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Control of particle segregation during drying of ceramic suspension droplets

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Abstract

Ink-jet printing of thick film combinatorial libraries involves the deposition and drying of drops of suspension containing many different powders. During drying, a peripheral ring of powder develops and segregation of the more mobile particles to the remaining liquid pool in the centre leaves behind a drop residue with non-uniform composition. The present work investigates the effectiveness of organic ink additives that contribute a degree of thixotropy to the ink in reducing particle mobility and inhibiting particle segregation.

Keywords: A: Drying; C: Chemical properties; Combinatorial

1. Introduction

Combinatorial methods now play a major part in drug discovery[1] and are beginning to be used in the Materials Sciences, particularly in the search for superconductors,[2] catalysts,[3] phosphors,[4] dielectric materials[5] and fuel cell anode materials.[6]

The approaches to ceramic library preparation are generally classified as thin film or thick film (>20 μm).[7] The former uses vapour deposition or sputtering techniques by either systematic masking[2] or multi-target chambers to produce submicron films of either discrete composition or as gradient libraries. Thick film methods make use of screen printing[8] or ink-jet printing.[9] Ceramic powders are put in suspension in vehicles such as water or alcohol and either the pH is adjusted to confer stability or steric dispersants added. These inks can then be mixed, deposited and fired to produce libraries for subsequent testing. Thick film methods deposit and sinter the same commercial powders that are used in the industrial manufacture of components. This allows sintering variables to be explored so that grain size and porosity ranges can be included, placing composition and processing parameters in the frame. Thin film effects such as residual stress and substrate influences are reduced.

One problem associated with thick film library preparation from powder is that powder segregation can occur as droplets of ink mixtures dry.[10] The problem is induced by particle behaviour during the droplet drying stage and has been reported and discussed recently.[7,11,12] There are two main types of flow that take place when a sessile drop of powder suspension dries. The first is outward radial flow from the droplet centre to the periphery,[13] which causes pile up of particles at the edge of the drop and pins the rim of the fluid. The second is vigorous recirculation flows driven by Marangoni forces[14,15] which take place in well-dispersed (non-flocculating) suspensions in the liquid pool bounded by the peripheral 'foot' of powder. When a droplet containing different powders dries, each particle has a choice of joining the growing 'foot' or participating in the recirculation flows in the liquid pool.[11,16] The resulting partitioning between 'foot' and pool for different powders results in inhomogeneous rearrangement of powders and often produces a surface layer enriched in the more mobile powder.[11] The focus of this work is to investigate the effectiveness of organic ink additives that contribute a degree of thixotropy to the ink and hence reduce particle mobility and inhibit particle segregation.

2. Experimental details

Two binary systems were examined $(La_{0.8}Sr_{0.2})_{0.98}CoO_x$ (LSC)–$La_{0.8}Sr_{0.2}MnO_x$ (LSM) designated the LSCM system

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Table 1
Details of oxide powders

Materials	Supplier	Purity (%)	Density ($kg\,m^{-3}$)
LSM	Pi-KEM Ltd., UK	99.99	6506
LSC	Pi-KEM Ltd., UK	99.9	7095
BT	Alfa Aesar, Karlsruhe, Germany	99.7	5850
ST	Alfa Aesar, Karlsruhe, Germany	>99.0	4810

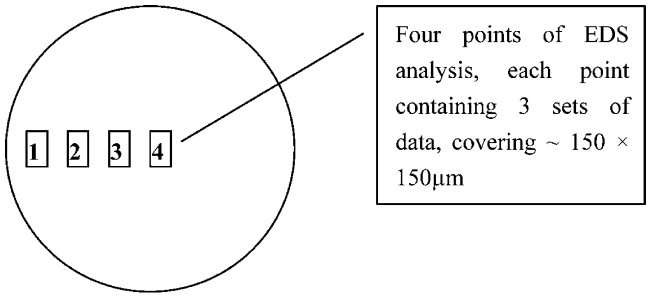

Fig. 1. Analysis positions on the sample surface.

and $BaTiO_3$ (BT)–$SrTiO_3$ (ST) designated the BST system. Details of the ceramic powders are given in Table 1. The powders were first inspected using scanning electron microscopy (SEM) and then their size distributions were measured using a Malvern Mastersizer 2000 (Malvern Instruments, Malvern, UK).

