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Chemical synthesis and microstructural analysis of superconducting $YBa_2Cu_3O_{7-\delta}$ ink deposited by drop-on-demand ink-jet printing on silver substrates

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Abstract The basis for the development of computer controlled printing techniques for $YBa_2Cu_3O_{7-\delta}$ (YBCO) coated conductors is discussed in detail. This method of continuous deposition of YBCO material potentially enables non-vacuum formation of complex multi-layer superconducting patterns on silver substrates. Sol–ink processes were used to print single droplets of YBCO on polycrystalline silver substrates under varying printing conditions. Droplet sizes were controlled from a range of 300 μm–1200 μm. The formation and the stability of the sol–ink with respect to pH and concentration has been studied and discussed herein. For optimum results, the pH of the ink had to regulated to 6.5. Printing and substrate parameters that alter solid–liquid interface properties were also investigated such as ink concentration and surface roughness, the best results produced were with an ink concentration of 0.025 M on a polished silver surface. In order to control the flow properties of the sol media dynamic viscosities were determined. Characterisation by X-Ray Diffraction, Differential Thermal Analysis, Thermal Gravitometry and Scanning Electron Microscopy was used to examine the sol–ink samples, whilst AC susceptibility was used to assess the superconductivity of the printed samples where they were discovered to have a characteristic T_c of ~83 K.

Introduction

$REBa_2Cu_3O_{7-\delta}$ (REBCO, where RE = Rare Earth) still remains the material of choice for high-T_c superconductors due to its ability to operate in and withstand high magnetic fields [1]. The main problems with REBCO materials is their difficult processing into highly textured forms. Processes such as Liquid Phase Epitaxy (LPE) and Physical Vapour Depositions (PVD) produce high quality material however problems arise with up scalability and cost [2].

Alternative low cost and non-vacuum processes is an area under considerable research, one of these routes is the sol–gel method. Groups worldwide are seeking to produce high quality REBCO superconductors using this technique; whilst some methods produce harmful by-products such as hydrofluoric acid [3] others are less harmful [4–6]. A review of a number of sol–gel processes are depicted in Table 1, leading to the acetate route which formed the basis of the acetate-oxide route used in this $YBa_2Cu_3O_{7-\delta}$ (YBCO) ink synthesis.

Standard deposition processes of sols impose restrictions on coating geometries; the aim of this study is to open up the possibility for the ink-jet deposition of sols (inks) with the aim of creating complex shapes, tracks and multilayered conducting structures.

The substrate material of choice for REBCO is silver as there is evidence to believe that it produces *c*-axis alignment in the growth of YBCO and hence improved conducting properties [7]. This is mainly due to the high surface diffusion coefficient of the metallic silver in comparison to the ceramic conductor (Figure 1) [8, 9].

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Table 1 Description and analysis of various sol–gel routes for the formation of YBCO through the use of different precursors and solvents. The acetate route was used as the basis of our sol–gel and ink formation with a few modifications

	Procedures	Comments
Fluorine route	Addition of barium acetate dissolved in trifluoroacetic acid with yttrium acetate tetrahydrate and anhydrous copper acetate in stoichiometric (1:2:3) proportions. Solution then diluted with methanol or isopropanol and 1,3 propanediol.	The biggest disadvantage of this process is the formation of hydrofluoric acid as a waste product during the synthesis of YBCO.
Nitrite route	Made by dissolving metal nitrates in stoichiometric (1:2:3) ratio in water and citric acid. The pH of the solution is then adjusted with ammonium.	Non-fluorine route however due to the high amount of organic compound in the material, violent reactions occur during the conversion to REBCO phase. The breakdown of citric acid to CO_2 also restricts the formation of thick coatings as foaming occurs. This destroys the integrity of the deposit, which is a major problem during deposition by ink-jet.
Acetate-hydroxide route	Yttrium trimethyl acetate, barium hydroxide and copper trimethyl acetate were dissolved in a mixture of propionic acid/amine solvent. Xylenes of alcohol were used to dilute the solution and hence alter its viscosity.	Another non-fluorine route that produces sols with shelf lives of over two years, the only downfall is the high cost of hydroxide precursors as well as the many variables present in creating such sols.
Alkoxide route	Commonly used form of sol-gel processing involving the addition of alkoxides with suitable solvents.	Expensive method with narrow working windows.
Acetate route	Created by dissolving metal acetates in stoichiometric quantities (1:2:3) in an acetic acid solution. The pH of the solution is then adjusted using ammonium.	A non-fluorine process with relatively low cost metal ion precursors and straightforward processes.

