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Synthesis of Functionally Graded Materials by Electrophoretic Deposition and Sintering

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- Committee members

  Prof. D. J. Benson

  Prof. K. B. Morsi

  Prof. Jin Sungho

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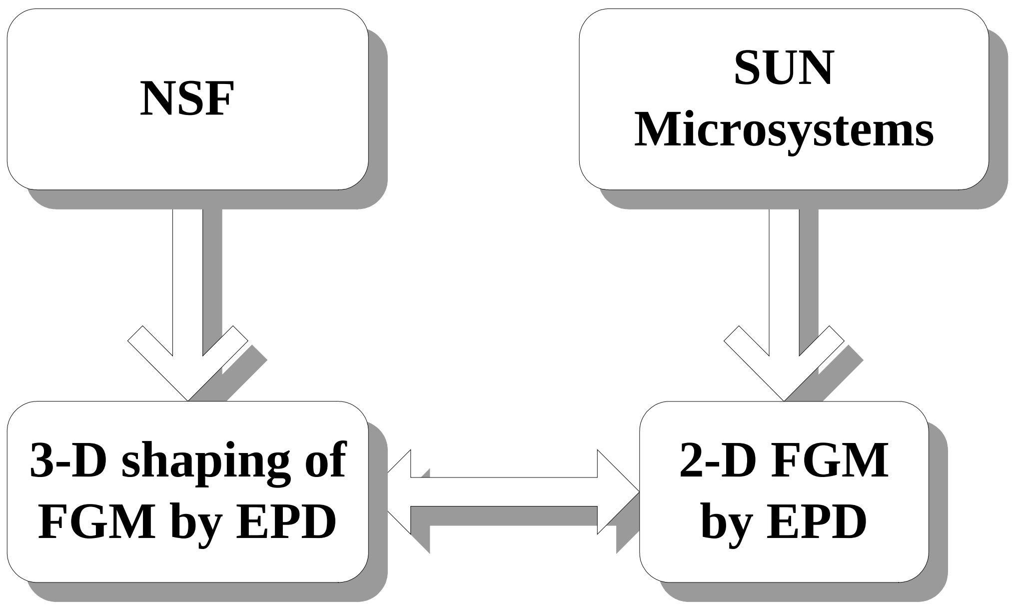

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Fabrication routes for FGM

- **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*

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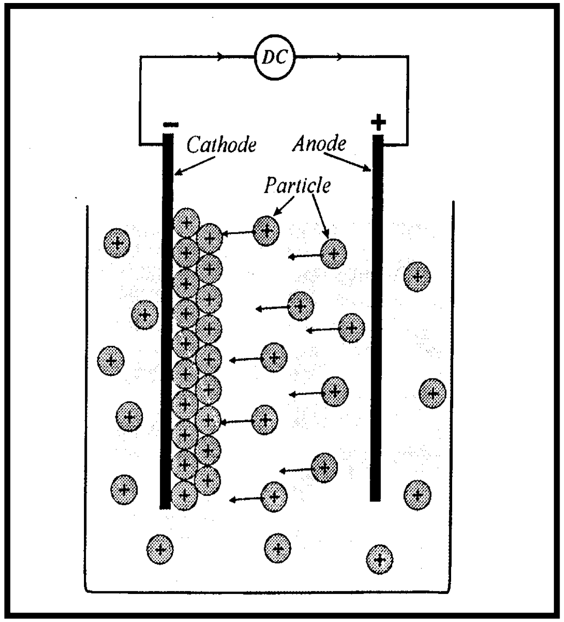
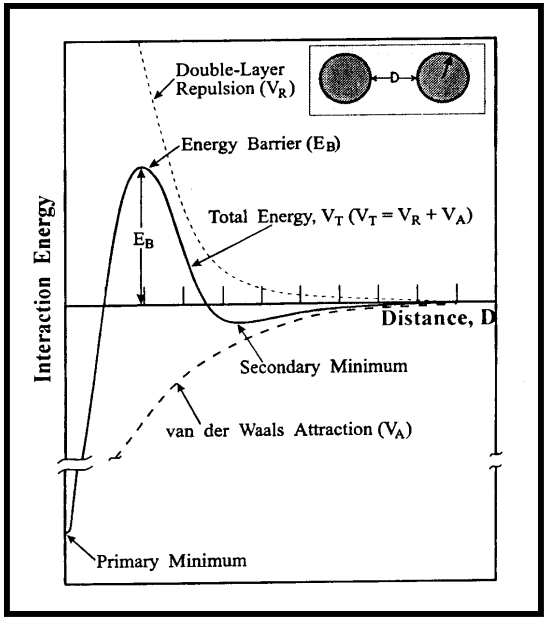
Electrophoretic Deposition (EPD)

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

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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

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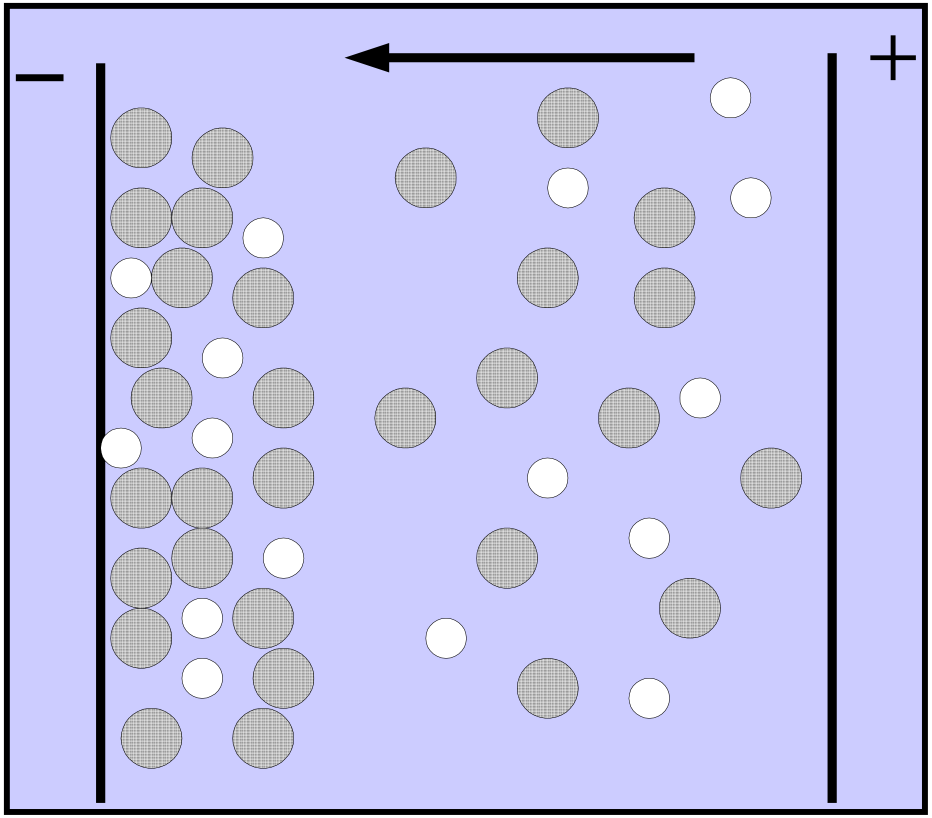
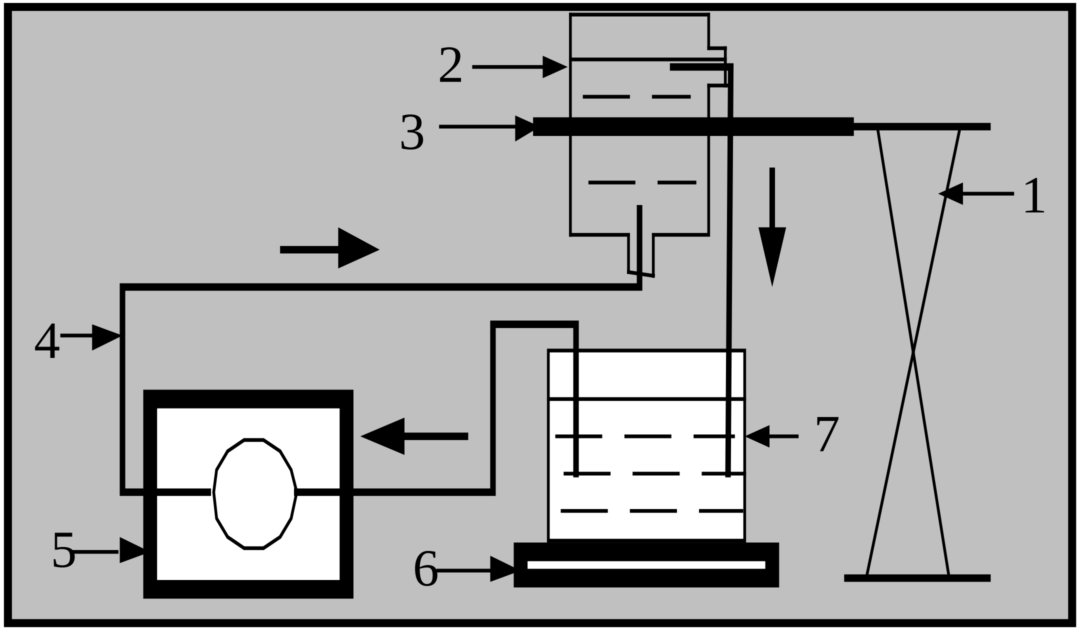
Research objectives