A high-energy Dyno mill (Model KDLA, Glen Creston Ltd., Middlesex, UK) charged with 1 mm diameter zirconia grinding media was used to mill the powders in distilled water. The suspensions were pumped through the mill 15 times to give a total milling time of approximately 60 min. The milling temperature was kept below 50 °C. A Micromeritics Gemini 2360 (Norcross, GA, USA) BET surface area analyser was employed to determine the surface areas before and after milling. Samples were first degassed at 200 °C for 1 h. The dried and degassed samples were then analysed using a five-point nitrogen adsorption method for surface area.

Sedimentation tests of the four powders were conducted on 1 vol.% suspensions to reduce particle interactions. Cloudy volume fraction as a function of time was recorded for 72 h. A dispersant, Darvan 821A (R.T. Vanderbilt Co. Inc., USA), which is an ammonium salt of poly(methacrylic acid) in aqueous solution was used to stabilize the suspensions. The dispersant dosages used were based on $2\,mg/m^2$ of powder.

Samples of a 50 wt.% LSC–50 wt.% LSM mixture and of a 50 wt.% BT–50 wt.% ST mixture were dispersed in water to form suspensions. Seven common thixotropic agents suitable for aqueous solutions were used as candidates to augment stability during drying. They were BYK-425&420 (Byk Chemie, Wesel, Germany), Acrysol 5000&12W (Rohm and Haas Company, Philadelphia, USA), TAFIGEL AP30, EDAPLAN 480 and METOLAT 355 (Munzing Chemie, Heilbronn, Germany).

To avoid introducing inorganic contaminants to the ink system, the thixotropic agents were first screened by ignition tests. Residues were considered to indicate the presence of inorganic components. Their solubilities in distilled water were examined and solutions with different loading levels were made at, above and below the recommended dosages for each additive. Viscosities of these solutions were measured at 25 °C using a reverse flow U-tube viscometer following BS 188:1977.

The LSCM and BST suspensions were mixed with different thixotropic additives to form inks. The details of ink compositions are given in Table 2. A clean, fine wire was dipped into the inks, and drops were deposited on silicone release paper (Grade SPT50/11, Cotek Papers Ltd., Glos., UK) dried at room temperature and separated from the substrate. The upper and lower surfaces of dried droplets were subjected to energy dispersive spectroscopy (EDS) analysis. For each dried sample, six sets of measurements were taken (three from each surface). Each set contained four points along the radius, and each point covered an area approximately 150 μm × 150 μm (Fig. 1). The microscope (SEM, Model 6300, JEOL, Tokyo, Japan) was equipped with an EDS system (Model eXL II, Oxford Instruments, Bucks, UK). The conditions for EDS were 20 kV acceleration voltage and 15 mm working distance. The data were corrected using INCA software (Oxford Instruments).

Table 2
Ink compositions for EDS analysis

Ink no.	LSM (wt.%)	LSC (wt.%)	Dispersant (wt.%)	Thixotropic agent (wt.%)			Distilled water (wt.%)	Ceramic (polymer) vol.% after drying
				I[a]	II[b]	III[c]		
1	15.9	15.9	1.9	–	–	–	66.3	74.1 (25.9)
2	14.4	14.4	1.7	1.9	–	–	67.6	56.4 (43.6)
3	14.4	14.4	1.7	–	1.9	–	67.6	56.5 (43.5)
4	15.1	15.1	1.8	–	–	1.8	66.2	58.6 (41.4)
5	16.1	16.1	1.3	–	–	–	66.5	84.4 (15.6)
6	14.6	14.6	1.2	1.9	–	–	67.7	66.1 (33.9)
7	14.6	14.6	1.2	–	1.9	–	67.7	66.1 (33.9)
8	15.1	15.1	1.2	–	–	1.8	66.8	69.1 (30.9)

[a] Acrysol 5000.
[b] Acrysol 12W.
[c] BYK-425.