The aim of this project is to understand the basis and parameters of ink-jet printing of sol–inks during synthesis, deposition and conversion. The optimum parameters need to be defined including ink pH and metal ion concentration, solid–liquid interface properties and finally the conversion steps from ink to the oxide compounds.

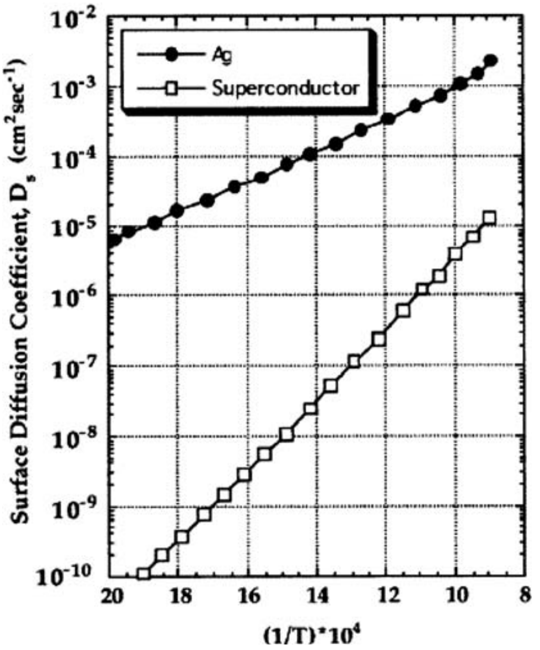


Fig. 1 Surface diffusion coefficients of ceramic superconductors and silver with respect to temperature [9]

Experimental procedures

YBCO ink synthesis

The inks were initially synthesised using an all acetate route. Yttrium acetate [$Y(OOCCH_3)_3 \cdot xH_2O$], barium acetate [$Ba(OOCH_3)_2$] and copper acetate [$Cu(OOCH_3)_2 \cdot H_2O$] were measured in stoichiometric metal quantities (1:2:3). All the acetates were dissolved separately in de-ionised water at 60 °C. The solutions were then added together and stirred continuously at 55 °C for 48 h in an oil bath to enable the uniform distribution of heat (hence avoiding 'hot spots'). The pH of the solution was then regulated using ammonia [NH_3] and an attempt to 'mass evaporate' the solvent to adjust the metal ion concentration of the ink was made.

A couple of problems were faced during mass evaporation. The severe recrystalisation of copper prevented a stable sol from forming. The unknown amount of water attached to the yttrium acetate compound also posed an uncertainty as to the amount of yttrium acetate required to form YBCO in its 1:2:3 stoichiometry.

An alternative yttrium acetate solution was then formulated to replace that of the first process; yttrium oxide [Y_2O_3] was dissolved in an acetic acid solution (0.2 M). This was then followed by the additions of the barium and copper acetate solutions (at stoichiometric

1:2:3 quantities). The addition of tartaric acid [$C_4H_6O_6$] to the solution helped overcome the problems of copper recrystalisation during mass evaporation and hence a stable sol could be formed. The pH of the ink was then varied in order to obtain the right value needed to avoid precipitation and form a stable sol. Inks of varying metal ion concentrations (0.4 M, 0.2 M, 0.15 M, 0.1 M, 0.05 M and 0.025 M) were created. Heating the ink to 60 °C causes it to turn into a viscous and dark blue gel.

The sols produced have a self-life in the order of a few months whilst the gels tend to precipitate after a few weeks. Figure 2 shows the flow chart of the successful route of ink synthesis utilising yttrium oxide as the yttrium precursor with tartaric acid and ammonium.

Differential thermal analysis and thermogravitometric analysis (DTA/TG) was carried out on the YBCO ink (using silver crucibles) on a Stanton Redcroft STA-780 in order to understand the different conversion steps of the ink. The viscosities of the inks were also measured using an RTI Visco-Elastic Rheometer.

Substrate and ink-jet printer

The synthesised inks were loaded into the ink-reservoir of the drop-on-demand ink-jet printer. Pressure is applied onto the reservoir and the outlet valve is then opened to ensure that all air pockets are removed. The substrate is placed 3 cm below the 90 μm ruby nozzle. As an electrical pulse (controlled by the computer interface) passes through the solenoid, the electromagnetic field lifts the piston off the surface of the nozzle. The pressure exerted onto the reservoir then forces a set amount of ink (~0.10 μl for a load of 60 kN/m^2) through the nozzle for deposition onto the substrate (Figure 3).