- **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



1. Adjustable stand 2. Deposition cell 3. Deposition cell holder 4. Tubes 5. Pump 6. Magnetic stirrer 7. Suspension container

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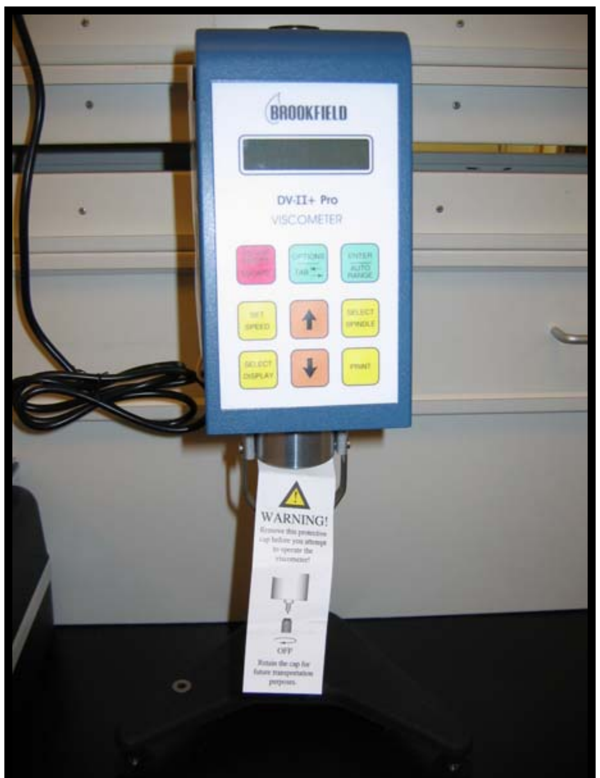
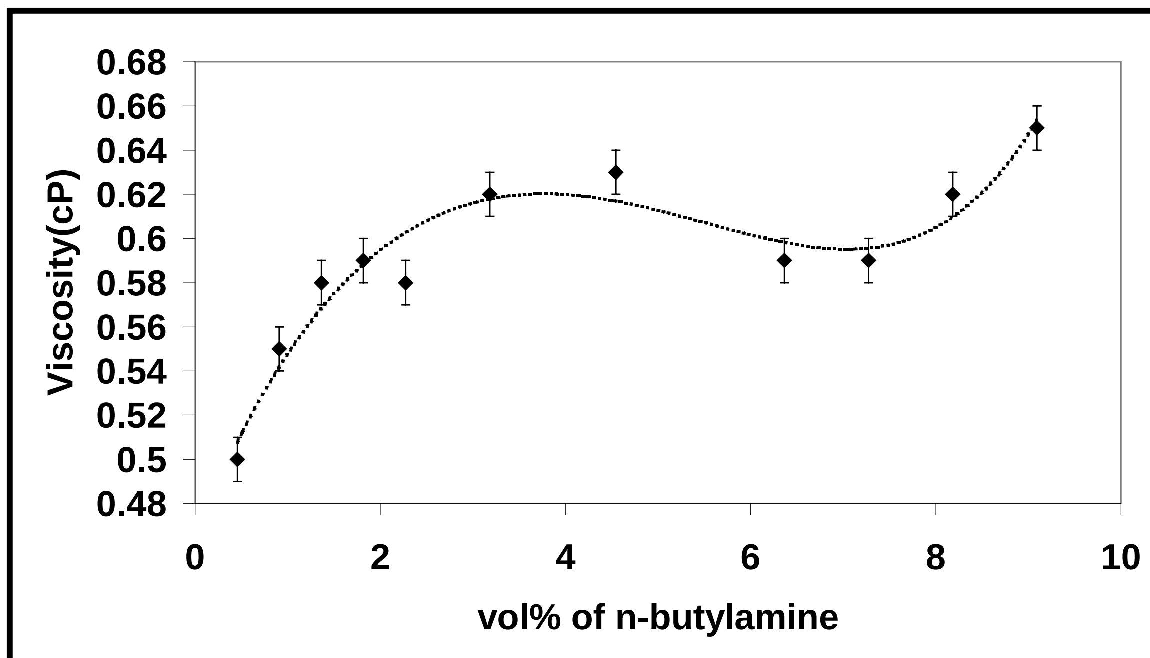
Characteristics of EPD suspension

- **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**





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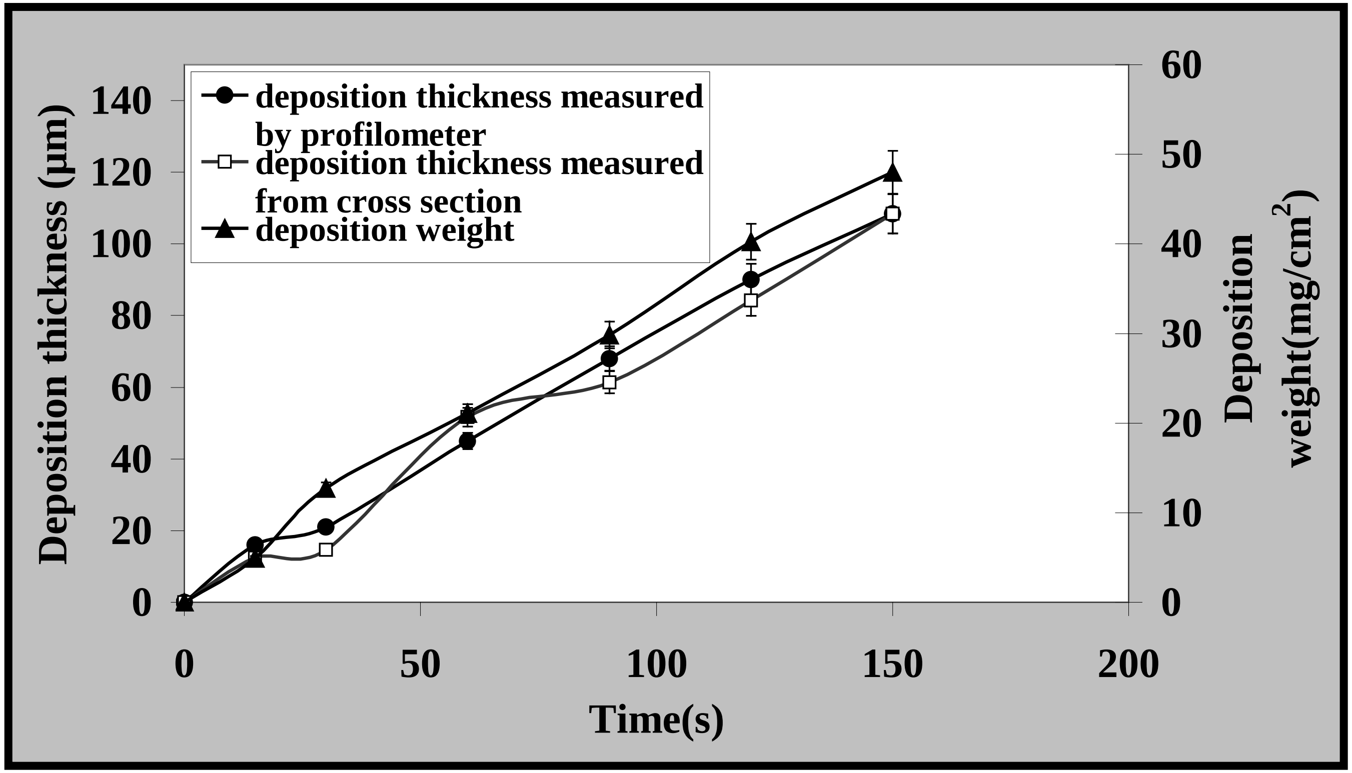
Kinetics of EPD (thin alumina film)