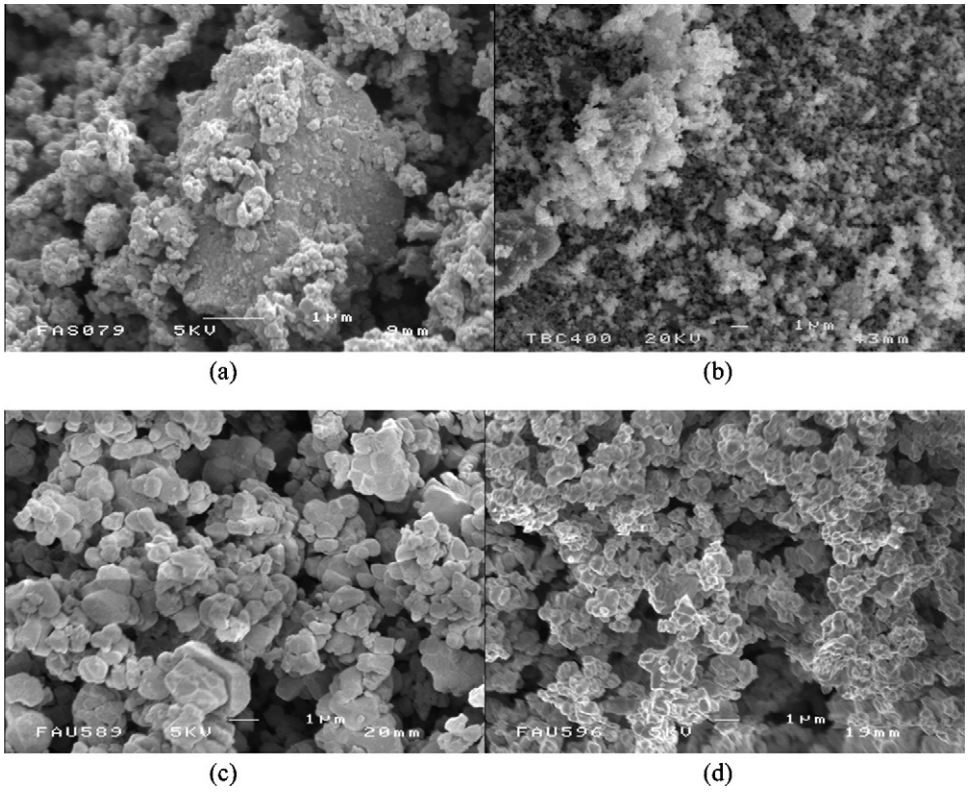

Fig. 2. The morphologies of the oxide powders: (a) LSM (b) LSC (c) ST (d) BT before milling.

3. Results

As Fig. 2 shows, the morphologies of the four powders were diverse. The LSC powder was finer than the LSM powder but the latter had a wider particle size distribution. Strong agglomerates were found in LSM. For BST powders, both BT and ST particles were around 1 μm diameter and demonstrated relative narrow size distribution. The particle size distributions by volume were obtained from the Malvern Matersizer 2000 (Fig. 3). The trend shown in Fig. 3 is consistent with the previous observation from SEM micrographs. LSM illustrates two peaks, indicating there were large particles in LSM (also seen in SEM, Fig. 2). The distribution and mean particle sizes of BT and ST were quite similar.

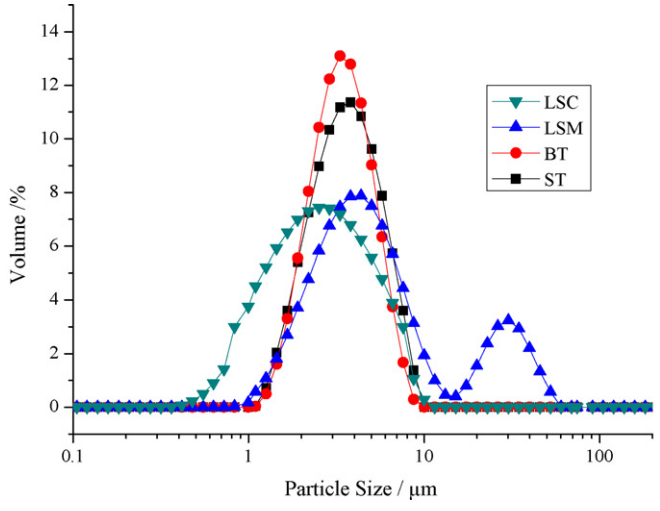

Fig. 3. Particle size distributions by volume before milling.