The silver substrates used for the deposition of the YBCO sols were prepared unpolished as well as polished to a 'mirror finish' result (using mechanical and chemical means). Droplets were printed onto the surface of the substrates in various conditions. The coatings were then sintered and analysed by scanning electron microscopy (SEM) using a JEOL 5800.

X-ray diffraction analysis (XRD) using a Phillips X'Pert PW1730 was conducted as well as AC-susceptibility (ACS) using an AC-Susceptometer Model 7000 with Lakeshore controls, this was only conducted for the 0.1 M sample as material properties do not vary with concentration.

Results and discussion

YBCO ink synthesis

Droplets of each ink (0.4 M, 0.2 M, 0.15 M, 0.1 M, 0.05 M and 0.025 M) were placed on a glass surface and gelled on a hot plate at 60 °C (Figure 4). High metal ion concentrations (0.4 M and 0.2 M) show signs of recrystalisation as a result of over saturation. The 0.15 M, 0.1 M, 0.05 M and 0.025 M samples at a pH of 3.5 show signs of early precipitation during gelation due to unsuitable charge (zeta-potential) of the colloidal particles. The 0.1 M, 0.05 M and 0.025 M inks show

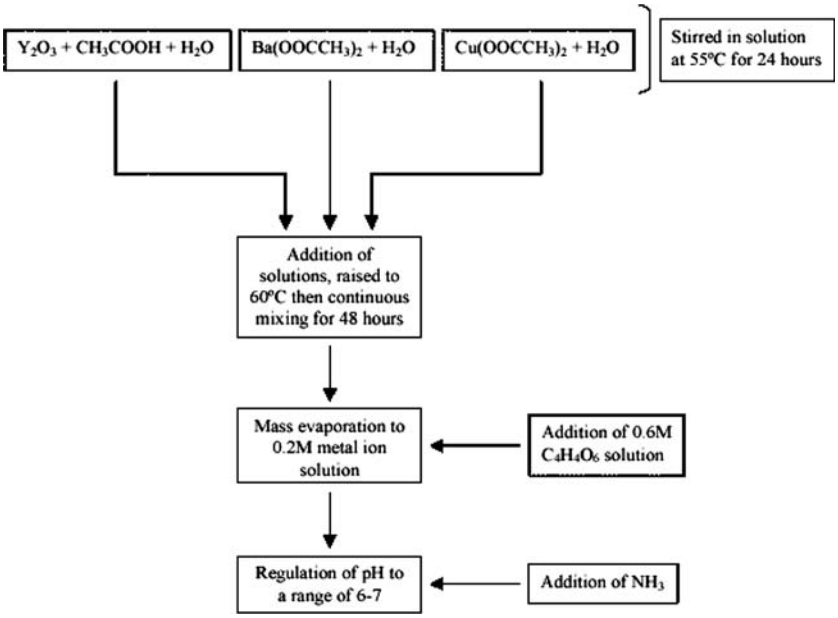