Objective: in order to control the thickness of EPD



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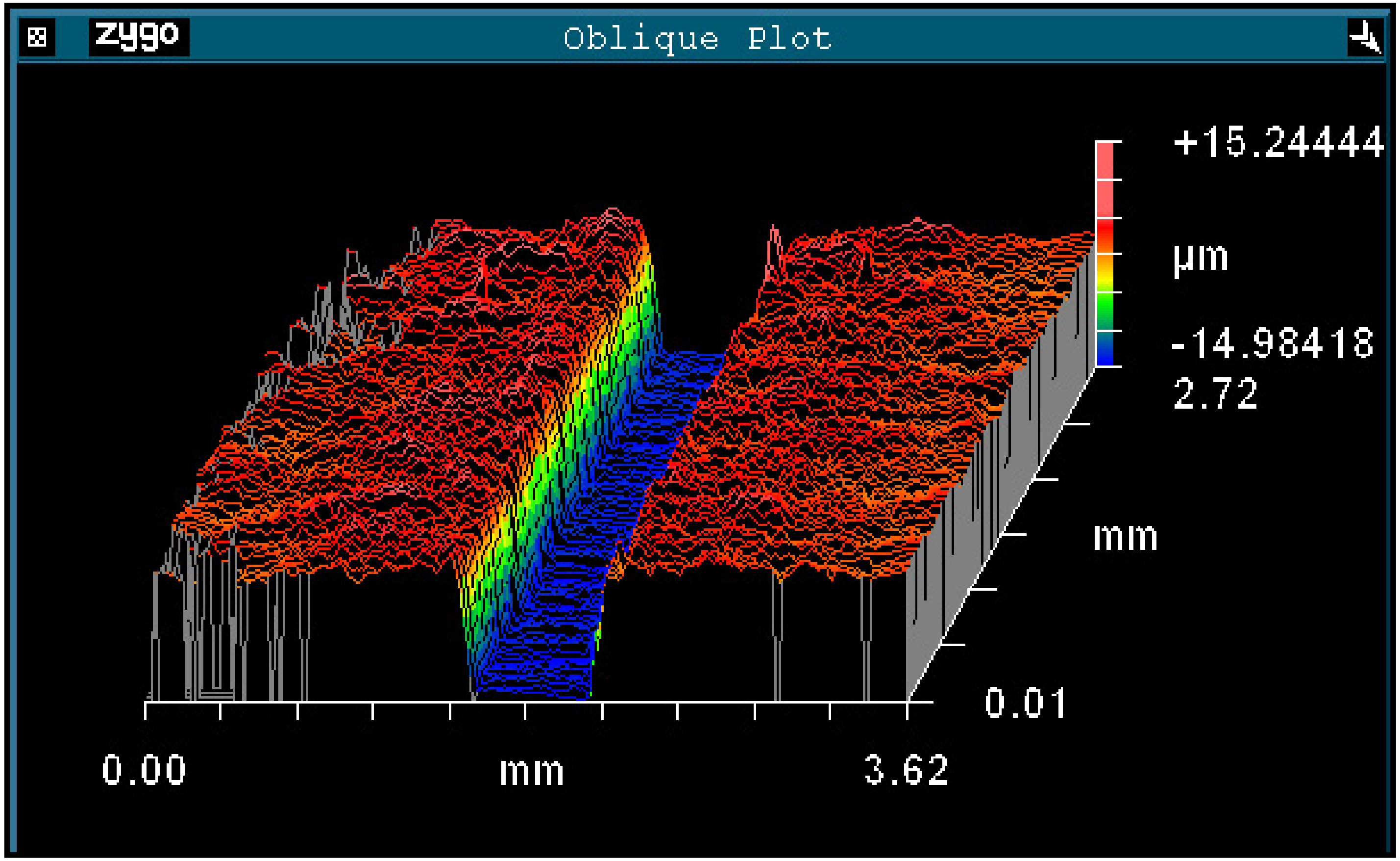
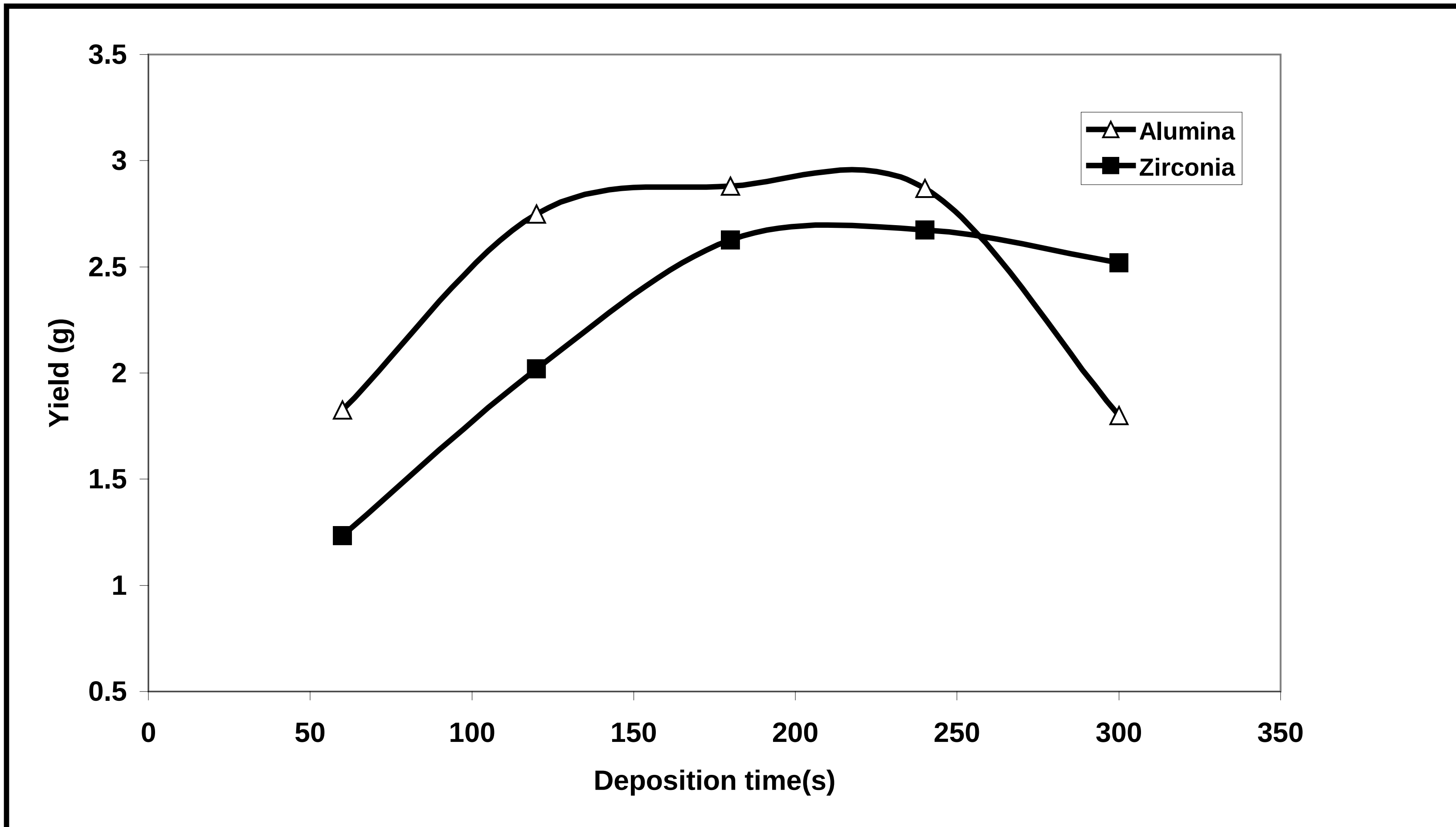
Measurement of EPD deposit thickness



Kinetics of EPD (thick alumina and zirconia deposits)



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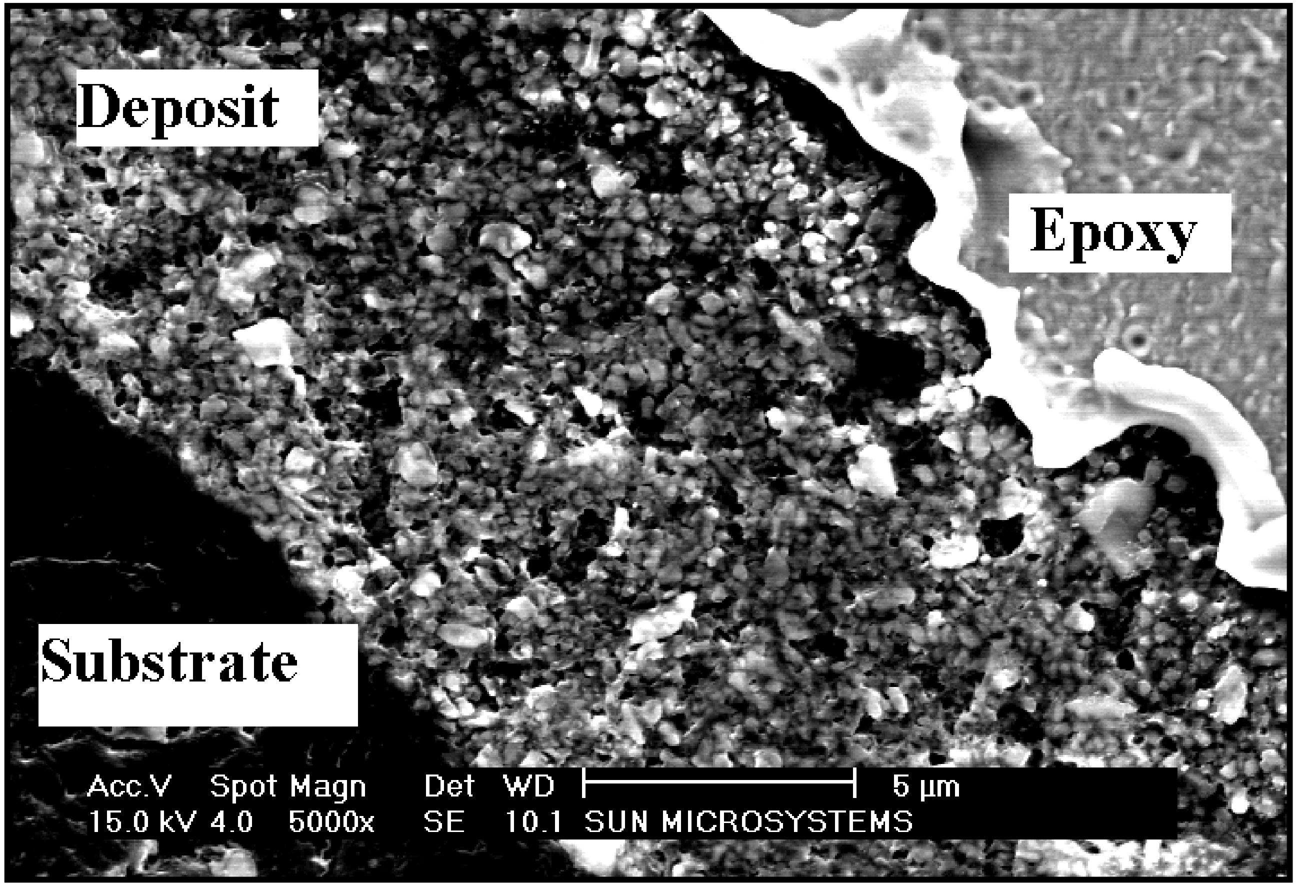
Cross section SEM of Alumina deposit obtained by EPD