Table 3 shows the changes in specific surface area before and after milling. Significant increases in surface area were found in all powders. The surface area difference between LSC and LSM was enlarged after milling; the surface area of LSC was three times than that of LSM. The specific surface areas of BT and ST were almost equal.

After 72 h of sedimentation, the LSC suspension demonstrated the best stability while LSM settled after 48 h. The stability of BT and ST suspensions were similar to each other as shown in Fig. 4.

The ignition test on a polished stainless steel spatula provided a rapid screening test for inorganic components in ink additives. Those testing positive by leaving a residue were eliminated from the candidate list. After ignition, there were only three additives left without residues; they were BYK-425, Acrysol 5000 and

Table 3
Surface area of the powders before and after milling

Materials	Specific surface area of original powder ($m^2\ g^{-1}$)	Specific surface area of milled powder ($m^2\ g^{-1}$)
LSC	3.9	46.8
LSM	3.4	12.3
ST	1.0	20.8
BT	1.5	20.0

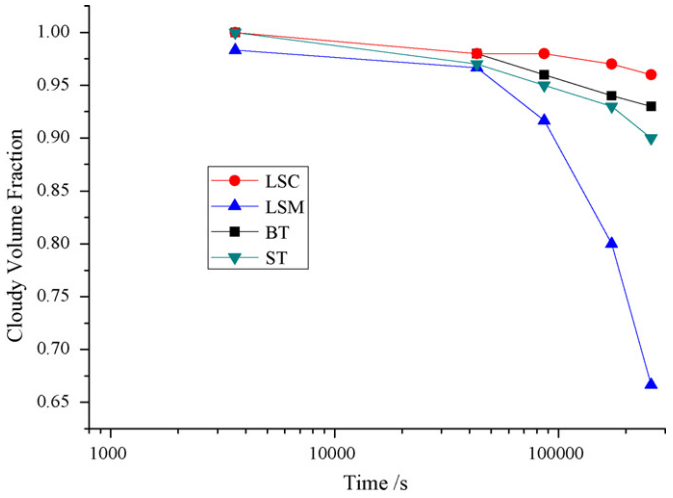

Fig. 4. Sedimentation tests of the four powders in 1 vol.% suspensions.

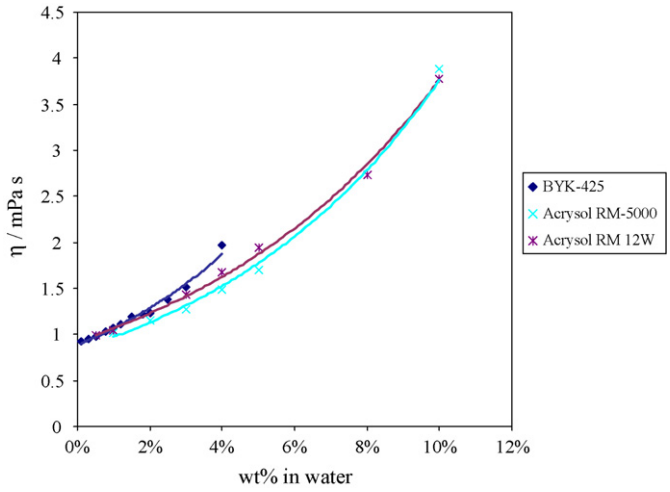

Fig. 5. Viscosities of ink additives in aqueous solution as a function of weight percentage in water.

Acrysol 12W. The rheological behaviour of these survivors was similar as shown in Fig. 5. No action was taken to shorten the candidate list further. After screening, the surviving thixotropic agents were BYK-425, Acrysol 5000 and Acrysol 12W.

