Inkjet Printing for fabrication of porous films

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Abstract—Thin film devices and structures are fabricated by adding layers of functional material one above the other. Drop on demand inkjet printing system is primarily used for precisely depositing nano particle suspension/inks of metals or nonmetals over different types and geometries of non porous substrates. However, in the case of porous substrate, inkjet printing entails to wetting and poor retention of the ink. Raising the substrate temperature to vaporize the solvent is one of the techniques used to control seepage of particles through the open pores of porous substrate. Moreover, it is also beneficial in controlling the spreading of the ink for developing highly accurate patterns over non porous substrates. In order to prepare stable inks, 5Mol% Yttria Stabilized Zirconia (YSZ) material is subjected to high energy milling in terpineol solvent and a polymeric dispersant. 3 batches of YSZ inks were prepared by varying milling speed. The inkjet printed YSZ films were subjected to low temperature sintering in Argon gas atmosphere. Inkjet printing of YSZ nano particle inks on AISI316L substrates produces a porous microstructure. SEM, XRD and micro hardness results confirmed that sintering of fine nano particle layer produced stable, non defective porous films. Deposition of multiple layers could produce graded porosity or even dense films.

Keywords—Inkjet Printing, high energy milling, sintering, porous films

I. INTRODUCTION

Inkjet printing is a non-contact type deposition technique for printing inks on paper. Inkjet printer was developed initially for the document and image printing community as a low cost, deposition system offering high resolutions in outputs. As the need for nanometer size products grew with demand for miniaturization of product features, this technique was adapted by researchers to coat/deposit nano particle suspensions for fabricating devices with layer architecture.

Inkjet printing is being used for fabrication of patterns and continuous coatings with precise control on drop size and layer thickness. Moreover, this technique reduces material wastage and allows trouble free maintenance. In order to print the material, it is necessary that the precursor powder be dispersed in a stable suspension. Inks are prepared through high energy milling process in non-aqueous medium. The resulting suspensions (also termed as inks) have a solid phase dispersed in a thick viscous solvent.

Pure zirconia exist in three crystalline phases i) Monoclinic (m-ZrO₂) till 1170°C, ii) Tetragonal (t-ZrO₂) till 2340°C and iii) Cubic (c-ZrO₂) above 2340°C. Each of these phases except m-ZrO₂ has tremendous applications. Zirconia is doped with Yttria in order to stabilize these phases at room temperature. Yttria stabilized Zirconia (YSZ) is a ceramic material with very good thermal and mechanical properties. YSZ is used as an insulating layer in thermal barrier coatings [1], as an electrolyte material in solid oxide fuel cells [2], as biomedical implant [3], as a membrane layer for gas sensors [4] and as a substrate material [5]. Most often, combined layer geometry of both ceramic and metal is very difficult to process and fabricate considering the large mismatch existing in thermal expansion coefficient, melting point etc. But, using inkjet printing process, we demonstrate a fabrication methodology of ceramic on metal supports. Generally, thin layers are subjected to sintering process to enable it for functional requirements like toughness, density, conductivity etc. Sintering YSZ layers over metal substrates is challenging due to sintering temperature limitation. It is also known that, YSZ material typically require very high sintering temperatures. Inkjet printing process bridges this gap in fulfilling the functional requirements of the ceramic film without causing any degradation of the substrate. Nano size particles could be sintered at relatively lower temperature due to the larger surface area to volume ratio. Higher surface energy of particles aids in densification and grain growth. Uniform stacking up of nano particles in layers is exploited for fabricating macro porous and nanoporous films. Highly stable YSZ layer deposited by inkjet printing process could possibly act as a corrosion resistance layer or an oxidation resistance layer for steel components. Moreover this coating could also marginally increase the operating temperature and service life of AISI316L components.

Recently, inkjet printing processes have been used for fabrication of solid oxide fuel cells [2], electromechanical
(MEMS) devices [6], organic light emitting devices [7], gas sensors [8], solar cells [9] and RFID antennas [10].

An extensive literature survey show no previous work done for fabricating stable defect free crystalline YSZ films on non porous flat metal substrates.

This research paper highlights steps involved in preparation of stable inks and describes the novel methodology in fabricating highly stable porous YSZ films on AISI316L metal substrates using inkjet printing process.

II. INK SYNTHESIS

A. Materials

5 Mol% Yttria stabilized zirconia (Screen-o-graphic, India) agglomerated precursor powder is dried in an oven for 1 hr at 100°C. The powder is mixed with 10 weight % Ethyl cellulose powder. Ethyl cellulose acts as a binder which promotes adhesion to the substrate and as a steric stabilizer/dispersant in promoting suspension stability [11].