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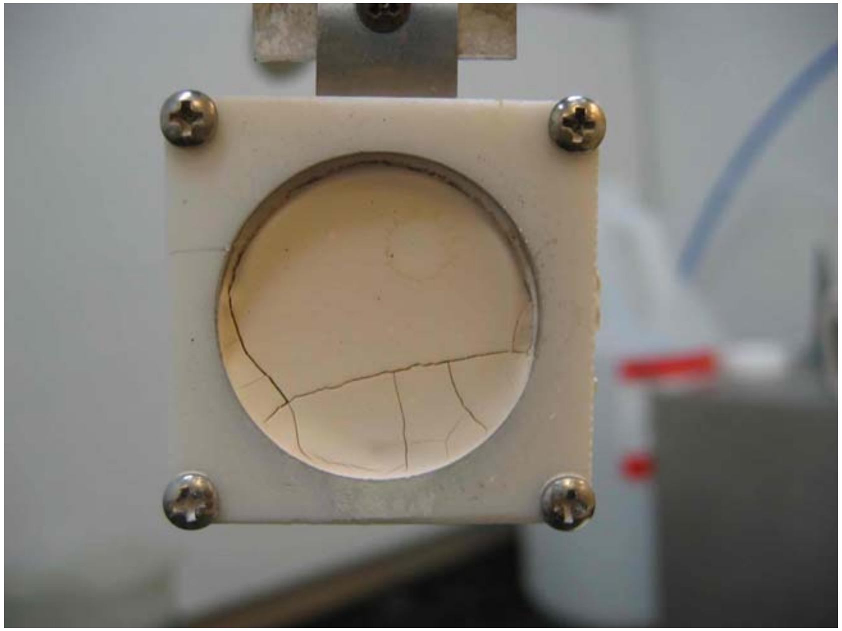
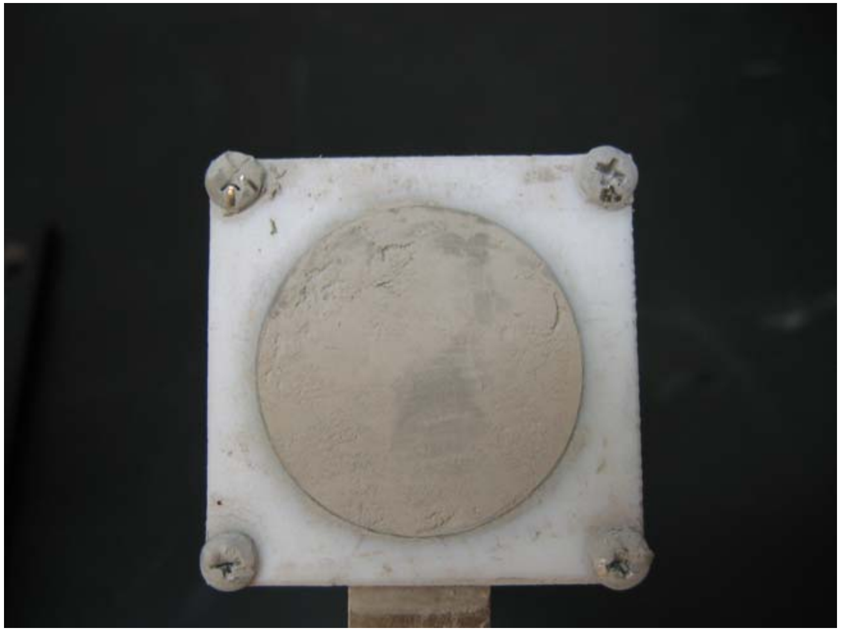
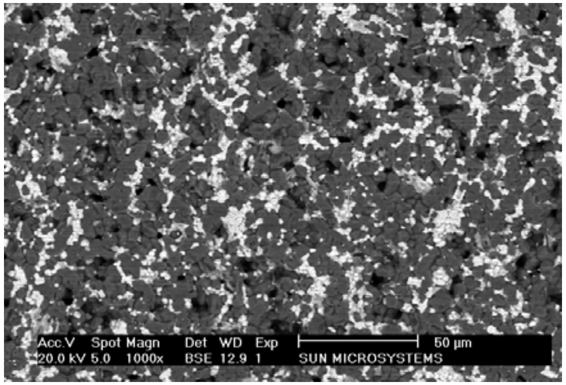
3-D EPD shaping

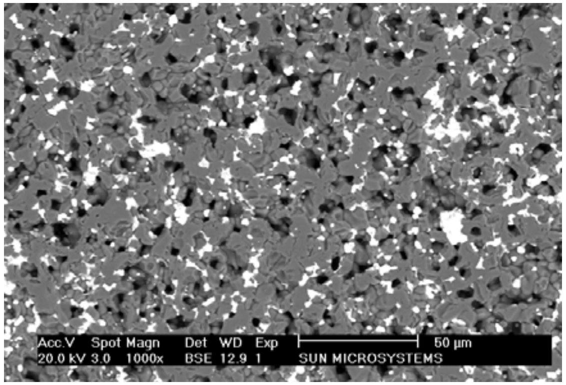
Cracking during drying

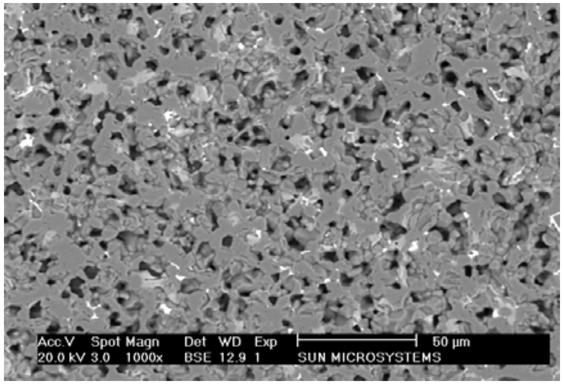




Microstructure of FGM cylinder







Zirconia rich side **Intermediate layer** **Alumina rich side**

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

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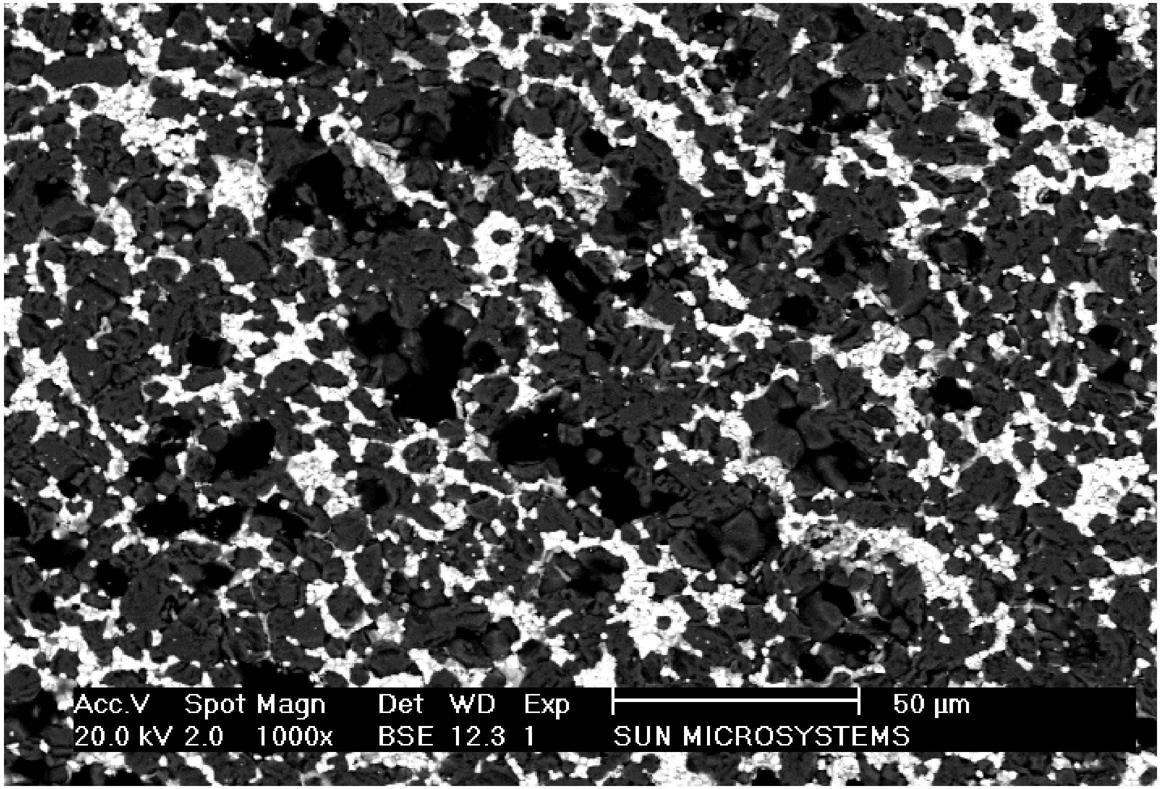
Microstructure of FGM disks



