Processing of Nanostructured Ceramics:
Shaping, Sintering and Properties

Mehdi Mazaheri
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Introduction - Ceramics?
low density, low sensitivity to corrosion, high rigidity and hardness even at high temperature

Introduction (1)- Ceramics?
Toughening Mechanism in Ceramics

Crack deflection


Introduction (1)- Ceramics?
(1) Crack deflection
(2) Crack bridging
(3) Fibers pullout

(1) Crack blunting
(2) Crack bridging
Introduction (1)- Ceramics?

Grain refining

- Increasing of fracture toughness at room temperature
- High temperature mechanical properties (e.g., sliding accommodated by diffusion or interface reaction mechanisms)

\[ \epsilon(\sigma, T) = A \left( \frac{\sigma}{E} \right) \left( \frac{T}{T_0} \right)^p \]

Nano-structured ceramics reinforced by nano-particles or fibers

- 3 times higher fracture toughness (Zhang et al., Nature Materials, 2003)

Interest on Nanostructured Ceramics

Functional Ceramics

Structural Ceramics

Problems

From: Nanopowders

Shaping

Sintering

To: Nanostructured

Particle porosity

Shaping?

Sintering of n-3Y.TZP
Master Sintering Curve

Non-Isothermal Sintering
(Dilatometric Study)

ρ = ρ0 [(1/T) - (1/T)]

Temperature (°C)
Density vs. (1/T)

Non-Isothermal Sintering (Dilatometric Study)
Master Sintering Curve for n-3Y.TZP

Sintering of n-3Y.TZP - Mechanical Behaviour

HARDNESS

Effect of Sintering Techniques
- Spark Plasma Sintering (SPS)
- Phase Transformation Assisted
- Pressure Assisted Sintering (HP & HIP)
- Using Additives
- Millimeter and Microwave Sintering
- Two-step Sintering (TSS)

Grain Growth Suppression
Two Step Sintering

Simple!  
Physically Powerful!

<table>
<thead>
<tr>
<th>Nano Ceramics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttria</td>
<td>Chen et al., Nature</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>Mazaheri et al., J. Am. Ceram. Soc.</td>
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<tr>
<td>ZnO Varistors</td>
<td>Duran et al., J. Am. Ceram. Soc.</td>
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<tr>
<td>YAG</td>
<td>Chen et al., J. Am. Ceram. Soc.</td>
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<td>Titania</td>
<td>Mazaheri et al., Scripta Mat.</td>
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Experimental:

1. Raw Material  
2. Shaping  
3. Sintering  
4. Mechanical properties  
5. Microstructural Observation

- SEM-TEM  
- BET  
- XRD  
- UP, CIP, Slip casting

Conventional Sintering of n-ZnO

Sintering of n-ZnO
CS-TSS and HP

Grain Growth Suppression

Effect of Shaping Techniques

- Experimental:
  - Raw Material
  - Shaping
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  - Mechanical properties
  - Microstructural Observation

- Conventional Sintering of n-ZnO

1. Conventional sintering (Non-isothermal and Isothermal)
2. Two-step sintering
3. Phase transformation sintering
4. Hot pressing
5. Microwave sintering

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Effect of Shaping Techniques
2 Step Sintering of n-ZnO

Discussion

Summarizes Results of TSS

Hot Pressing of n-ZnO

Application?
Sintering of n-Titania
CS, TSS and assisted by phase-transformation

Processing of 8YSZ
Sintering methods: CS, TSS and Microwave Sintering
Shaping methods: Uniaxial pressing, Slipcasting
Processing of 8YSZ
Sintering methods: CS, TSS, MS

Microstructure and Mechanical behaviour

Conclusion 1
Spark Plasma Sintering

&

Thermo-Mechanical Properties
Pressure effect

For Coble creep based grain boundary sliding

In intermediate stage
\[
\frac{d(\Delta L/L_0)}{dt} = \frac{95}{2} \left( \frac{D_0 \delta T G}{kT} \right) \left( \frac{\rho \phi + \gamma_{sv}}{r} \right)
\]

In final stage
\[
\frac{d(\Delta L/L_0)}{dt} = \frac{15}{2} \left( \frac{D_0 \delta T G}{kT} \right) \left( \frac{\rho \phi + 2\gamma_{sv}}{r} \right)
\]

\(D_0\): GB diffusion coefficient, \(\delta\): GB width, \(G\): atomic volume, \(\rho\): grain size, \(k\): Boltzmann constant, \(T\): the absolute temperature, \(\gamma_{sv}\): the solid-vapour surface energy, \(r\): pore size, \(\rho_a\): applied stress.

Sintering or packing?

MgO Superplasticity

— Grain boundary sliding

0.3 T_m vs 0.5T_m

Strain rate: 10^7 s^-1

Compressive deformation under constant cross-head speed
**Consolidating YAG under high pressure**

In intermediate stage, $32\% \leq V_p \leq 10\%$, no linear relation

Final stage, $V_p \leq 10\%$, no linear relation

$$\frac{d(-\Delta L/L_0)}{dt} = \frac{9D_{\text{av}}\rho_0^2}{2G(K')^{1/2}}P_{\phi + \frac{1}{2}r}$$

Intermediate stage, $32\% \leq V_p \leq 10\%$, no linear relation

Final stage, $V_p \leq 10\%$, no linear relation

$$\frac{d(-\Delta L/L_0)}{dt} = \frac{15D_{\text{av}}\rho_0^2}{2G(K')^{1/2}}P_{\phi + \frac{1}{2}r}$$

**Densification rate**

- Grain sliding
- Diffusion

**Densification rate: P at T_f**

Strain rate: $10^{-2} s^{-1}$

- $100P$
- $75P$
- $50P$
- $25P$

**Relative Density**

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**Strain rate: $>10^{-4} s^{-1}$**

- $100MPa$
- $75MPa$
- $50MPa$
- $25MPa$

**Grain Sliding**

**Diffusion**

**J. of Euro Ceram. Soc. (2007), 27(11), 3331-3337**
Densification while retarding solution-reprecipitation

Bright-field TEM image, beta-powder, grain size: 76 nm, SPS 1500°C under 50 MPa for 3 min. Note the aggregate feature of the large grains.