Fig. 2 Flow chart of successful YBCO ink synthesis via oxide-acetate route

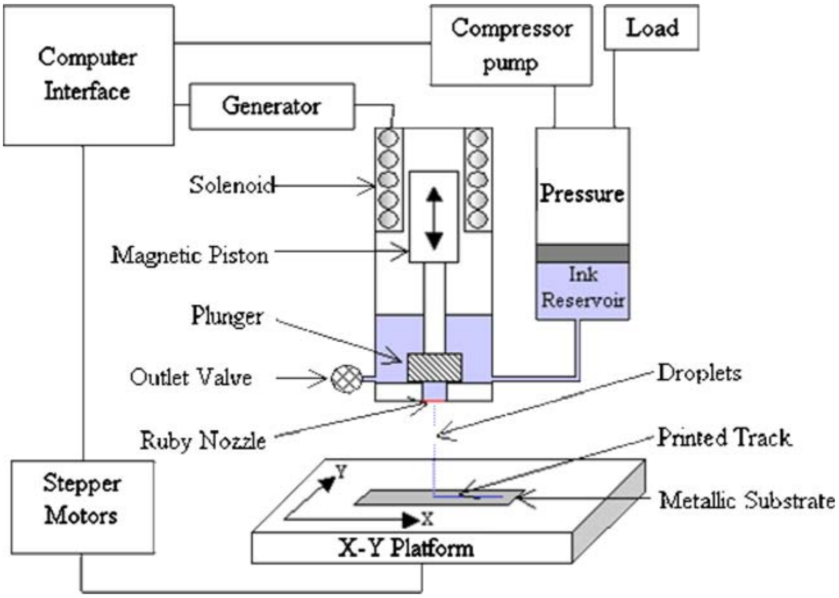


Fig. 3 Schematic of in-house built drop-on-demand ink-jet printer

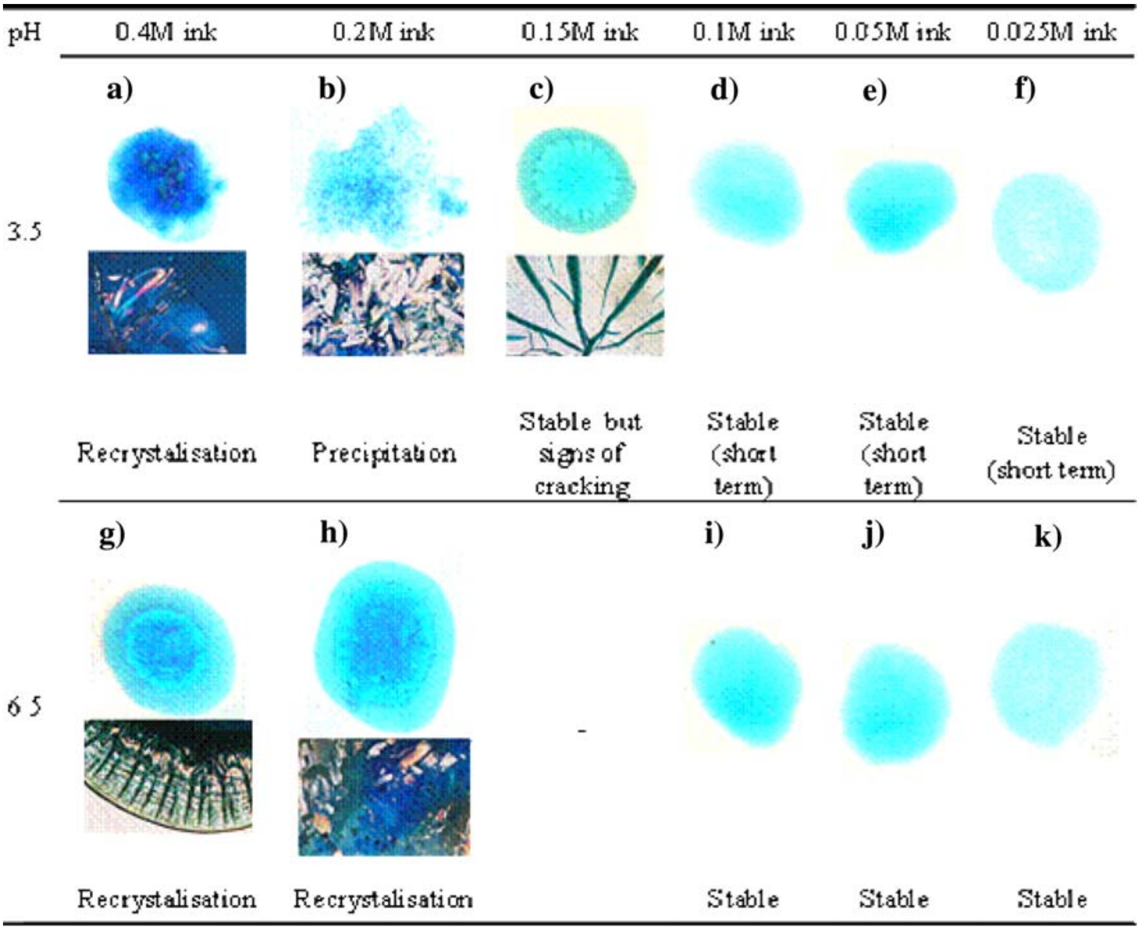


Fig. 4 Molar concentration and pH parameter optimisation of the YBCO inks

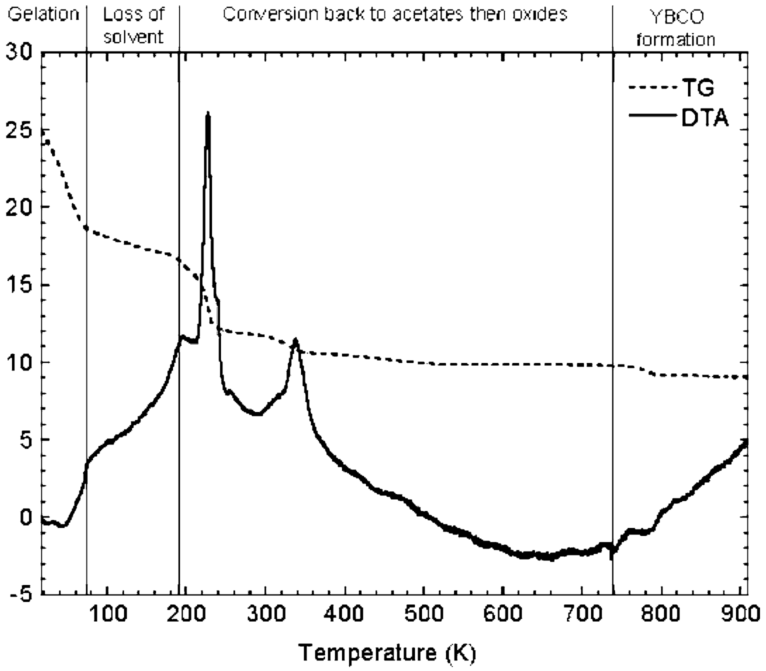


Fig. 5 DTA and TG analysis of the 0.1 M ink from the so to YBCO oxide compound at a heating rate of 0.5 °C/min in an O_2 atmosphere

stability at a pH of 6.5, the necessary pH value needed in obtaining stability.

DTA analysis is shown in Figure 5. Gelation commences at 60 °C where most of the solvent has been trapped by the macro-chains created within the ink. From 60 °C to 200 °C the gel is converted to solid acetates as the remaining trapped solvent is evaporated. From 200 °C to 450 °C the organic compounds present are removed and the ink is converted to Y_2O_3, $BaCO_3$ and CuO, the $BaCO_3$ is then broken down to BaO at 780 °C. The conversion and sintering of the oxides to YBCO occurs around 860 °C.