B. High energy Milling

The powder mixture is homogenized in a single bowl planetary ball mill (Retsch, Germany) in Terpineol (Fine chem, India) using tungsten carbide jar and balls. Powder to ball weight ratio was maintained at 1:10 for all the milling experiments. Apart from size reduction, high energy milling enhances the interaction among the particles in the suspension. Milling was done for a total duration of 4 hours 30 minutes at three different speeds. Three batches of suspensions were prepared at 120, 140 and 160 RPM. The inks are identified as YSZ1, YSZ2 and YSZ3 respectively. In order to prevent evaporative loss, the inks are collected in glass vials and stored at 20°C. YSZ ink synthesis is elaborated in our previous article [12].

C. Particle size analysis

Particle size analysis was conducted for three batches of YSZ ink using dynamic light scattering technique in Nano Partica (Horiba, Japan). Sample preparation was done by diluting 25µl (Macro pipette controller, Brand GMBH, Germany) of concentrated ink in 5ml terpineol, followed by homogenization in an ultrasonic bath [12]. All the three batches of inks were highly stable and showed a narrow size distribution. Mean diameters YSZ1 (coarse), YSZ2 (medium) and YSZ3 (Fine) inks are 1164nm, 1015nm and 572nm respectively [12]. Fig.1 shows the relationship between mean diameter and milling speed.

With increase in milling speed a decrease in particle size is observed till 160 RPM. Particles in a stable suspension develop a charged double layer which maintains charge equilibrium with the ions in the suspending medium. Likewise, these particles also exhibit random Brownian motion allowing interactions within the suspension. These interactions in the form of attractive/repulsive forces contribute to stability in suspensions. Instability in the form of sedimentation or agglomeration is primarily caused due to reduction in ionic charge over time or by charge neutralization by an external chemical agent.

Figure 1 Mean dia Vs Milling speed relationship [12]

III. INKJET PRINTING PROCESS

A. Classification

Inkjet printing is a solution deposition technique by which material in a suspension state is jetted out in the form of droplets under pressure. The droplet could be targeted on to a substrate to develop the required pattern and thickness of material. Based on the type of print heads, inkjet printing systems are classified into continuous and drop on demand. Continuous system produces ink drops continuously even at idle time. The jetted drops are targeted on paper/substrate for developing the layer. During idle time, these are deflected and collected in a collector which circulates the ink back to an ink reservoir for re-use. Increased exposure of the ink with the atmosphere degrades the quality of the solvent based ink. Moreover, drying up of the ink in the head is a major issue for these systems. On the other hand, drop on demand systems use a trigger source which produces the inkjet drop only when it is required (on demand). These systems are more rugged and durable compared to continuous system, providing more life for the ink and the head. Most often these print heads are attached on a carriage mounted over XY stage for precise positioning over a fixed substrate.

Drop on demand systems are broadly classified into thermal, electromagnetic piezoelectric and acoustic heads. Fig.2 shows the classification of inkjet printing systems based on the type of print heads. Thermal inkjet heads rely on a localized heating source for producing a vapor bubble in the ink column which is jetted out through an orifice on to the target surface. Drop size and drop volume is a function of temperature, viscosity and
frequency of trigger signal [13,14]. Electromagnetic heads have a solenoid plunger valve moving up and down for opening and closing an orifice. A positive pressure applied on the ink in the print head jets out a drop during the open time interval.

![Image of Inkjet Printing System](image)

**Figure 2** Classification of inkjet printing systems

Piezoelectric heads employ a piezo crystal encased in tubular or diaphragm geometry. A signal pulse is used for deforming the crystal which produces a pressure wave that propagates through the ink column and causes jetting through an orifice [15]. Acoustic inkjet print heads produce a pressure wave from an ultrasound field [16]. This pressure wave is used for jetting the ink on the substrate.

### B. Inkjet Printing

Inkjet printing system (ASCG, University of Cambridge, UK) with 16 plunger electromagnetic print head (Domino, UK) was used for this study. Fig.3 shows the schematic diagram of the print head. At idling position, plunger slug with rubberized tip seals the orifice in the nozzle plate. The spring loaded plunger slug is connected to the electromagnetic coil by means of a SS wire inside SS tube. Actuation of the plunger (Open Time duration) is controlled by Macrojet controller hardware through a PC software interface. Pneumatic control panel is equipped with a precision needle valve and pressure sensor (Janatics, India) for controlling the ink chamber pressure from 0.1 to 0.5 bar. In order to print the ink, concentrated ink is diluted in methanol solvent and agitated in an ultrasonic bath. Diluted ink is inserted into the ink reservoir. Ink flows through silicone rubber tubes to the print head and gets collected in the ink chamber under pressure.

