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Controlling micro ceramic patterns via multiple/sequential drop-on-demand inkjet printing of dilute colloidal suspensions

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ABSTRACT

Drop-on-demand (DOD) inkjet printing has great potential for fabricating miniature ceramic devices that are currently constructed by more complicated, time consuming, and costly procedures. In this study, micro $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFC) patterns are crafted via DOD inkjet printing. A dilute solid-solvent colloidal ink suspension composed of LSFC, a common solid oxide fuel cell (SOFC) cathode material, suspended in α-terpineol solvent, was printed with multiple, sequential inkjet passes. Critical process parameters were identified and tuned to achieve acceptable layer to layer deposition accuracy. Micro 0-D dots and micro 1-D lines with x/y dimensions $<100\,\mu m$ and z-axis dimensions $<1\,\mu m$ were demonstrated. Addition of ethyl cellulose to the ink resulted in unique 'volcano' features which may benefit miniature SOFCs with a density shift between the feature's center and ridge.

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1. Introduction

Drop-on-demand (DOD) inkjet printing is capable of producing micrometer ceramic features through precise deposition of 1–100 picoliters droplets onto a designated site [1]. By controlling ink formulation, droplet/substrate interactions, and judicious placement of the jetted droplets, DOD inkjet printing has the potential to produce tiny patterns and thin films with dense, porous, or networked microstructures. This approach can be a promising alternative to MEMS fabrication for micro ceramic devices such as micro solid oxide fuel cells (μSOFC) [2–4]. For these applications, smaller inkjet nozzles in the tens of micrometers have been employed to produce a range of features using a variety of colloidal suspensions [5–9]. However, numerous challenges remain which have prohibited their broad commercial proliferation. For instance, dilute ceramic suspensions are often employed to prevent nozzle clogging but that necessitates the use of multiple ink passes to achieve the desired feature dimensions. Further, high sample throughput is often desired, necessitating higher operating temperatures which can lead to clogged jetting nozzles. Overcoming challenges such as these is a principal motivation for this work.

Colloidal droplet deposition onto a solid surface can conceptually be described as a fluid sphere spreading and drying into a circular solid film upon impaction with the surface and evaporation of the solvent [10]. Following the initial contact, the droplet will experience a stage dominated by inertial forces that are a function of drop velocity, ink density, and drop volume. It is characterized by a time scale of microseconds as well as a rapid increase in diameter as the inertial forces are dissipated by viscous resistance as well as deformation in free surface area [11]. If the inertial forces are sufficient to exceed the cohesive forces, the droplet can disintegrate in flight and/or be lifted from the substrate on impact resulting in splash and other printing defects. In our previous study, focus was on this inertia dominated stage and the Weber number was found to be a good indicator for stable jetting. Above the Weber threshold, printing defects from splashes and satellites resulted which eventually were detrimental to the final printing quality of micro patterns [12].

Following the inertia dominated stage, the droplet will experience a capillary dominated stage during which it continues to expand in diameter as a result of surface tension forces between the substrate, ink droplet, and air. Throughout this stage, the viscous forces and the gravitational force are negligible [13]. This stage is characterized by a longer time scale of milliseconds in which the droplet will transform into an increasingly thinner

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spherical cap of ink. The capillary dominated stage of small droplets in the pico to micro liter range has recently been the subject of much investigation due to the ever expanding body of inkjet research. Yarin et al. [10] reviewed droplet behavior in the inkjet drop volume range and determined that the dimensions of the final evaporated drop, if splashing does not occur, were primarily determined by the initial droplet size and the ink-substrate contact angle. Derby et al. [11] described a geometric model which predicted the final diameter of the dried droplet using the initial droplet diameter prior to deposition based on the assumption that the solvent wetted the solid surface as a spherical cap. For the case when ink droplets contain dispersed solids, a dense, ring-like deposit is often observed at the periphery of the droplet after the solvent has evaporated, which is referred to as the 'coffee ring effect' [14]. Deegan et al. attributed the 'coffee ring effect' to the pinning of the contact line in a drying droplet which promotes an outward flow of solvent/solid colloidal solution to the pinned outer boundary [15]. Factors that affect a 'coffee ring effect'include the size of the droplet [16], density of the suspended solid relative to the solvent [17], adsorption of particles at the air/water interface [17], inward directed flow (i.e., Marangoni) [18], and interparticle interactions [19].

DOD printing of 0-D drops is done by depositing non-overlapping droplets. In contrast, printing of 1-D lines is done by overlapping jetted droplets to achieve the desired line microstructure. Additional factors must be considered for this structure such as the line edge characteristics (i.e., straightness and parallelism) and line continuity (i.e., absence of gaps). Soltman et al. [20] studied 1-D line morphologies as a function of overlapped droplet spacing using a polymeric aqueous solution. They identified an ideal drop spacing threshold that achieved the most desirable line shape with straight, parallel sides. Below this threshold, the line began to exhibit instabilities in the form of bulging of the line edges due to solvent pooling. Duinveld et al. [21] submitted that the bulging occurrence resulted from the instability of droplets in the advancing contact line as it flowed over the solid substrate. 'Drawback' is another common defect in line printing that occurs slightly above the 'ideal' spacing threshold. During drawback, the leading edge of a printed droplet recoils sufficiently to prevent overlap with the subsequent neighboring droplet, thus creating a printing discontinuity. A mathematical relationship was developed by Li et al. [22] to predict the 'drawback threshold'. The model was verified experimentally by studying the overlapping behaviors of molten wax droplets.