The heat-treatment for the printed droplets on silver follows the results depicted by the DTA analysis. The sample is gradually heated in oxygen at 1 °C/min and held at 60 °C, 200 °C and then 450 °C for 30 min; finally the temperature is raised to 930 °C whilst heating at 5 °C/min and held for 3 h, the sample was then cooled to room temperature in flowing oxygen.

Bulk material was then prepared by sintering it in custom made silver crucibles. XRD analysis was then performed to show phase-pure orthorombic YBCO (Figure 6). The ceramic material also exhibited preferential growth in the *c*-axis direction as speculated.

Before loading the ink into the printer, its viscosity was determined using a visco-elastic rheometer. Ideally, the viscosity of the ink should match that of water (~1 cP) in order to ease the process of printing. The

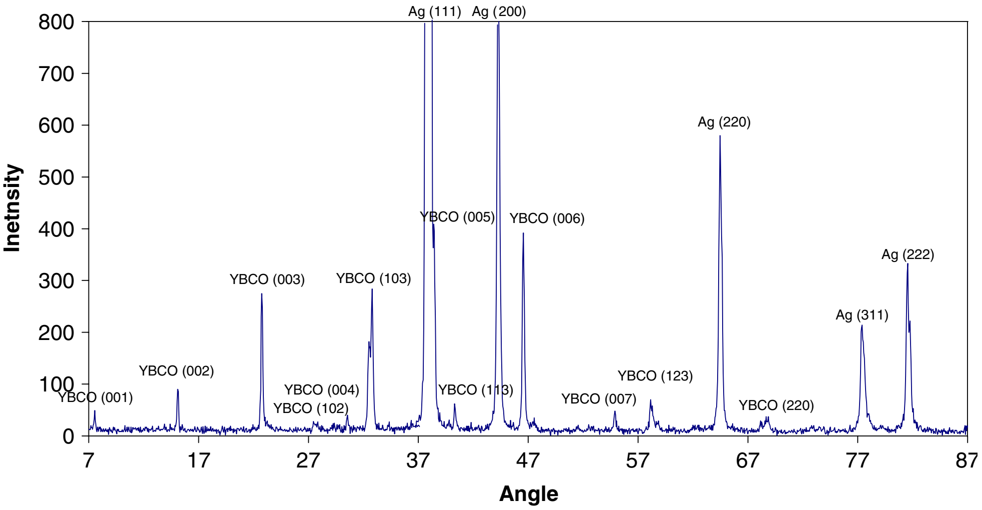


Fig. 6 XRD analysis of 0.1 M heat-treated YBCO ink at 930 °C in O_2

viscosities determined from all the ink samples are comparable to that of water (Table 2). Although ink viscosities can be altered by dissolving in solvent or initiating gelation (solvent evaporation) it was decided to commence deposition by using the existing viscosity and not introduce a new variable in the early stages of the project.