When the actuation signal is received by the controller, the plunger opens the orifice for a very short interval (~400µsec). During this interval diluted ink is jetted out in the form of droplets. The drop in mid air takes the shape of a sphere to reduce the surface area. Satellite drops are also produced while jetting. Often these satellite drops which come as a part of the discharge joins with the larger drop falling within the same jetting axis. In another case, these could fall away from the jetting axis producing an irregular drop pattern on the substrate. The defects produced during layer build up could be reduced by printing multiple layers successively [12]. Longer open time duration allows more discharge through the orifice. Thickness of the film is a function of open time duration and the concentration of solids in the suspension [2]. Inkjet printing system is also equipped with a hot stage for printing at elevated temperatures. Inkjet printing over porous substrates is extremely difficult because of penetration of nano particles through the pores of the substrate leading to significant loss of material in the form of seepage. Increasing the temperature of the substrate allows rapid evaporation of the carrier solvent allowing material retention. Moreover, the dried up ink tends to act as a barrier which closes the open pore structure leading to thick layer of film on the surface. In case of non-porous substrates, hot stage printing is also beneficial in preventing wetting and island formation. This is apparently useful in fabrication of thin patterns.

![Image of Electro Magnetic Print Head](image)

**Figure 3** Schematic diagram of Electro Magnetic print head in Inkjet printing system

The most significant print parameters [17] contributing to layer thickness over flat substrates is as given below

i) **Open Time duration** (variable from 400µsec to 1000 µsec in 50 µsec steps)

ii) **Ink content** (manually varied from 10% to 30%)

iii) **Substrate Temperature** (variable from 100°C to 180°C in 1°C steps)

AISI316L substrates are mechanically polished and cleaned ultrasonically in acetone and positioned over the hot stage set at 100°C. A masking tape is attached at one end of the polished substrate in order to measure the thickness of the deposited layer. YSZ1, 2 and 3 inks were diluted in 70% by volume of methanol and agitated in an ultrasonic bath. Diluted inks were passed through 3μm glass multi fiber syringe filter (Cronus, UK). YSZ inks were deposited on metal substrates with offset overlaps of droplets [12]. All 16 plungers were activated with a
fixed drop spacing of 2.1mm. 20 layers were deposited for each sample. Offset measurements were changed once after every 5 depositions as shown in Table I.

### TABLE I. PRINT HEAD OFFSET MEASUREMENTS

| Sample | Ink | L(100|5) | L(60|10) | L(11|00S) | L(16|020) |
|--------|-----|------|--------|---------|---------|
| YSZ1-SS | YSZ-1 | X0.0 | Y0.0 | X 0.5 | Y 1.0 | X 1.5 |
| YSZ2-SS | YSZ-2 | X0.0 | Y0.0 | X 0.5 | Y 1.0 | X 1.5 |
| YSZ3-SS | YSZ-3 | X0.0 | Y0.0 | X 0.5 | Y 1.0 | X 1.5 |

*Offset measurements are in mm

### C. Sintering of YSZ films

In order to develop functional films, as printed layers are sintered at low temperatures. Ceramic-metal composite substrates are subjected to sintering process under Argon (UHP Grade, BOC, India) atmosphere at 200 mbar pressure in a resistance heating furnace (Hind Hi-Vac, India) at 1180°C for 2 hrs. Inkjet printed and sintered YSZ samples are designated as YSZ1-SS, YSZ2-SS, and YSZ3-SS.

### IV. RESULTS AND DISCUSSIONS

The sintered YSZ films were subjected to visible examination to check for delamination, cracks and defective regions. YSZ1-SS and YSZ2-SS samples show YSZ films with surface cracks. Whereas, YSZ layer on YSZ3-SS with very fine nano particles exhibit a stable layer with minor surface cracks X-ray diffraction studies were performed using X’pert MPD (PANanalytical, Netherlands) using Cu Ka (λ=1.5405Å) source with step size=0.01° and X-Ray beam power of 40kV/30mA. Analysis of precursor powder showed the significant phase as tetragonal zirconia t-ZrO$_2$ (101) at 20= 30.19° with trace amounts of monoclinic zirconia m-ZrO$_2$ (111) at 20= 28.17°. Table II shows the XRD data of precursor powder and sintered YSZ films. It is observed that fine particles in the film caused moderate crystal growth leading to significant reduction in crack development within the film during sintering. Crack could be caused due to residual stresses, phase transformations [18] or due to thermal expansion mismatch between the substrate and coating [19]. After sintering process, YSZ films exhibit completely stabilized t-ZrO$_2$ crystalline phase. Single phase YSZ formation is highly beneficial in preventing crack resistance and coating failure during service conditions [20]. Peak shifts to lower 2θ positions indicate compressive stresses in the film [21]. Thicknesses of sintered YSZ films were measured using Talyssurf (Taylor Hobson, UK). Fine particles in YSZ3-SS resulted in higher thickness of the film. Fig.4 shows the XRD spectrum of sintered YSZ films with complete absence of monoclinic phases and showing stabilized tetragonal (t-ZrO$_2$) phases. Substrates peaks identified at higher 20 positions in Fig.4 show a typical composition of AISI316L material having a chemical formula Fe$_{0.64}$Ni$_{0.36}$ (JCPD ref code 47-1405).