Alumina rich side of an FGM disk (FGM02)

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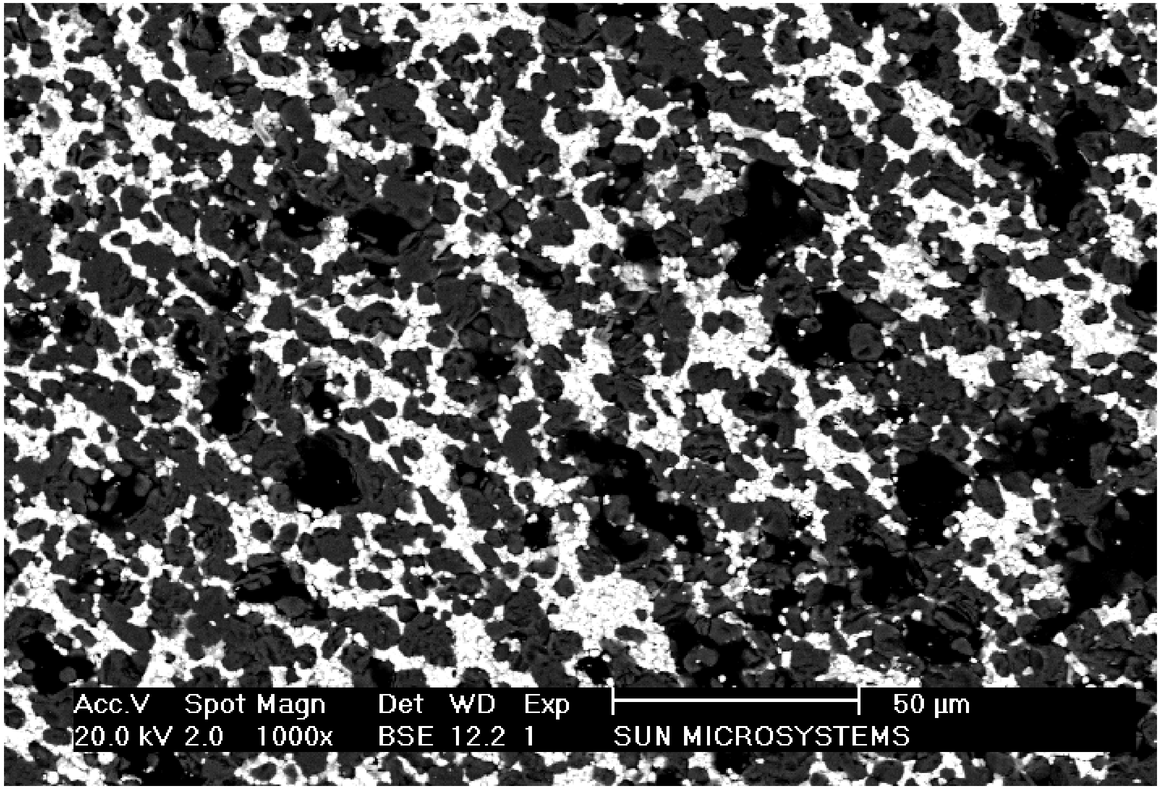
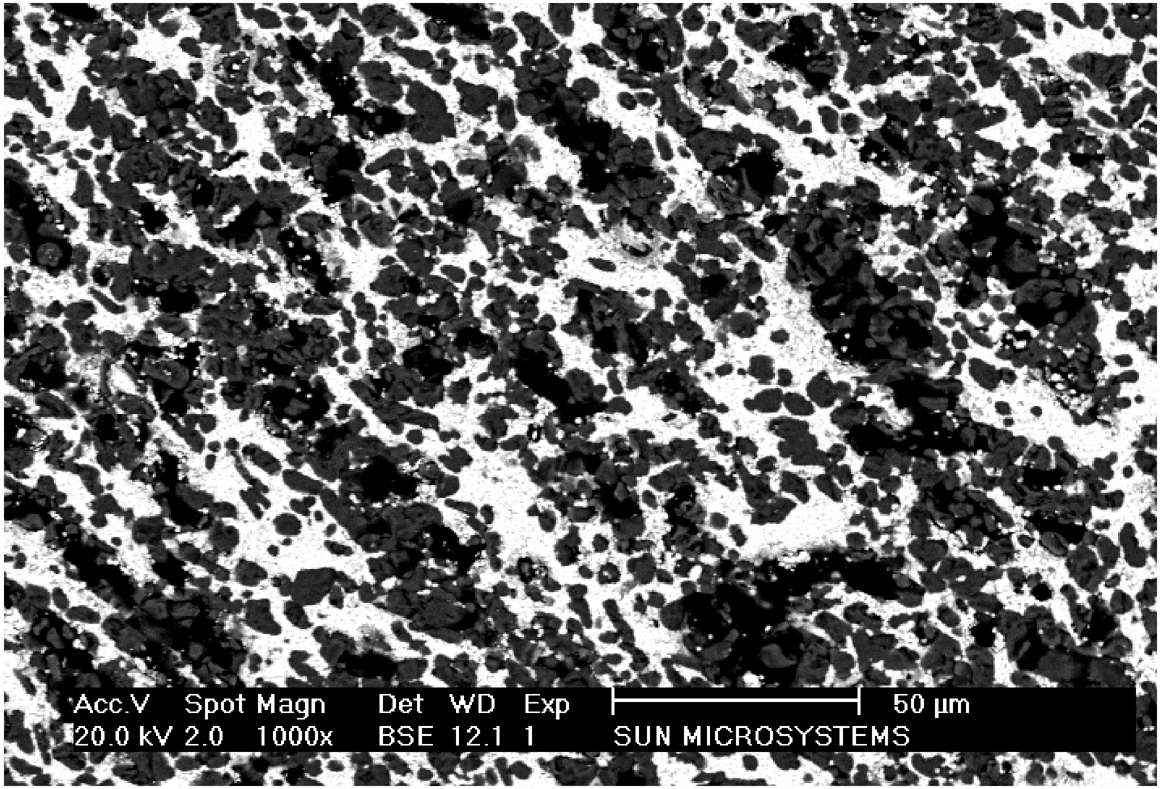
Microstructure of FGM disks



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

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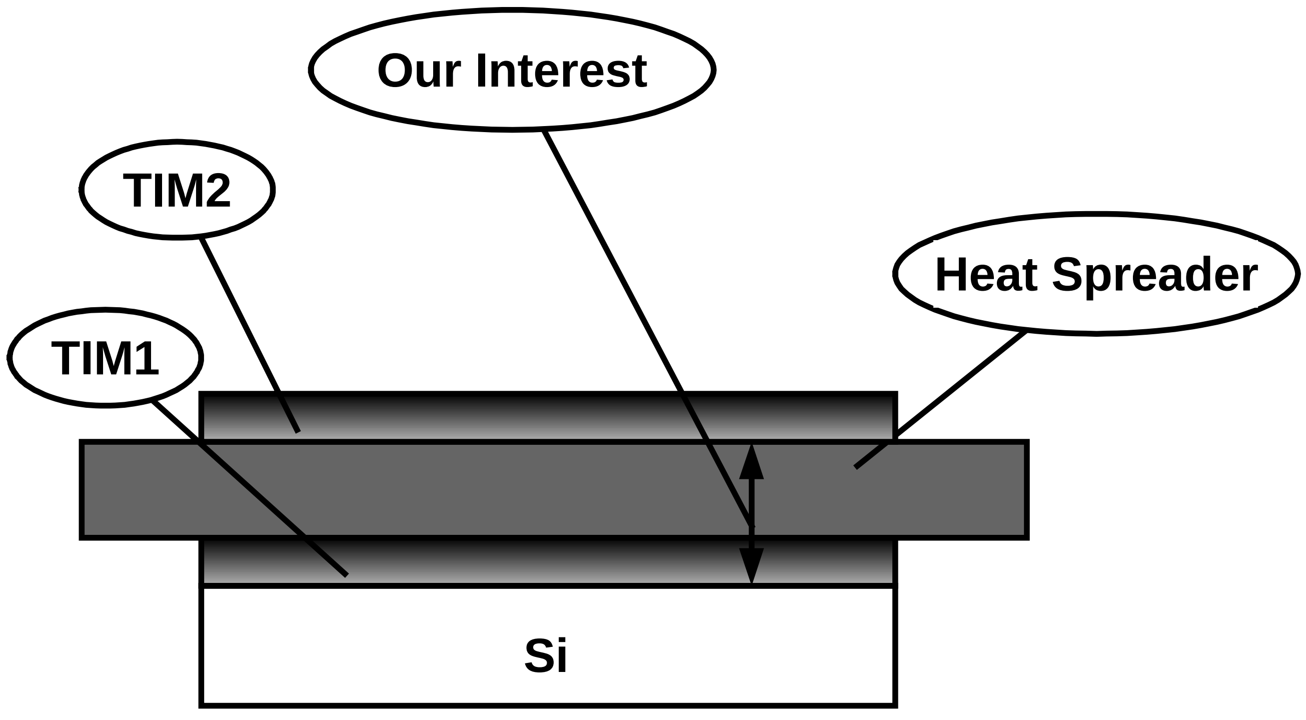
Background