Ink-jet printing deposition

Substrate effects

Initial print sequences consisted of the 1.5 M ink at a pH of 3.5. Single droplets deposited on polished and non-polished silver (pressure of 60 kN/m^2) were dried in air and by hot plate at 60 °C. SEM images were then taken of the sintered samples (Figure 7).

The two parameters varied (surface friction reduced by polishing and rapid gelling by hot plate) have a profound effect on the structure of the YBCO layer. Polishing the surface reduces the size of the deposit droplet to about 300 µm (Figure 7b); this is a result of the high wetting angles created between the ink and the silver substrate (Figure 8a). The non-polished surface hinders this relationship as it immobilises the droplet and does not allow the liquid to pull together as the friction exerted on it pins it down as shown in Figure 8b) as opposed to the natural profile illustrated in Figure 8a). This increases the sintered droplet size to a range of about 800 µm. Polished surfaces create wetting/contact angles greater than 90° (>90°) and surfaces with high friction create wetting angles of less than 90° (<90°). The sample printed on polished silver and rapidly gelled (Figure 7c), had no time to pull together to the profile created in Figure 8a) hence the similar results to that of Figure 7a).

Table 2 Dynamic viscosity of varying YBCO ink concentrations at 25 °C measured using a visco-elastic rheometer

	Viscosity (cP)
Deionised water	0.98
0.025 M ink (pH 6.5)	0.86
0.050 M ink (pH 6.5)	0.87
0.100 M ink (pH 6.5)	0.89
0.150 M ink (pH 6.5)	0.94
0.200 M ink (pH 6.5)	1.13

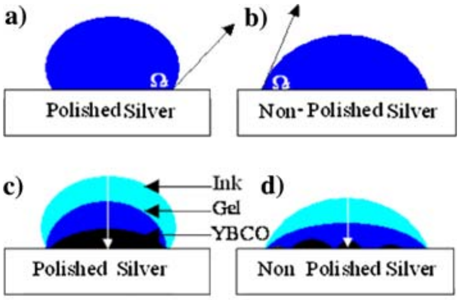


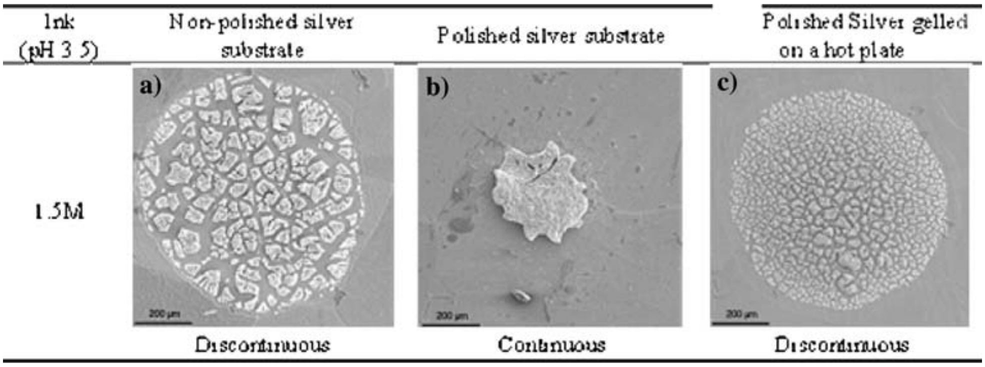
Fig. 8 Schematic representations of contact angles (Ω_c) of printed ink on substrate (**a**) >90° on polished silver (**b**) <90° on non-polished silver and conversion of ink to YBCO on substrates with contact angles (**c**) >90° and (**d**) <90°

As the contact area is smaller with the polished sample as opposed to the non-polished sample (Figure 8c, d) a smaller but thicker coating is formed. All deposits will convert to the same volume of YBCO therefore inks that are deposited over a larger surface area of silver (i.e. wetting angles less than 90°) would create coatings that are less thick and maybe even discontinuous.

