Synthesis of Functionally Graded Materials by Electrophoretic Deposition and Sintering

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Fabrication routes for FGM

- **Constructive processes**
  - Conventional solid state powder deposition
  - Liquid phase sintering
  - Infiltration
  - Reactive powder processes
  - Plasma spray forming
  - Laser cladding
  - Electroforming
  - Vapor deposition
  - Lamination processes

- **Transport based processes**
  - Mass transport processes
  - Thermal processes
  - Setting and centrifugal separation
Electrophoretic Deposition (EPD)

EPD is a powder processing technology based on colloids.

3 steps of Electrophoretic deposition:
- Particle surface charging in solvent
- Particle migration under external electric field
- Particle coagulation at electrode

Picture by courtesy of P. Sarkar and P.S. Nicholson
Advantages of EPD

– Fast and convenient, easy to scale up
– Low investment and high flexibility (almost any materials: metals, ceramics and polymers)
– Capable of producing thick, thin films (ranging from micrometers to centimeters) and 3-D complex geometries
– Easy to produce composite materials with precisely tailored properties
Research objectives

• Net-shape manufacturing by sintering → inverse sintering problem solution: green specimen with special shape and with special (composite) structure;
• Fabrication of a special shape functionally structured (graded) green specimen → EPD;
• An ambient temperature processing technology for FGM fabrication as a parallel problem → the EPD-EP approach provides application in electronic packaging.
Fabrication of FGM by EPD
Equipment for EPD

Characteristics of EPD suspension

• The suspension is acetone. N-butylamine was added to enhance particle charging.

• The optimal concentration of n-butylamine was determined by viscosity measurement to make the suspension stable.
Kinetics of EPD (thin alumina film)

Objective: in order to control the thickness of EPD

![Graph showing the kinetics of EPD](image)
Measurement of EPD deposit thickness
Kinetics of EPD (thick alumina and zirconia deposits)
Cross section SEM of Alumina deposit obtained by EPD
3-D EPD shaping
Cracking during drying
Microstructure of FGM cylinder

Zirconia rich side

Intermediate layer

Alumina rich side

SEM pictures of different positions of FGM: white spots are zirconia, gray spots are alumina
Microstructure of FGM disks

Alumina rich side of an FGM disk
(FGM02)
Microstructure of FGM disks

Intermediate part of an FGM disk
(FGM02)
Microstructure of FGM disks

Zirconia rich side of an FGM disk
(FGM02)
Shape distortion of FGM after sintering
Background

- High thermal conductivity
- Resolve CTE mismatch
Requirements for fabrication of TIM

- Thermal properties of TIM should fall between silicon and copper: composite of metal and ceramics should be used
- Synthesis method should avoid high temperature processing
- Our approach: Electrophoretic deposition (deposition of ceramic particles) and electroplating (deposition of metal) to produce TIM without thermal processing
The approach-sequential deposition

Sequential Deposition: EPD+Electroplating in two steps
The Main Constitutive Relationship

\[ \sigma_{ij} = \frac{\sigma(W)}{W} \left[ \varphi \dot{e}_{ij} \right] + \left( \psi - \frac{1}{3} \varphi \epsilon \delta_{ij} \right) + P_L \delta_{ij} \]

- Strain rate component
- Bulk modulus: Resistance to the volume change, function of porosity
- Shear modulus: Resistance to the shape change, function of porosity
- Volume strain rate
- Effective sintering stress: function of porosity
- Generalized viscosity: corresponds to the constitutive properties of particle material
- Externally applied material resistance, sintering stresses

**Linear Viscous:** \( \sigma(W) = 2\eta_0 W \)

**Rigid Plastic:** \( \sigma(W) = \sigma_y \)

**Power Law Creep:** \( \sigma(W) = AW^m \)

\[ W = \frac{1}{\sqrt{1-\theta}} \sqrt{\varphi \dot{y} + \psi \dot{e}^2} \]
Formulations to model sintering of composite and FGM

Linear viscous case:

\[ \sigma_{ij} = 2\eta_0 \left[ \phi \dot{\varepsilon}_{ij} + \left( \psi - \frac{1}{3} \varphi \right) \dot{\varepsilon}_{ij} \right] + P_L \]

Skorohod model:

\[ P_L = \frac{3\alpha}{r} (1 - \theta)^2 \]