3.1. LSCM system

EDS data obtained from LSCM dried samples are summarized in Table 4. Severe segregation occurred on the top surface of Sample 1, which was formed by the ink with dispersant only and without thixotropic agents. Element Mn was lost and in contrast Co remained, especially in the middle region of the sample surface (Points 2 and 3) which represents the last liquid to dry. Samples 2–4 contain the three surviving thixotropic agents and in these samples, the segregation phenomena were not apparent. The compositions examined were consistent with the planned compositions to within 1–3 at.%, which is the error that is to be expected from EDS analysis of unpolished surface.[17] One exception was Sample 2, Point 4, which was the centre of the sample. Combined with the elemental dot map image in Fig. 6(b), there was a deep sunken region in the centre, leading to collection of insufficient information by the spectrometer.

However, no apparent segregation was found on the lower surface, including that for Sample 1. The measured compositions were all coincident with the planned compositions typically to within 1–3 at.%. These results are consistent with previous observations of droplet drying which found that even where segregation is pronounced on the upper surface, the lower surfaces and cross-sections had uniform and planned compositions[7] thus dismissing preferential sedimentation during drying as a causative factor. The particle behaviour is discussed in more detail below.

The shapes of the samples were various, Sample 1 was nearly the classic 'doughnut' shape. Sample 2 had a sink in the middle, while Sample 3 had an approximate dome shape, and Sample 4 had a small hole in the centre.

Table 4
EDS analyses of upper and lower surfaces of LSCM samples with different additives

Sample (ink) no.	Planned composition (at.%)	Point 1 upper/lower (at.%)	Point 2 upper/lower (at.%)	Point 3 upper/lower (at.%)	Point 4 upper/lower (at.%)
1	La 40	41 ± 3/40 ± 1	41 ± 1/40 ± 1	40 ± 1/40 ± 1	39 ± 1/40 ± 1
	Sr 10	11 ± 4/10 ± 1	11 ± 2/10 ± 1	10 ± 1/10 ± 1	13 ± 2/10 ± 1
	Mn 26.25	16 ± 1/23 ± 1	1.5 ± 1/24 ± 2	1 ± 1/26 ± 2	23 ± 1/24 ± 1
	Co 23.75	30 ± 1/24 ± 2	45 ± 1/21 ± 1	47 ± 1/21 ± 2	22 ± 1/22 ± 1
2	La 40	43 ± 5/41 ± 1	40 ± 1/40 ± 2	40 ± 1/40 ± 1	41 ± 1/40 ± 1
	Sr 10	9 ± 4/10 ± 1	12 ± 1/12 ± 1	12 ± 2/10 ± 2	10 ± 1/10 ± 1
	Mn 23.75	21 ± 2/21 ± 1	23 ± 1/22 ± 1	22 ± 1/22 ± 1	0.5 ± 1/22 ± 1
	Co 26.25	25 ± 3/25 ± 1	24 ± 1/25 ± 1	24 ± 1/26 ± 1	46 ± 1/25 ± 1
3	La 40	44 ± 5/42 ± 1	42 ± 2/39 ± 1	40 ± 1/40 ± 1	40 ± 1/40 ± 2
	Sr 10	8 ± 5/12 ± 1	9 ± 3/12 ± 2	11 ± 1/10 ± 1	12 ± 2/9 ± 1
	Mn 23.75	21 ± 2/22 ± 1	24 ± 1/22 ± 1	24 ± 1/23 ± 1	25 ± 1/24 ± 1
	Co 26.25	25 ± 2/25 ± 1	24 ± 1/25 ± 1	22 ± 1/25 ± 1	22 ± 1/24 ± 1
4	La 40	40 ± 2/43 ± 1	40 ± 1/40 ± 2	40 ± 1/40 ± 2	39 ± 1/40 ± 1
	Sr 10	10 ± 2/10 ± 1	11 ± 1/10 ± 2	11 ± 2/10 ± 1	13 ± 2/10 ± 1
	Mn 24	23 ± 1/22 ± 1	25 ± 1/24 ± 1	22 ± 1/22 ± 1	23 ± 1/22 ± 2
	Co 26	23 ± 1/24 ± 1	23 ± 1/25 ± 1	25 ± 1/25 ± 1	22 ± 1/25 ± 1