- High thermal conductivity
- Resolve CTE mismatch



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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

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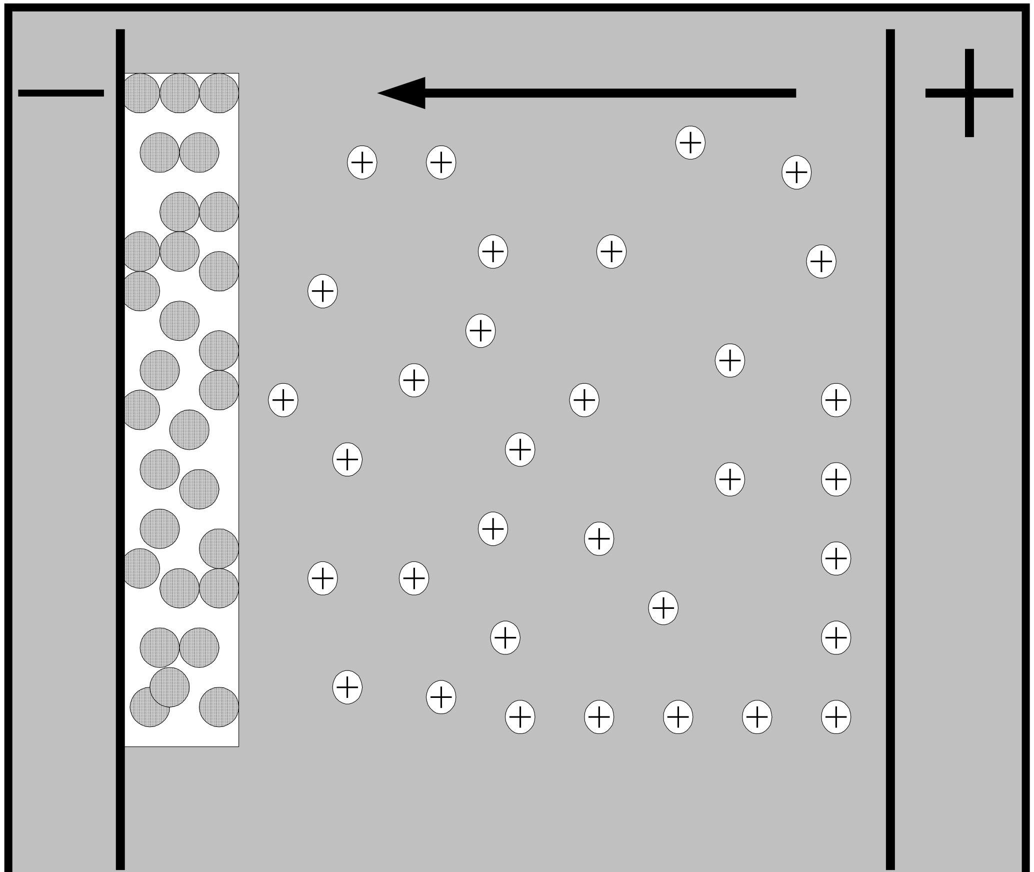
The approach-sequential deposition



Sequential Deposition:

EPD+Electroplating in two steps

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The Main Constitutive Relationship

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

Strain rate component

Bulk modulus:
Resistance to the volume change
<u>function of porosity</u>

Shear modulus:
Resistance to the shape change
<u>function of porosity</u>

Volume strain rate

Generalized viscosity:
corresponds to the constitutive properties of particle material

Effective sintering stress:
<u>function of porosity</u>

externally applied stresses — material resistance — sintering

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

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

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

$$W = \frac{1}{\sqrt{1-\theta}}\sqrt{\varphi\dot{\gamma} + \psi\dot{e}^2}$$

Formulations to model sintering of composite and FGM

Linear viscous case:

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

Skorohod model:

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

Sintering stress for composite materials:

$$P_L = -\frac{\alpha\gamma(1-\theta)N_c}{4}\left\{\begin{array}{l}\dfrac{\phi_s c_{ls}}{R_s(\phi_l + c_{ls}\phi_s)}[\phi_s + \dfrac{(1-\frac{\sqrt{3}}{2})\phi_l(1+c_{ls})}{1+c_{ls}-\sqrt{1+2c_{ls}}}] + \\ \dfrac{\phi_l c_{sl}}{R_l(\phi_s + c_{sl}\phi_l)}[\phi_l + \dfrac{(1-\frac{\sqrt{3}}{2})\phi_s(1+c_{sl})}{1+c_{sl}-\sqrt{1+2c_{sl}}}]\end{array}\right\}$$

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

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

$$\dot{\rho} = A \frac{\exp(-Q/R_g T)}{T} \frac{f(\rho)}{R^4}$$

$$f(\rho) = \frac{1-\rho}{\rho}$$

$$Q = \begin{cases} 440 + 5200\phi_{ZrO_2} \\ 700, 0.05 \le \phi_{ZrO_2} \le 0.95 \\ 615 + 1700(1-\phi_{ZrO_2}), \phi_{ZrO_2} > 0.95 \end{cases} \quad kJ/mol$$

*J. Wang, R. Raj, Activation energy for the sintering of two-phase alumina/ zirconia ceramics, J. Am. Ceram. Soc., 74 (1991) 1959

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

Equivalent particle size*: $R = \dfrac{R_l}{\chi(c_{sl}, \phi_s)}$

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

Bulk viscosity: $K_v = -\dfrac{P_L \rho}{\dot{\rho}}$

Shear viscosity: $S = 1.5 f(\rho) K_v = \dfrac{3(1-\rho)}{2\rho}$

*J. Pan, H. Le, S. Kucherenko, J. A. Yeomans, A model for the sintering of spherical particles of different sizes by solid state diffusion, Acta Mater., 46 (1998) 4671.

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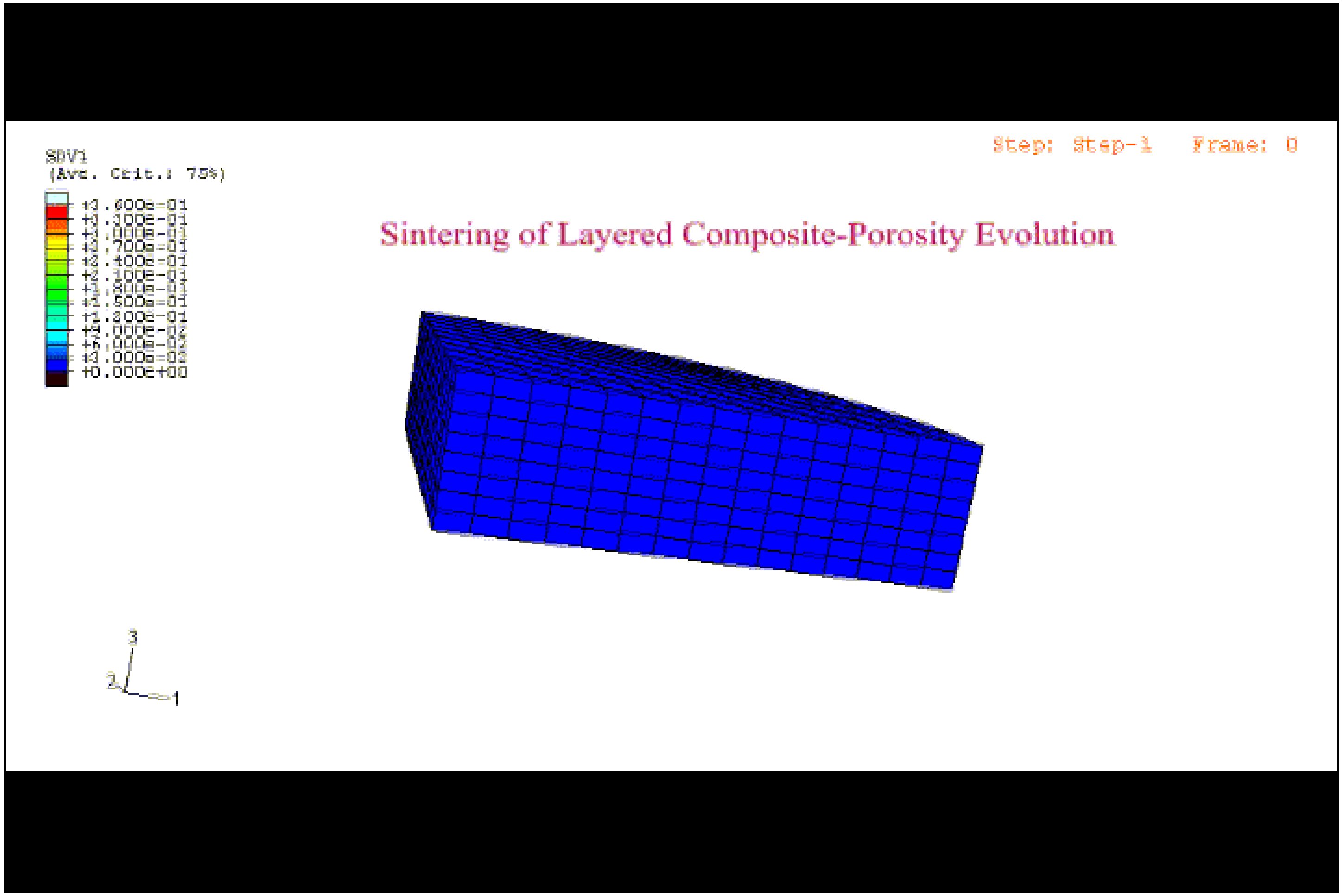
Finite Element Modeling of shape distortion of FGM sintering