Sintering stress for composite materials:

\[
P_L = -\frac{\alpha\gamma(1-\theta)N_c}{4} \left\{ \begin{array}{c} \frac{\phi_s c_{ls}}{R_s (\phi_l + c_{ls} \phi_s)} \left[ \phi_s + \frac{(1 - \frac{\sqrt{3}}{2})\phi_l (1 + c_{ls})}{1 + c_{ls} - \sqrt{1 + 2c_{ls}}} \right] + \\ \frac{\phi_l c_{sl}}{R_l (\phi_s + c_{sl} \phi_l)} \left[ \phi_l + \frac{(1 - \frac{\sqrt{3}}{2})\phi_s (1 + c_{sl})}{1 + c_{sl} - \sqrt{1 + 2c_{sl}}} \right] \end{array} \right\}
\]
Formulations to model sintering of composite and FGM (cont’d)

Densification rate of mixed alumina and zirconia (from experimental results of Raj*):  

\[ \dot{\rho} = A \frac{\exp\left(-\frac{Q}{R_g T}\right)}{T} \frac{f(\rho)}{R^4} \]

\[ f(\rho) = \frac{1-\rho}{\rho} \]

\[ Q = \begin{cases} 440 + 5200\phi_{\text{ZrO}_2} & 0.05 \leq \phi_{\text{ZrO}_2} \leq 0.95 \\ 700 & 0.95 < \phi_{\text{ZrO}_2} \end{cases} \text{kJ/mol} \]

\[ 615 + 1700(1-\phi_{\text{ZrO}_2}), \phi_{\text{ZrO}_2} > 0.95 \]

Formulations to model sintering of composite and FGM (cont’d)

Equivalent particle size*:

\[ R = \frac{R_i}{\chi(c_{sl}, \phi_s)} \]

\[ \chi = \frac{c_{sl}^3 (1 - \phi_s)^2 + \phi_s (1 - \phi_s)(1 + c_{sl})c_{sl} + \phi_s^3}{c_{sl}^3 (1 - \phi_s)^2 + 0.5\phi_s (1 - \phi_s)(1 + c_{sl})^2 c_{sl} + \phi_s^2 c_{sl}} \]

Bulk viscosity:

\[ K_v = -\frac{P_L \rho}{\dot{\rho}} \]

Shear viscosity:

\[ S = 1.5 f(\rho)K_v = \frac{3(1 - \rho)}{2\rho} \]

Finite Element Modeling of shape distortion of FGM sintering
Comparison with experimental results
Iteration process to optimize initial shape of FGM

Start

Initial shape \( S=S_0 \)

Compute final shape \( S=S_i \)

\[ Z_i = S_i - S_0 \]

\[ Z_i < \text{Tolerance?} \]

No \( S_{i+1} = S_i - Z_i \)

Yes

End
Inverse optimization of initial shape
Conclusions

• The characteristics of EPD suspension were studied. 8% vol. n-butylamine was added into the suspension to enhance particle charging. Particle agglomeration problems were solved by the ultrasonic vibration.

• The kinetics of the deposition of both thin films and 3-D shape components were studied. The obtained kinetics shows good agreement with Hamaker’s law.

• The green Al₂O₃/ZrO₂ 3-D FGM was successfully synthesized by EPD. Disks and cylinders were deposited using a self-designed device. It was found that large particles help avoiding cracking problems during drying. The fabricated specimens were sintered and the resultant SEM micrographs show the desired graded structures.
Conclusions (cont’d)

- A user subroutine, which implements the developed constitutive formulations, was developed and linked to the commercial finite-element software ABAQUS.
- The sintering of a disk-shape FGM made of Al₂O₃/ZrO₂ was simulated. The results showed that the FGM disk has undergone warping because of the difference between the sintering kinetics of Al₂O₃ and ZrO₂.
- The “inverse” methodology was successfully employed to obtain the initial shape in order to get the desired final shape after sintering.
- A sequential deposition process which consists of electrophoretic deposition and following electroplating was investigated. A copper sulfate plating bath was used for electroplating. An Al₂O₃/Cu composite was successfully fabricated.
Possible future work: freeze drying

- Powder and water
- Fluorocarbon
- Liquid Nitrogen
- Aluminum
- Powder and water
Microstructures

Regular freezing

Unidirectional freezing
CTE range of composite predicted by modeling