization was found equal to the wavelength of the capillary waves generated by the third harmonic frequency. The silicon resonator is made of one or multiple Fourier horns in cascade (see Fig. 2), each with half-wavelength design and vibration amplitude magnification of two. A unique advantage of the multiple-horn nozzle is that the longitudinal vibration amplitude gain at the nozzle tip can be increased considerably without a reduction in tip cross-sectional area (Tsai et al. 2004). Therefore, the required electric drive power should be drastically reduced, decreasing the likelihood of transducer failure in ultrasonic atomization. Ultrasound-modulated two-fluid atomization combines ultrasonic and two-fluid atomization, and is capable of reducing the peak drop diameter to 22 μm (Tsai et al. 2006).

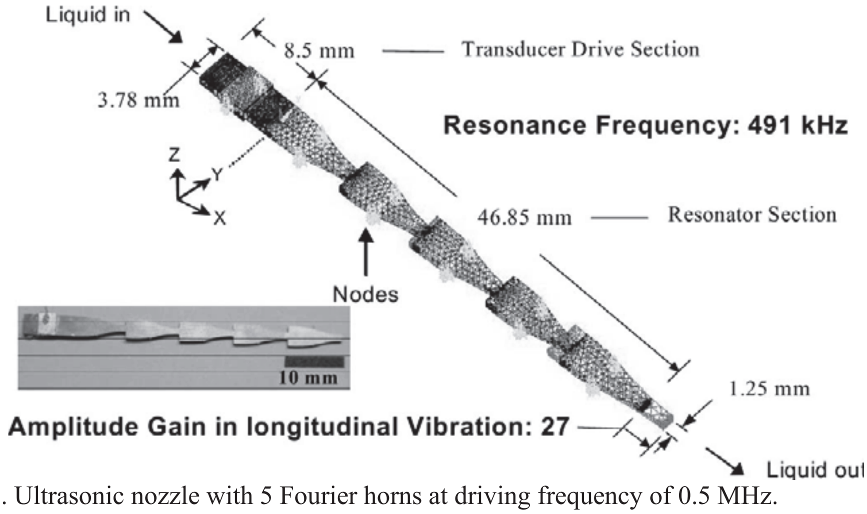

Figure 2. Ultrasonic nozzle with 5 Fourier horns at driving frequency of 0.5 MHz.

ULTRASONIC SPRAY PYOLYSIS

Ultrasonic spray pyrolysis (USP) is a new method in which a thin film is deposited by spraying a solution with an ultrasonic nozzle onto a heated surface, where the constituents react to form a desired chemical compound. In comparison to the conventional methods, the USP method provides advantages such as low equipment cost, good thickness uniformity over a large area, low temperature and low vacuum requirement in processing, and so forth. Spray pyrolysis involves four major steps: (1) generation of drops from a precursor solution, (2) drop size shrinkage due to evaporation, (3) conversion of precursor into oxides, and (4) solid particle formation. Drops are typically generated through either two-fluid atomization (liquid atomization by high velocity air) or ultrasonic atomization (without air). The PZT film manufactured by USP has strong piezoactivity, high resistivity, and good thickness uniformity (Lee et al. 2001). The mesoscopic α-Fe_2O_3 layers produced by USP consist mainly of 100 nm-sized platelets with a thickness of 5-10 nm. The mesoscopic leaflet structure has the advantage that it allows for efficient harvesting of visible light, while offering at the same time the very short distance required for the photo-generated holes to reach the electrolyte interface before recombining with conduction band electrons (Duret and Grätzel 2005).

Two-fluid atomization has the advantage of high throughput but with broad distribution of drop size. In contrast, UMTF) atomization has a higher throughput and produces a narrower drop size distribution and a smaller peak drop diameter than conventional ultrasonic atomization (without air) at the same ultrasonic frequency, resulting in greater control over particle size during spray pyrolysis. Furthermore, the drop size can be decreased by increasing the ultrasonic frequency. However, the mechanisms of spray pyrolysis are at present not fully understood. It is widely believed that the drops, when sprayed into a tubular reactor under pyrolysis conditions, serve as micro-reactors and yield one particle per drop. The drop sizes obtained by different atomization techniques have been found to significantly affect the size and morphology of the particles produced. However, the actual relationship between precursor drop size and the resulting product particle size has yet to be determined. The drop diameter calculated using the Kelvin equation multiplied by 0.34 often underestimates the drop diameter, which illustrated the invalid of the one particle per drop mechanism (Tsai et al. 2004).

SUMMARY

Ultrasonic nozzle could be used in the 3D printing to reduce the drop size and narrow its size distribution, broaden the application field to highly viscous fluid as well as to feed solid nanoparticles at soft slow speed and high controllability. Spray pyrolysis using ultrasound would further enhance the quality of the film. However, the mechanism of ultrasonic atomization is not completely known. Novel design of ultrasound nozzle, especially those in the microscale, and real-time feedback control in the process are highly desired for the technological improvement.

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