Ink and processing effect

The problems of discontinuity could be solved by (1) reducing concentration of the ink and therefore avoiding cracking when thicker coatings are being made and/or (2) reducing the actual size of the droplet (and hence the material) deposited on the surface

Fig. 7 Deposition of 1.5 M YBCO sol at a pressure of 60 kN/m^2 on (**a**) non-polished silver dried in air (**b**) non-polished silver dried on a hot plate (**c**) polished silver dried in air (**d**) polished silver dried on a hot plate



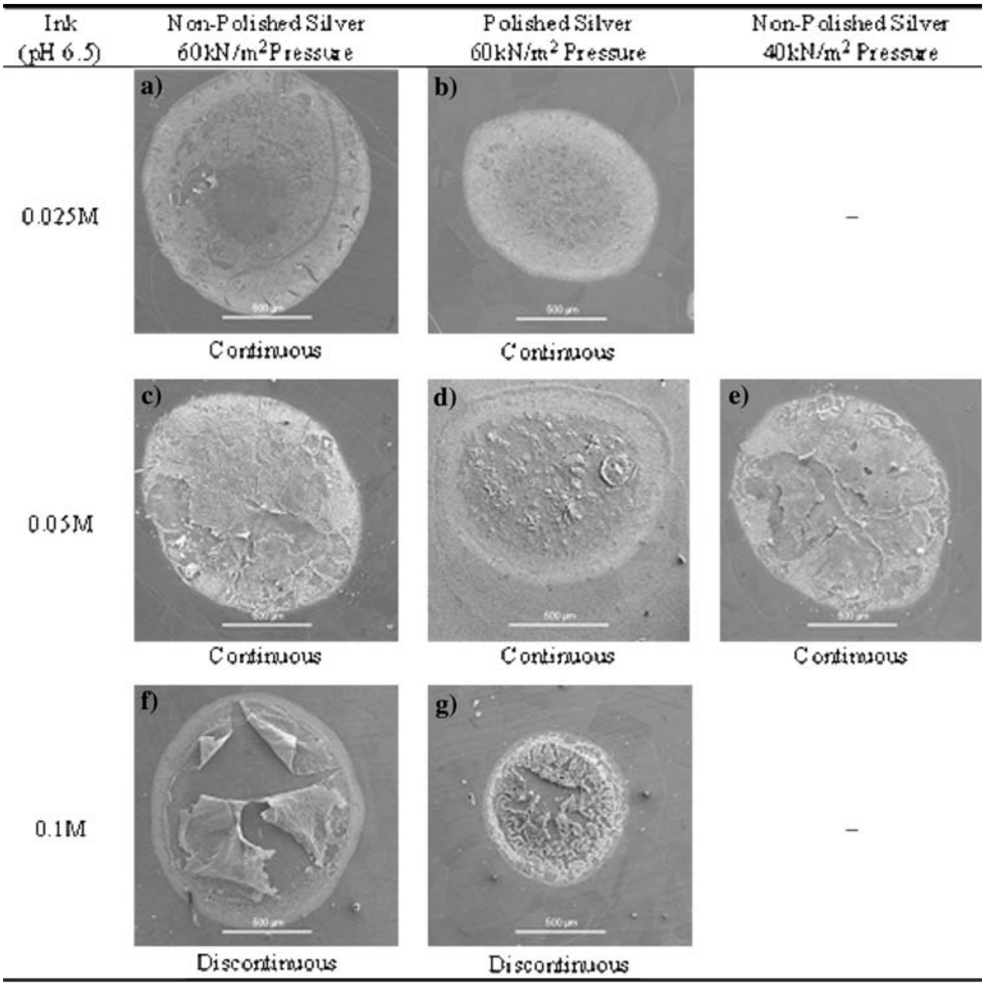


Fig. 9 Printed droplets of YBCO on silver dried in air (**a**) 0.025 M non-polished (**b**) 0.025 M polished (**c**) 0.05 M non-polished (**d**) 0.05 M polished (**e**) 0.05 M at 40 kN/m^2 non-polished (**f**) 0.1 M non-polished and (**g**) 0.1 M polished

therefore as the internal organic compounds try and escape they do not ‘rupture’ the surface of the deposit and destroy its integrity.