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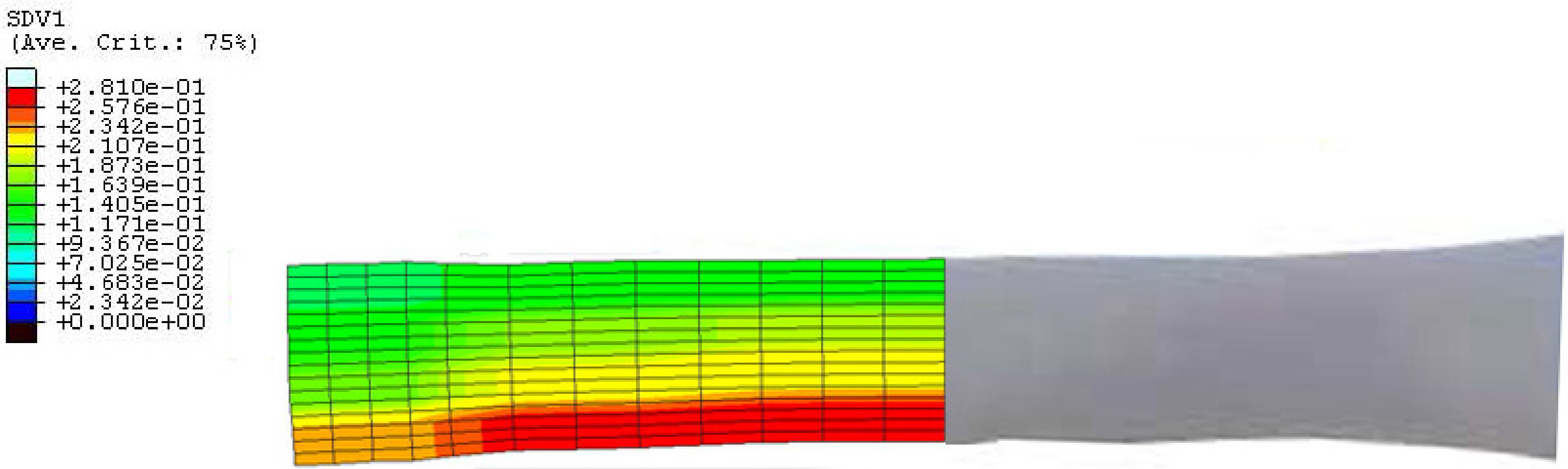
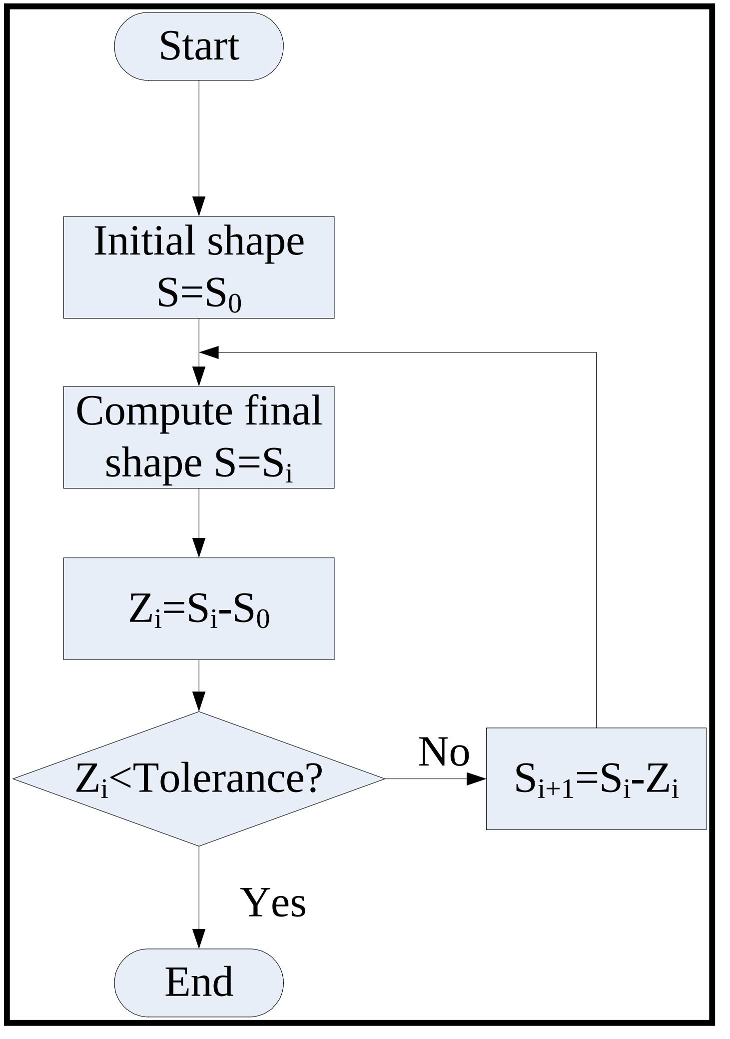
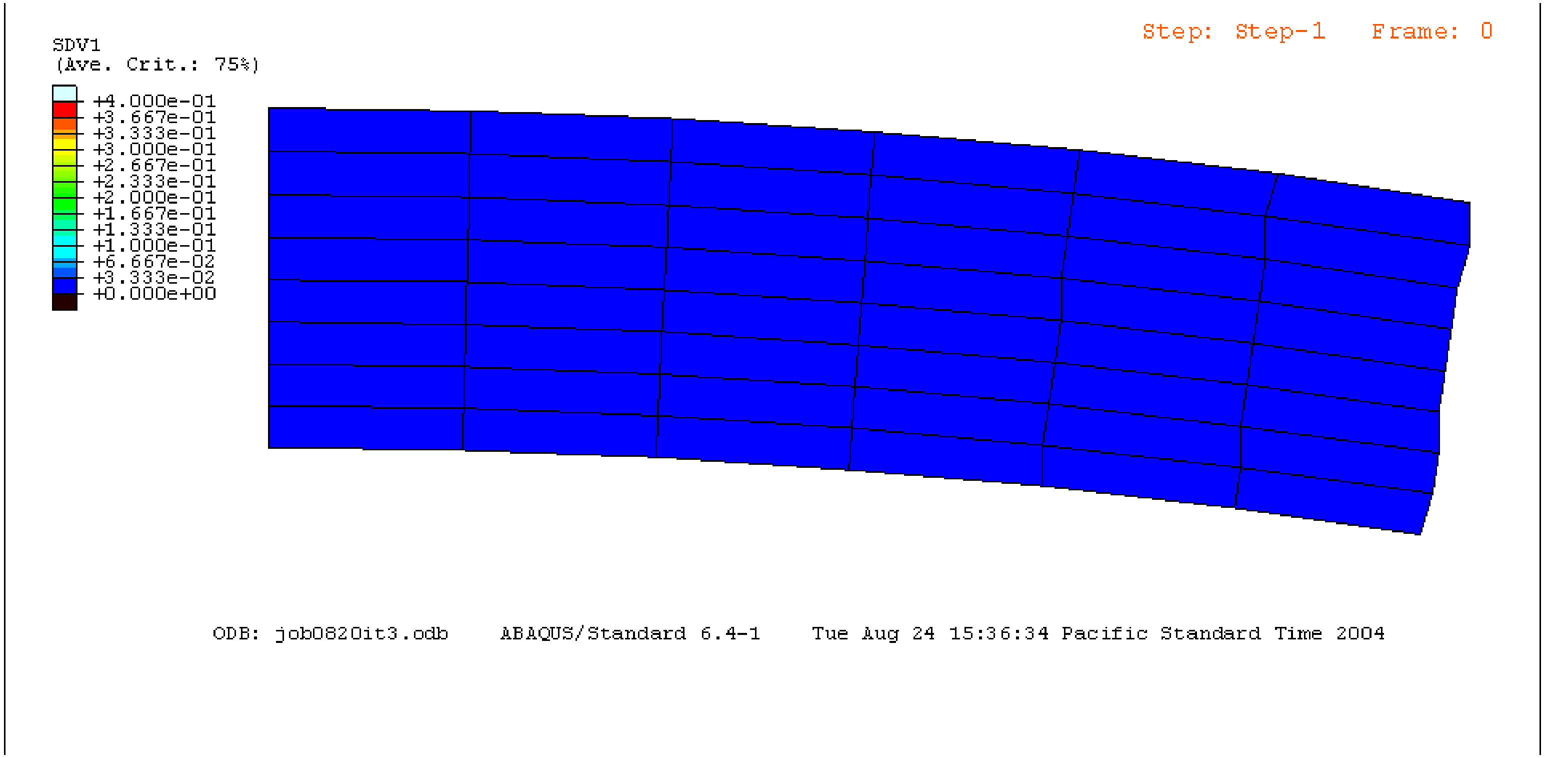
Comparison with experimental results