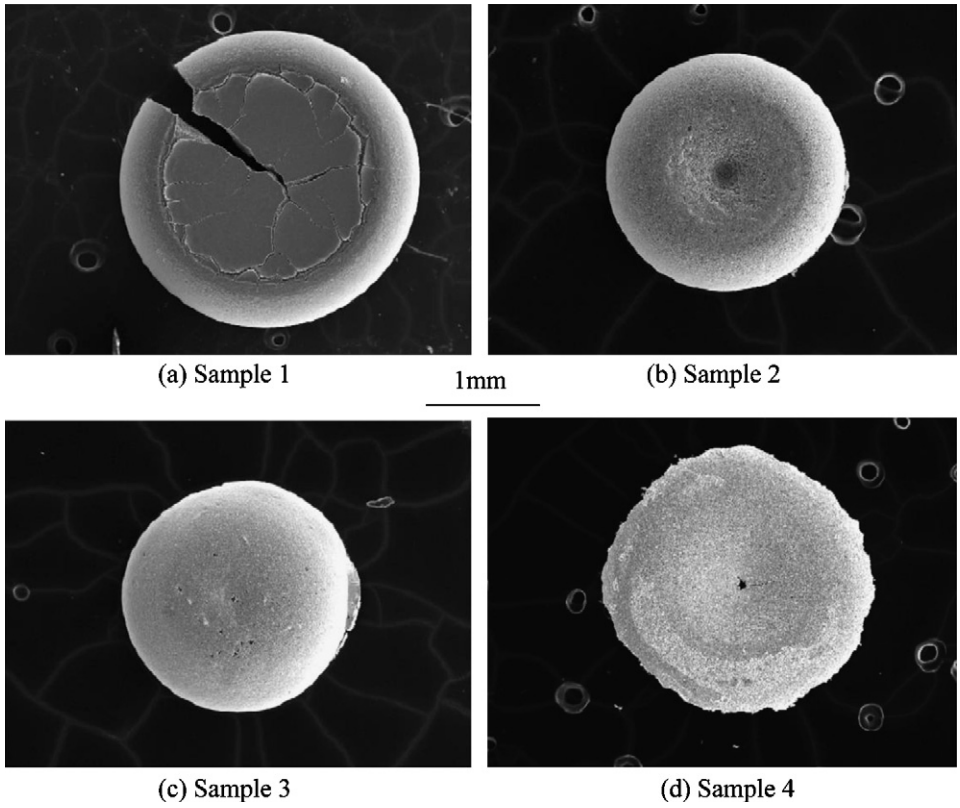

Fig. 6. LSCM samples for EDS analysis: (a) Sample 1, LSCM sample with dispersant only; (b) Sample 2, LSCM with Acrysol 5000; (c) Sample 3, LSCM with Acrysol 12W; (d) Sample 4, LSCM with BYK-425.

3.2. BST binary system

EDS results for this system are given in Table 5. Unlike the LSCM system, there is negligible segregation in the BT/ST system on both top and lower surfaces (Fig. 7). Even in Sample 5, which had no thixotropic additive, the measured compositions were all coincident with the planned compositions typically to within 1–3 at.%. This is discussed in terms of the similar particle characteristics for these two powders (*vide infra*).

4. Discussion

Two kinds of flow occur during droplet drying. The first is radial flow of liquid to the periphery of the drop to produce the classic 'doughnut' shape.[13] The second is vigorous recirculation flows that take place in the remaining central liquid region driven by Marangoni flows.[14,15] Different particles have different mobility in suspension and different inter-particle potentials and it is these differences that result in segregation in multi-component compositions. Factors affecting particle mobility are

