

Towards manufacture of thick film thermoelectric devices

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Introduction



- Functional materials
- Towards sustainability through additive manufacturing for micro scale structures
- Impact on synthesis of functional materials
- Impact on processing functional additively manufactured structures











Innovate UK Technology Strategy Board



Environmentally safe and sustainable functional materials









PZT film before sintering



Temperature induced degradation:

- Interdiffusion
- Evaporation
- Degradation

Solutions:

• Low temperature

e.g. Compsite sol gel < 750°C for PZT/Si

• Diffusion barrier e.g. ZrO₂

R.A. Dorey, S.B. Stringfellow, R.W. Whatmore, Effect of sintering aid and repeated sol infiltrations on the dielectric and piezoelectric properties of a PZT composite thick film, J.Euro.Ceram.Soc., 22, 2921-2926, 2002.









Manufacture of film based devices





Micro coordinate measurement tool sensor/actuator

Fabrication stages

Additive manufacturing: knock-on effects







Additive manufacturing techniques for structured films

Structuring – micromoulding





PZT features created by micro moulding

D. Wang, S.A. Rocks, R.A. Dorey, Micromoulding of PZT film structures using electrohydrodynamic atomization mould filling, J.Euro.Ceram.Soc., 29, 1147–1155, 2009.

Structuring – micromoulding





Structuring – pad printing







Silver NPs deposited by pad printing







PZT features created by ink jet printing

Structuring – direct writing





Bi2Te3 features created by ink jet printing an aqueous ink

Deposition – screen printing





Bi₂Te₃ features created by screen printing

Structuring – direct writing





*Bi*₂*Te*₃ *powder prepared for ink jet printing*

Sb₂Te₃ powder prepared for screen printing

Structuring – direct writing





Ink jet printed Bi₂Te₃

screen printed Sb₂Te₃



Additive manufacturing techniques for structured films

Design criteria Building block size << feature size

Friday, 10 February 2017

18



Powder synthesis

Need small functional (multi-element) materials particles

Fusion based techniques #1: particle growth





Particle growth due to coalescence of multiple primary particles = Fundamental limit on particle size

Fusion based techniques #2: phase evolution





Fusion based techniques #2: phase evolution





Friday, 10 February 2017

Fusion based techniques #2: phase evolution (950°C hold)



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Powder synthesis

Liquid phase/bottom up required

24

Molten salt synthesis





PbO soluble in NaCl/KCL – ZrO₂ slight solubility

F. Bortolani, R.A.Dorey, Molten salt synthesis of PZT powder for direct write inks, J. Euro.Ceram.Soc., 30, 2073-2079, 2010

Friday, 10 February 2017





Molten salt synthesis – NaCo₂O₄





NaCo_xO_y evolution (MSS@900°C)





NaCo_xO_y evolution (MSS@900°C)







Processing of films

How about films during manufacture?





Cross section of PZT following heat treatment at 800°C for 4 hours



10 min at 100°C in air



10 min at 350°C in air



Extensive reaction with atmosphere oxygen at low temperatures

KNN thick films - challenges







KNN thick films – loss of volatile elements





- Compositional fluctuations occur through-thickness of sample
- During early stages of sintering porous nature dominates for oxidation/evaporation effects
- Substrate interactions more important at longer times
- Substrate interactions lead to compositional gradient (inward & outward diffusion)
- Pattern has little effect provided aspect ratio > 1



Summary

- Film forming techniques are continually improving
- Cheaper & quicker to fabricate than bulk systems
- Thick films are reliant on consolidation of powders

 i.e. heat required
- Control of content of volatile elements difficult to manage at T > 900°C without containment & excess.

Robert A. Dorey,

Integrated Powder-based Thick Films for Thermoelectric, Pyroelectric and Piezoelectric Energy Harvesting Devices IEEE Sensors Journal, vol 14, no 7, pp 2177-2184, 2014











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