Applications of Spark Plasma Sintering

Takashi Goto

Institute for Materials Research, Tohoku University, Japan

Outline

1. Introduction
   - Spark Plasma Sintering (SPS)
2. Transparent Lu-based Oxide Ceramics by SPS
   - Lu₂O₃, Lu₂Al₅O₁₂ (LuAG), Lu₂Ti₂O₇, Lu₃NbO₇, Lu₂Hf₂O₇
3. Non-Oxide High-Temperature Ceramic Composite by SPS
   - Carbide-Boride Eutectic Composite (SiC-ZrB₂)
4. Covalent Bond Ceramic Composite by SPS
   - cBN-Based Composites
5. Summary
**SPS Forum of Japan**

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>SPS Started in Japan</td>
</tr>
<tr>
<td>1992</td>
<td>First SPS in IMR</td>
</tr>
<tr>
<td>1996</td>
<td>Forum in IMR</td>
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<tr>
<td>2000</td>
<td>Forum in IMR</td>
</tr>
<tr>
<td>2006</td>
<td>New SPS in IMR</td>
</tr>
<tr>
<td>2009</td>
<td>Forum in IMR</td>
</tr>
<tr>
<td>2012</td>
<td>17th Forum in IMR</td>
</tr>
</tbody>
</table>

![Papers of SPS](image)

**Spark Plasma Sintering**

- ON-OFF direct pulse voltage, current
- Pressure/Current
- Graphite spacer
- Graphite punch
- Graphite die
- Vacuum chamber
- Materials

![Spark Plasma Sintering Diagram](image)
Transparent Materials

Single crystal
- High transparency
- Expensive, size and composition limitation, brittle

Polycrystalline
- Opaque
- Cost effective, no size-limit, wide range of composition, good mechanical property

1950s: First translucent Al₂O₃ ceramics were prepared (R.L. Coble), but contained many scattering sources: pores, grain boundary phases.

1990s: Laser oscillation was demonstrated using Nd:YAG ceramics (A. Ikose).

- Polycrystalline ceramics with no pores, no secondary phases, less defects and atomically clean grain boundary can be transparent.
  - We can prepare transparent ceramics having high melting point, which are difficult to grow single crystals.
  - Ceramics sometimes shows excellent property than single crystals.

Transparent Single Crystalline Ceramics

Verneuil Method

Czochralski Method

Floating Zone Method

BaTi₂O₅
Spark Plasma Sintering (SPS)

**Strategy**
- Easy way
- Cost-effective
- Short-time
- Low-temperature

**Characteristics:**
- Consolidation in a short time and at a relatively low sintering temperature
- Precise pressure control
- High speed cooling

SPS and Post-annealing

- Consolidation in a short time and at a relatively low sintering temperature
- Precise pressure control
- High speed cooling

**Sintering Mechanism**

<table>
<thead>
<tr>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image Cu" /></td>
<td><img src="image2.png" alt="Image Ni" /></td>
</tr>
</tbody>
</table>

- **1st Stage** (Density < 65%)
  - Neck growth and re-aggregation of particles

- **2nd Stage** (Density = 65~92%)
  - Continuous pore channel
  - Spherical to polygonal pores

- **3rd Stage** (Density > 92%)
  - Diffusion and disappear of pores through grain-boundary
Spark Plasma Sintering (SPS)

I. Increased packing density
II. Sintering with increased grain sliding and diffusion
III. Removal of the pores via diffusional creep

Two-step sintering profile for no/minimal grain growth
I & II. Pressure loading
III. Heating rate

Lutetium (Lu)-based Oxides

Lu$_2$O$_3$ (Bixbyte, $Ia3$)
LuAG (Garnet, $Ia3d$)
C-type rare-earth

Pyrochlore
Lu$_2$Ti$_2$O$_7$

Defect fluorite
Lu$_2$Hf$_2$O$_7$
Lu$_2$NbO$_7$

Lu$^{3+}$ (C$_2$)
O
Lu$^{3+}$ (S$_6$)
AlO$_6$
Lutetium (Lu)-based Oxides

- Practical transparent Lu-based oxide
  
  \[ \text{Lu}_2\text{O}_3 \]  
  (Hot pressing + Hot isostatic pressing)
  
  \[ \text{Lu}_3\text{Al}_5\text{O}_{12} \text{(LuAG)} \]  
  (Vacuum sintering)


Main issues: **High sintering temperature** and **large grains**

There is no report on Lu$_2$O$_3$ and LuAG prepared by SPS.