Table 5
EDS analyses of BST samples with different additives

Sample (ink) no.	Planned composition (at.%)	Point 1 upper/lower (at.%)	Point 2 upper/lower (at.%)	Point 3 upper/lower (at.%)	Point 4 upper/lower (at.%)
5	Ba 22	23 ± 3/22 ± 2	22 ± 1/22 ± 1	23 ± 1/22 ± 1	25 ± 2/23 ± 2
	Sr 28	30 ± 3/31 ± 1	33 ± 2/28 ± 2	32 ± 1/31 ± 1	25 ± 6/27 ± 2
	Ti 50	46 ± 4/48 ± 2	45 ± 1/47 ± 3	45 ± 1/46 ± 2	51 ± 4/52 ± 2
6	Ba 22	22 ± 2/22 ± 1	21 ± 2/22 ± 1	21 ± 1/23 ± 1	21 ± 1/22 ± 1
	Sr 28	29 ± 4/28 ± 2	32 ± 2/31 ± 1	33 ± 1/32 ± 2	32 ± 2/31 ± 3
	Ti 50	49 ± 4/50 ± 3	47 ± 2/49 ± 2	46 ± 2/45 ± 1	47 ± 1/48 ± 2
7	Ba 22	23 ± 2/23 ± 1	22 ± 1/22 ± 1	22 ± 1/22 ± 1	21 ± 1/22 ± 1
	Sr 28	29 ± 4/27 ± 2	32 ± 2/30 ± 3	30 ± 1/32 ± 1	33 ± 1/31 ± 2
	Ti 50	48 ± 5/49 ± 2	46 ± 2/47 ± 2	47 ± 1/48 ± 2	46 ± 1/47 ± 1
8	Ba 22	21 ± 1/23 ± 1	20 ± 1/21 ± 1	21 ± 1/23 ± 1	21 ± 1/21 ± 1
	Sr 28	33 ± 1/30 ± 2	33 ± 1/30 ± 2	32 ± 1/31 ± 2	32 ± 2/30 ± 1
	Ti 50	46 ± 1/51 ± 2	46 ± 1/47 ± 1	46 ± 1/47 ± 2	46 ± 1/49 ± 2