### TABLE II. X-RAY DIFFRACTION DATA OF PRECURSOR POWDER AND SINTERED YSZ FILMS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Phase</th>
<th>Position (2θ)</th>
<th>(hkl)</th>
<th>Chemical formula</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>JCPD Ref code</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ powder</td>
<td>t-ZrO$_2$</td>
<td>30.19</td>
<td>(101)</td>
<td>ZrO$<em>{0.92}$O$</em>{0.08}$</td>
<td>3.6110</td>
<td>3.6110</td>
<td>5.1675</td>
<td>48-0224</td>
<td>-</td>
</tr>
<tr>
<td>YSZ1-SS</td>
<td>t-ZrO$_2$</td>
<td>29.82</td>
<td>(101)</td>
<td>ZrO$_{1.00}$</td>
<td>3.6136</td>
<td>3.6136</td>
<td>5.1909</td>
<td>81-1545</td>
<td>22.19</td>
</tr>
<tr>
<td>YSZ2-SS</td>
<td>t-ZrO$_2$</td>
<td>29.74</td>
<td>(101)</td>
<td>ZrO$_{1.06}$</td>
<td>3.6227</td>
<td>3.6227</td>
<td>5.2056</td>
<td>81-1546</td>
<td>25.12</td>
</tr>
<tr>
<td>YSZ3-SS</td>
<td>t-ZrO$_2$</td>
<td>29.73</td>
<td>(101)</td>
<td>ZrO$_{1.06}$</td>
<td>3.6499</td>
<td>3.6499</td>
<td>5.2483</td>
<td>81-1549</td>
<td>27.51</td>
</tr>
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</table>

a. YSZ film thickness measured using Talyssurf

Figure 4 XRD spectrums of sintered YSZ films on AISI316L substrates. * symbol indicates t-ZrO$_2$ phases, ● indicates substrate peaks.

Coated YSZ films were analyzed for microstructure using Scanning Electron Microscope (Tescan, Czech Republic) at 20kV. Prior to SEM examination, all the three YSZ layers were gold sputtered (90 sec, 15-20mV) with copper tape attached over the film to ensure electronic conducting path. This is done so as to reduce charge accumulation in the sample. Fig.5 shows the secondary Electron SEM micrographs of sintered YSZ layers of a) YSZ1-SS, b) YSZ2-SS, c) YSZ3-SS at 50kX magnification and d) YSZ1-SS, e) YSZ2-SS, f) YSZ3-SS at 100X magnification. Sintered YSZ films exhibit porous microstructures with average pore size of approximately 300nm, 250nm, 150 nm for YSZ1-SS, YSZ2-SS and YSZ3-SS respectively.
Micrographs also reveal that YSZ film on YSZ3-SS has less number of pores which is attributed to increased density due to finer particles in the deposited layer. Fig.5d), e) and f) show a diminishing trend in crack formation on YSZ films. From SEM micrographs, approximate average crack width observed for YSZ film is 10μm, 4μm and 1μm for YSZ1-SS, YSZ2-SS and YSZ3-SS respectively.

![SEM microstructures of sintered YSZ films](image)

Figure 5 SEM microstructures of sintered YSZ films in a) YSZ1-SS, b) YSZ2-SS, c) YSZ3-SS at 50 KX magnification (500nm scale) and d) YSZ1-SS, e)YSZ2-SS, f) YSZ3-SS at 100X magnification (50μm scale). Circled regions show the area of examination.

Micro hardness measurements were done with micro hardness tester (UHL VMHT 104, Germany) by applying 50gms load with a diamond indenter. Five indentations were made on crack free regions of YSZ film. Average Vickers hardness of 186, 221 and 240 has been reported for YSZ1-SS, YSZ2-SS and YSZ3-SS respectively. Higher hardness of YSZ film with fine particles signifies the presence of a dense and defect free sintered layer.

V. CONCLUSIONS

Inkjet printing of 5 Mol% YSZ films on flat metal substrates has been successfully demonstrated. Low temperature sintering of ceramic-metal substrates was done in controlled atmosphere resistance heating furnace. Low temperature sintering aided in complete stabilization of tetragonal phase of zirconia. Finer particles in the ink resulted in reduced pore size and increased hardness. Solvents and dispersants in the ink lead to fabrication of porous films. Deposition of multiple layers through inkjet printing process could produce graded porosity or even dense films.

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