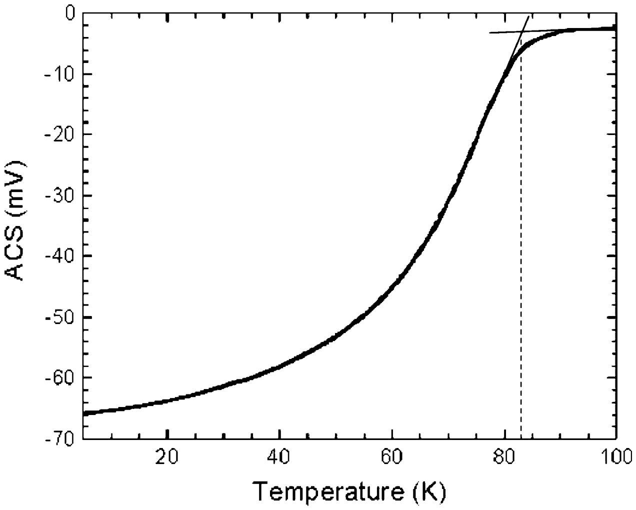


Fig. 10 ACS analysis of the 60 kN/m^2 printed and sintered 0.1 M YBCO ink sample at 1Oe and 333.3 Hz from 5 K to 100 K

The other stable variations of ink at lower concentration and at a higher pH were explored. Single droplets were printed on polished and non-polished silver at 60 kN/m^2 and one sample at 40 kN/m^2 to find out the effect of varying pressure (less material is deposited). The results can be seen in Figure 9.

The ink with the highest metal ion concentration (Figure 9f, g), exhibit discontinuous coating on the silver during sintering. As a solution, it would be necessary to reduce coating thickness (by reducing pressure on the ink reservoir) to obtain continual YBCO coatings using the 0.1 M ink. Alternatively, reducing the concentration of the ink should solve the problem. Both the 0.05 M and 0.025 M inks show continual coverage of the silver substrate post-sintering (Figure 9a, b). The main difference between the samples is the uniformity of the coatings. As the 0.05 M is still a high concentration for such thick coatings (thickness is in the order of a few microns) slight cracking is evident, the 0.025 M samples show no cracking.

Table 3 Summary of results and required parameters depicted by initial studies

Parameters					Results		
Substrate	pH	Viscosity (cP)	Metal ion concentration	Pressure (kN/m^2)	Wetting Angle	Layer	Droplet size (μm)
Non-polished	6.5	0.86	0.025M	60	<90°	Continuous	~1250
Non-polished	6.5	0.87	0.050 M	60	<90°	Continuous	~1000
Non-polished	6.5	0.89	0.100 M	60	<90°	Discontinuous	~1000
Polished	6.5	0.86	0.025 M	60	>90°	Continuous	~1000
Polished	6.5	0.87	0.050 M	60	>90°	Continuous	~750
Polished	6.5	0.89	0.100 M	60	>90°	Discontinuous	~600
Non-polished	6.5	0.87	0.050 M	40	<90°	Continuous	~1000

It was expected that the profiles of the polished samples would look like that represented in Figure 8a. This is exactly the case when sessile drop tests were conducted on polished silver (wetting angles of above 100° were achieved). With the non-polished surface, a lot more friction is exerted onto the droplet by the silver surface and hence there is no freedom for movement; the deposits cover a wider area (up to 1.25 mm). The samples printed on the polished silver exhibit smaller diameters (from 0.5 mm).

Superconducting properties

The printed sample (0.1 M at 60 kN/m^2) was analysed by AC-Susceptibility (Figure 10). A superconducting transition within the material begins at the onset critical temperature of ~83 K, however, the transition (ΔT) is broad, which is typical of a granular superconducting YBCO material. The smooth curve also suggests that the material is phase pure. The ink-jet printed ink is fully converted to superconducting YBCO.

Conclusions

Studies on the ink-jet printing of YBCO superconductors and oxide buffer layers show promising results. Parameters such as ink concentration, substrate surface preparation and ink-jet printer settings (such as pressure and distance) have large effects on the coatings produced (Table 3). For optimum results, the ink had to have a pH of 6.5 and a concentration of 0.05 M or less, in order to get improved morphology after sintering, the ink with a concentration of 0.025 M printed on polished silver proved best.

Alternative methods for the production inks are now being considered such as an organic polymeric route based on the Pecchini method as well as nitrites for the precursor materials. Further research on parametric optimisation of printing inks is needed, as well as solid-liquid interface studies. Current work being conducted concentrates on the requirements needed for the production of tracks and long lengths as well as opening up the possibility for three dimensional structures.

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