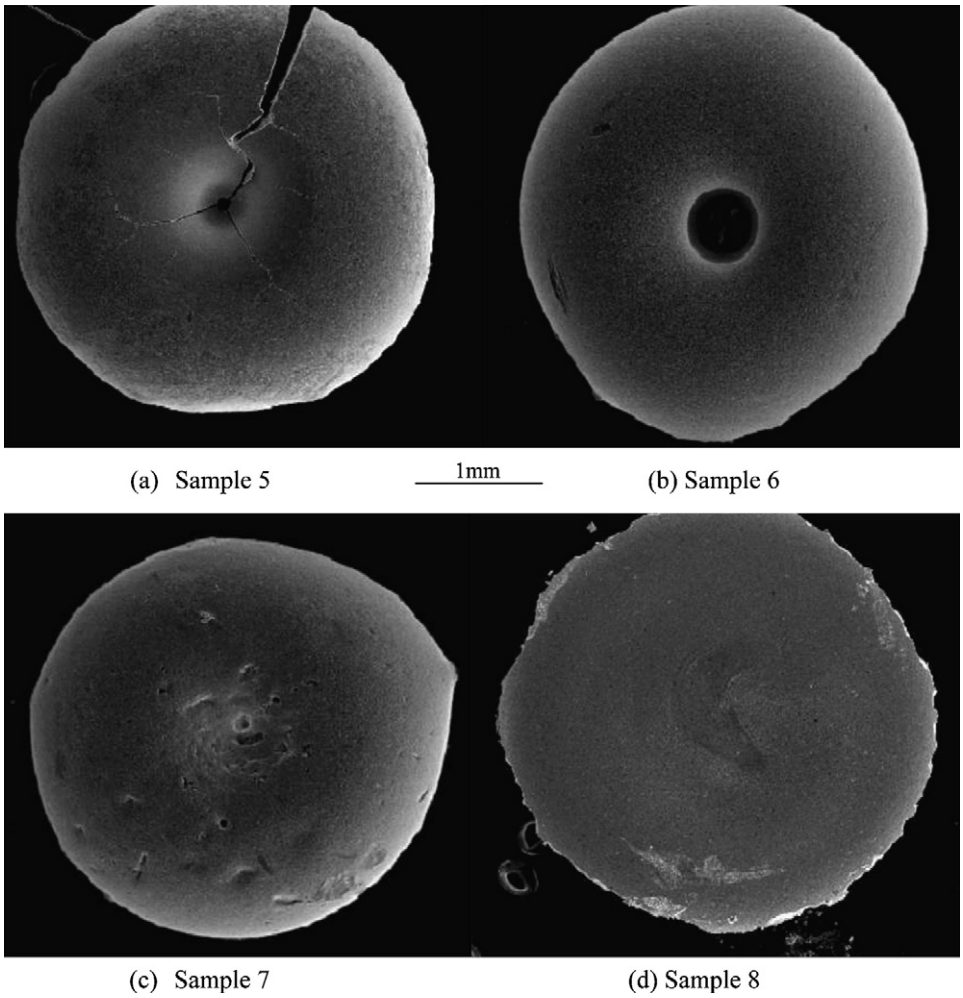

Fig. 7. BST samples for EDS analysis: (a) Sample 5, BST with dispersant only; (b) Sample 6, BST with Acrysol 5000; (c) Sample 7, BST with Acrysol 12W; (d) Sample 8, BST with BYK-425.

expected to affect the extent of segregation. These include, *inter alia*, particle size distribution and dispersant interaction. BT and ST powders were very similar to each other, including the particle size distribution (Fig. 3), surface area (Table 3) and dispersion stability as judged by sedimentation tests (Fig. 4). Segregation was not observed for this pair of powders. But for other systems, like LSCM as investigated here, the ZrO_2–AL_2O_3–Y_2O_3 system[10] and the TiO_2–Al_2O_3–ZrO_2 system[7,18,19] as reported previously, the segregation problem is severe and becomes an impediment for thick film combinational ink-jet printing.

The results demonstrate that all three thixotropic agents are effective in stopping segregation. While sessile drops are drying, the thixotropic agents increase the viscosity of the stationary fluid and slow down the recirculation flow significantly and therefore stop or weaken segregation. Notably, thixotropic agents provide outstanding shear thinning property for inks. During printing, shear stresses produced by aspirating and dispensing decrease the ink viscosity and maintain printability. Therefore, thixotropic agents are ideal and indeed may be essential for thick film combinatorial ink-jet printing with different types of powder.

In addition, these additives inhibited cracking during droplet drying. Cracks were found in samples without the thixotropic agents (Samples 1 and 5). On the other hand, no cracking was found in the samples with thixotropic agents. This effect is probably caused by the increased organic volume fraction of the ink based on the dry composition (Table 2).

In previous work there was a strong correlation between the incidence of segregation and the resulting droplet shape after drying. Thus, when entanglement flocculation was induced by excessive addition of dispersant or when the suspensions were naturally flocculating, the drops dried to form a dome shape rather than the 'doughnut' shape associated with radial particle migration to the periphery of the drop. In these mixtures (e.g. Samples 2–8) various sample shapes were obtained, but no obvious segregation was observed in these samples. This implies that the radial flow inside the drops was still taking place to some extent but that the recirculation flows attributed to Marangoni stresses[14,15] had been quenched.

Thus, the addition of a thixotropic agent prevents segregation but does not appear to offer control of drop shape. In previous work,[12] the three methods used to control segregation also

offered some control over the shape of the droplet residue. They were: (i) printing onto a porous substrate which gave rapid drying, (ii) use of excessive dispersant addition which appeared to produce entanglement flocculation and (iii) the use of naturally flocculating suspensions. The first is of limited use because non-porous substrates are generally preferable while the third is undesirable because well-dispersed suspensions are used to prevent sedimentation during printing and to encourage a densely packed residue. Flocculation appears to control droplet shape by locking the particles in a three dimensional structure early in the drying process. The addition of these thixotropic agents does not encourage flocculation but is effective in restricting particle motion in the liquid pool and hence prevents compositional segregation.

5. Conclusions

For most thick film ceramic combinatorial libraries, segregation occurs and is a severe problem challenging the implementation of thick film combinatorial ink-jet printing. Uniform compositional distribution was obtained by adding thixotropic agents to printing inks. Thixotropic agents are probably effective in stopping or weakening the recirculation flows inside drops during drying but offer less control over the final droplet residue shape.

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