Iteration process to optimize initial shape of FGM



Inverse optimization of initial shape



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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 Al_2O_3/ZrO_2 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 Al_2O_3/ZrO_2 was simulated. The results showed that the FGM disk has undergone warping because of the difference between the sintering kinetics of Al_2O_3 and ZrO_2.**
- **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 Al_2O_3/Cu composite was successfully fabricated.**

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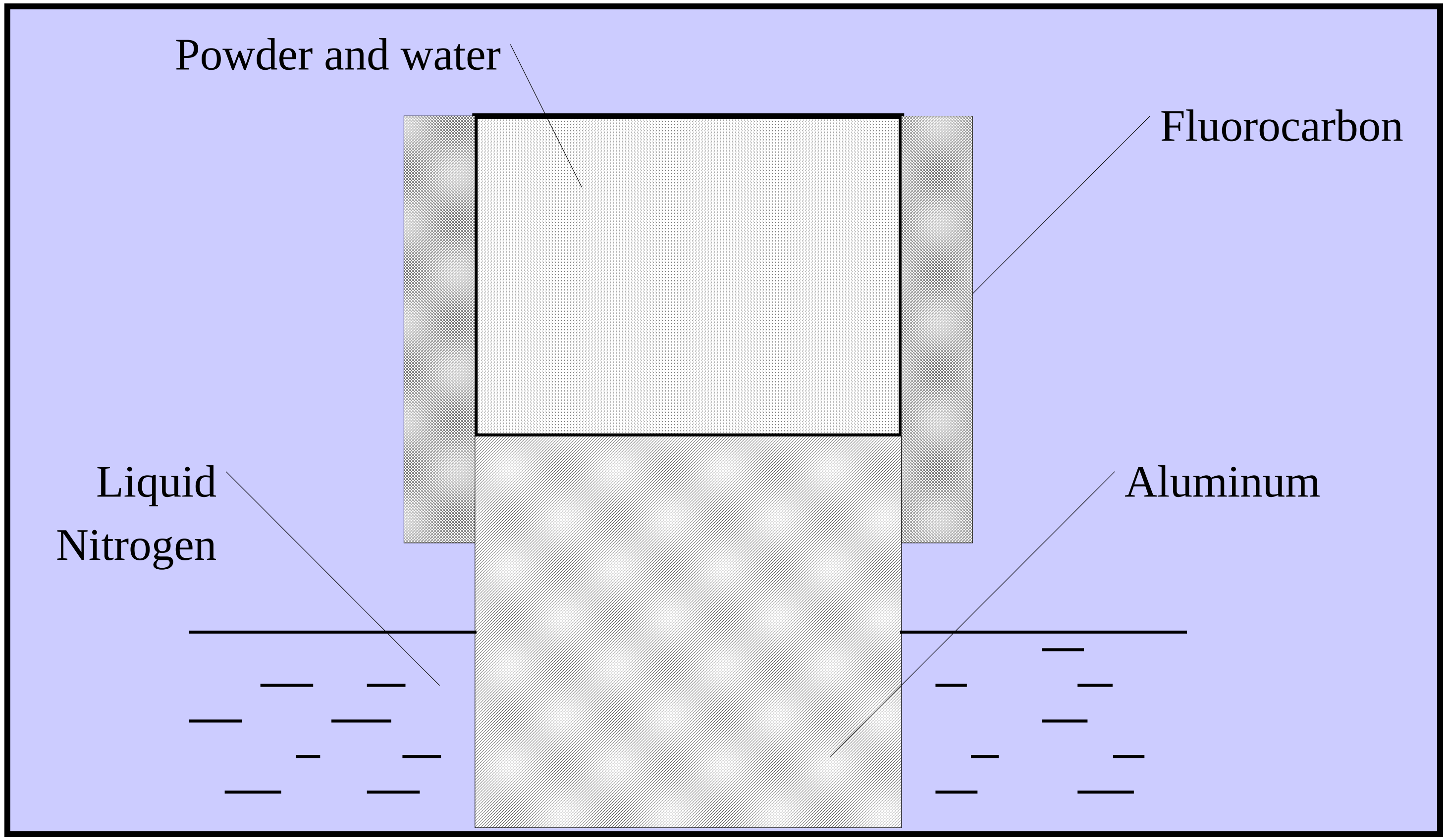
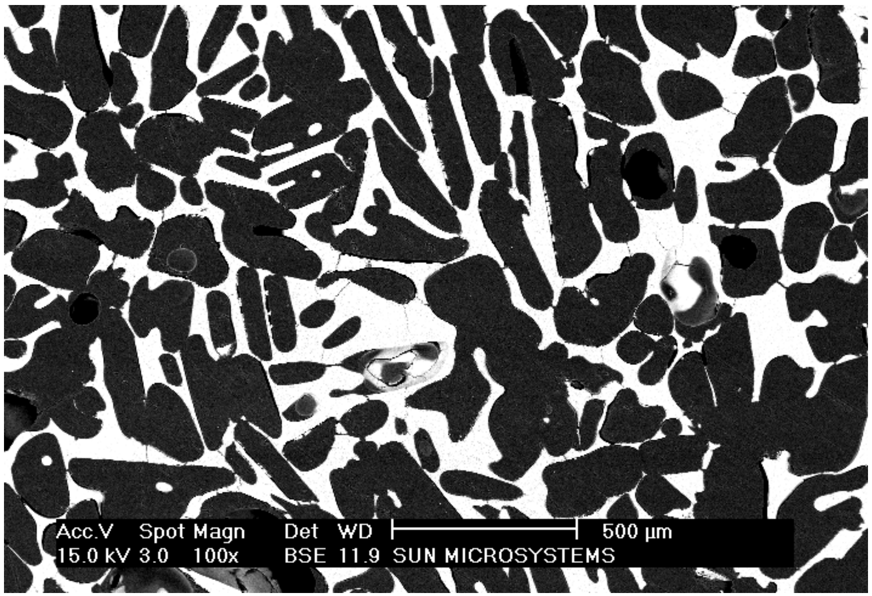
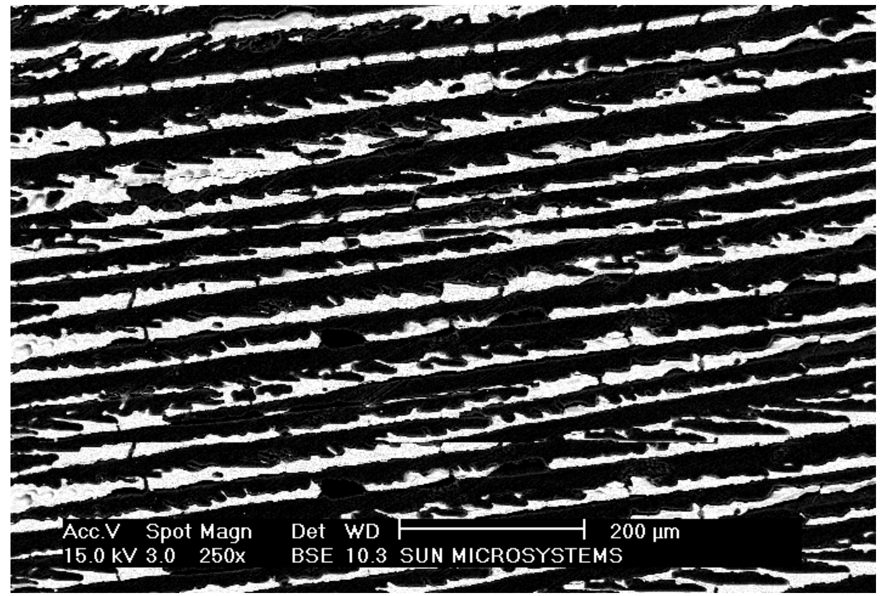
Possible future work: freeze drying



Microstructures





Regular freezing

Unidirectional freezing

CTE range of composite predicted by modeling