Introduction 2- Anelasticity

Anelastic Relaxation

\[ \Delta \sigma = \sigma - \sigma_e = \Delta \sigma + \Delta \sigma_e \]

Introduction 2- Mechanical spectroscopy

Periodic stress: \( \sigma = \sigma_e + \sigma_d \)

Strain response: \( \varepsilon = \varepsilon_e + \varepsilon_d \)

Mechanical spectroscopy is applicable for investigations of significant features such as local distortion of lattice (point defect relaxation), dislocation motions and grain-boundary sliding processes.

Debye equations

\[ \tan \theta = \frac{\lambda}{\beta n} = \frac{\lambda}{\beta} n \]

Introduction (2)- Ceramics?

Grain refining

Increasing of fracture toughness at room temperature

High temperature mechanical properties (G.B. sliding accommodated by diffusion or interface reaction mechanisms)

\[ \epsilon = A \left( \frac{\sigma}{E} \right)^n \]

Nano-structured ceramics reinforced by nano-particles or fibers


3 times higher fracture toughness (Zhang et al., Nature Materials, 2003)

\[ f_1 \sigma + f_2 \theta = \varepsilon + \varepsilon_d \]
Introduction 2- Mechanical spectroscopy

High temp. mechanical behavior

Crystallization in glassy phase

Onset of creep

Mechanical spectroscopy

* Forced torsion pendulum in sub-resonant mode
* Temperature: RT - 1600 K
* Frequency: 10⁻⁴ and 10 Hz
* Vacuum: 10⁻³ Pa

Introduction (3) – Application of M.S. in ceramics

High-temperature plasticity of fine-grained ceramics proceeds by mutually accommodating grain boundary sliding and diffusion creep.

Grain boundary sliding creates voids or overlaps that have to be accommodated by diffusion.

Diffusion processes are:
- Nabarro-Herring creep
- Coble creep
First results (2) – 3Y.TZP

Donzel et al., Acta Mater. 2000

Theoretical model for GB sliding

Lakki’s model for GB sliding

\[ \tan(\phi) = \frac{G}{d} \frac{\phi^2}{(\phi^2 + k^2)^{1/2} + \phi^2} \]

\[ \sigma_y = \frac{\delta}{\eta} K_\gamma K^2 G \]

\[ K(\phi) = \frac{\sigma_y}{\phi^2 + k^2} \]

\[ K = \text{cat} \]

\[ K = 0 \]
What is the aim of this work?

Silicon nitride based ceramics (SiAlON)

Yttria Stabilized Zirconia (3Y.TZP)

Spark plasma sintering (SPS)

Materials

Hot Press & Spark Plasma Sintering

Hot Press

2073 K, 35 MPa and 4 h

Materials

Ca-SiAlON (Si₃N₄, AlN, CaN)

Ca-SiAlON (Si₃N₄, AlN, CaO)

Ca₃Al₂O₆N₁₆₋ₓ

x=0.4, 1.4

Ca₃Si₃Al₂O₆Nₓ

x=0.4, 1.4

Si₃N₄ + 6wt% Al₂O₃ + 6wt% Y₂O₃

Two-step sintering

SPS apparatus in Lyon

Hot Press & Spark Plasma Sintering

1773 K, 50 MPa and only 3 min

Si₃N₄ + 6wt% Al₂O₃ + 6wt% Y₂O₃
Si$_3$N$_4$ based ceramics


1. Equiaxed grains (as same!)
2. Grain size (as same!)

(Y4O and Y4N)
Results (Yb\textsubscript{4}O and Yb\textsubscript{4}N)

Si\textsubscript{3}N\textsubscript{4} based ceramics

- Real Si\textsubscript{3}N\textsubscript{4} system

To be published in Acta Materialia
Results

Mechanical loss spectrum of Si$_3$N$_4$ Processed via SPS

First results (2) – 3Y.TZP

F= 1 Hz
Heating rate = 1 K/min
As received Si$_3$N$_4$

(1) Pure zirconia
(2) 3Y-TZP + 3 wt% CNTs
(3) 3Y-TZP + 3 wt% CNTs (2nd test) + 30h anneal
Power law equation of creep

\[ \dot{\epsilon}(\sigma, T) = A \left( \frac{\sigma}{G} \right)^n \exp \left( \frac{-\Delta H_{\text{act}}}{R T} \right) \]

\[ \ln(\dot{\epsilon}) = \ln(A) + n \ln \left( \frac{\sigma}{G} \right) - \frac{\Delta H_{\text{act}}}{R T} \]

\[ \delta(\log(\dot{\epsilon})) = \delta(\log(\sigma)) - \frac{\Delta H_{\text{act}}}{R T} \delta(\log(T)) \]
Slope \( p/n = -0.319 \)

\[ \log(\tan(\theta)) = 3Y-TZP + 1.5\% \text{CNTs} \]

As received

Aneal temperature = 1600 K

Creep model:
Interface reaction, \( p=1, n=3 \)

This model to be submitted by end of year

**What is the plan for future?**

Is the model correct?

1- More investigation on SPS results
2- Different additives and microstructures

Processing new nano-CMCs by
1- grow up CNTs directly (in collaboration with Dr. Magrez)
2- application of TSS and SPS (in collaboration with Prof. Shen and Prof. Fantozzi)
Acknowledgment

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