In this endeavor, we aim to investigate the limiting factors that affect the fabrication and quality of micro ceramic patterns and thin films via DOD inkjet printing using a dilute colloidal ink suspension in combination with multiple, sequential print passes. The colloidal suspension ink was composed of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFC), a common SOFC cathode ceramic material, and α-terpineol solvent. In contrast to other molten wax inks or polymeric inks, the solidification process of the droplet occurs through evaporation of the carrier solvent rather than by gelation or chemical reaction. Droplet formation, transport and deposition were precisely maintained based upon our previous results [12] to ensure no splashing or satellite defects. This permits a careful focus on the capillary phase wherein the ink solvent vehicle is evaporated and the loaded solid in the drop precipitates to produce the desired micro ceramic features. These features include micro-dots and micro-lines which are herein referred to as 0-D dots and 1-D lines, respectively. In terms of the feature dimensions, the x and y axes are the direction of the print carriage and platen movement, respectively, while the z-axis is the direction perpendicular to the platen. The 0-D dots are constructed by stacking multiple layers of drops directly on top of each other in z-direction to increase the feature thickness. Consequently, the layer to layer deposition must have a high degree of accuracy at the designated print point in the x/y plane. Perfectly shaped 0-D dots will be circular with an x-axis dimension identical to the y-axis dimension. The 1-D lines are constructed by sequentially overlapping one droplet onto another in the x-direction and then stacking additional layers in z-direction to increase feature thickness. As with the 0-D dot, the deposited lines must have a high degree of accuracy in printing line on line. In addition, the 1-D line should be continuous, straight and narrow with parallel sides. This requires regulating the spacing between droplets to minimize line width as well as to avoid discontinuities and/or bulging at the line edges.

2. Materials and methods

The inkjet printer used was a Dimatix DMP 2831 by Fujifilm which is DOD piezoelectrically-driven with capabilities of adjusting print head temperature, platen temperature, firing voltage of individual jets, print-height, and drop spacing. The print head has 16 nozzles each with a hydraulic diameter of ~22 μm at the orifice. The printer ejects droplets with a nominal volume of 10 picoliters. The waveform of a single pulse voltage pattern was selected with the voltage ramping up or down to the target firing voltage within ~1 μs at a firing frequency of 2 kHz. A vacuum of 5 inches of water is needed to minimize issues with the ink flowing freely out of the print cartridge. Video cameras are integrated into the printer system to tune the drop velocity at each nozzle, to monitor the trajectory of the droplet flight, and to estimate evaporation rates of the carrier solvent. Using the video camera integrated into the carriage print head in conjunction with a stop watch, the evaporation rates of the carrier solvent were measured.

Prior to this micro pattern research, four key operating conditions were studied for their potential to affect layer to layer print accuracy. These were print height, interlayer delay time, substrate smoothness and evaporation rates. The print height, which is the distance of the inkjet nozzles above the substrate, was varied from 0.25 mm to 1.5 mm. The interlayer delay time, which is the time it takes for the print head to complete one pass and start the next, was varied from 0 to 240 s. The substrate smoothness was varied using smooth and rough glass substrates. Evaporation rate was evaluated by varying the platen temperature from ambient conditions (~25 °C) to 60 °C.

As mentioned earlier, 0-D dots were fabricated by stacking multiple layers of drops directly on top of each other. To avoid any drop to drop interactions, the 0-D drops were printed 254 μm apart on the x and y axes. 1-D lines were fabricated by overlapping jetted drops on the x-axis, in rows of 1 mm or more in length. The "drawback" effect was assessed by evaluating five droplets overlapped on the x-axis with varied drop spacing from 40 to 120 μm. The thickness of the micro features was tuned by varying the number of inkjet print passes from 1 to 10.

The ink used in this study consisted of the SOFC cathode material LSFC suspended in the solvent α-terpineol. To study the 'coffee-ring effect', polymeric ethyl cellulose (EC) was added to the ink. The inks were ball-milled for a minimum of 1 week to break up the LSFC agglomerates. The printer's nozzle diameter necessitates the use of particles <200 nm and low solid loadings. To eliminate particles larger than 200 nm, the ink was filtered through a 1.0 μm syringe filter. Also, the maximum solid loadings that would jet were experimentally determined to be 12 wt% (1.5 vol%) for this colloidal suspension ink. Above this level, the nozzles clogged immediately upon printing.

Top view optical images of the printed 0-D and 1-D micro features were captured using a MEIJI MX optical microscope with the help of Motic Plus software. Detailed morphological information was further examined by scanning electron microscopy (SEM)