- New Lu-based oxides

  There is no report on **optical property** of Lu-based oxide single crystal and sintered body.

Introduction - Lu$_2$O$_3$

Previous study on transparent Lu$_2$O$_3$ ceramic

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis method</th>
<th>Sintering conditions</th>
<th>Grain size</th>
<th>Transmittance at 550 nm (Thickness)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 at% Nd:Lu$_2$O$_3$</td>
<td>NPS(H$_2$)</td>
<td>2153 K for 8 h</td>
<td>~50 μm</td>
<td>64% (1.4 mm) 50% for Lu$_2$O$_3$</td>
<td>D. Zhou, J. Am. Ceram. Soc., 92, 2182-7 (2009).</td>
</tr>
</tbody>
</table>

VS: vacuum sintering, NPS(H$_2$): pressureless sintering in H$_2$

- **Transparent** Lu$_2$O$_3$ ceramics have been prepared by conventional sintering techniques.
- The main issues are **high sintering temperature** (over 1973 K), **long sintering time** (> 5 h) and **large grains** (> 50 μm).

There is no report on preparation of Lu$_2$O$_3$ by SPS.
Polycrystalline Ceramic Process

![Diagram of the Polycrystalline Ceramic Process]

Table 1: Sintering techniques to prepare transparent ceramic

<table>
<thead>
<tr>
<th>Sintering Temperature</th>
<th>Vacuum sintering</th>
<th>Pressure-less sintering in H₂</th>
<th>Hot pressing</th>
<th>Hot isostatic pressing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Sintering time</td>
<td>Long</td>
<td>Long</td>
<td>Long</td>
<td>Long</td>
</tr>
<tr>
<td>Grain size</td>
<td>Large</td>
<td>Large</td>
<td>Medium</td>
<td>Small</td>
</tr>
</tbody>
</table>

Issues:
- Home-made powder
- High sintering temperature
- Long sintering time
- Large grains

Experimental Procedure

![Diagram of the Experimental Procedure]

**STEP I**

- Pre-treatment of starting powder

**STEP II**

- SPS shaping and densification

**STEP III**

- Post-annealing

**Sintering profile**

- Preload pressure ($P_{\text{pre}}$): 10-100 MPa
- Final Pressure: 100 MPa
- Heating rate ($V_H$): 0.08-1.67 K s⁻¹
- Sintering temperature: 1723 K
- Holding time: 2.7 ks

**Phase**

- XRD

**Microstructure and grain size ($d$):**

- FESEM

**Relative density (RD):**

- Archimedes method

**Transmittance ($T$):**

- UV-VIS-IR
Sintering Curves of Lu$_2$O$_3$ at Different $P_{\text{pre}}$ and $V_F$

$V_F = 0.17 \text{ K s}^{-1}$

- Relative density increased significantly at the point where final pressure was applied under low $P_{\text{pre}}$.

- Relative density increased significantly at a high heating rate.

$P_{\text{pre}} = 10 \text{ MPa}$

Effect of $P_{\text{pre}}$ on Microstructure of Lu$_2$O$_3$ at $V_F = 0.17 \text{ K s}^{-1}$

- Grain size decreased with increasing final pressure.
Effect of $P_{\text{pre}}$ on Microstructure and Transmittance of Lu$_2$O$_3$

- Grain size decreased with increasing final pressure.
- Transmittance exhibited the maximum at $P_{\text{pre}}=30$ MPa at $V_F=0.17$ Ks$^{-1}$.

Effect of $V_F$ on Microstructure and Transmittance of Lu$_2$O$_3$

- Porosity slightly increased with increasing $V_F$.
- Transmittance exhibited the maximum at $V_F=0.03$ Ks$^{-1}$.

at $P_{\text{pre}}=30$ MPa
Effect of annealing on Transmittance of Lu$_2$O$_3$

Annealing can improve the transparency.
The optimal annealing temperature was 1323 K.

Comparison on Transparency and Grain Size of Lu$_2$O$_3$

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<th>Grain size</th>
<th>Transmittance at 550 nm(Thickness)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 at. % Nd:Lu$_2$O$_3$</td>
<td>VS</td>
<td>about 1973 K for 5 h</td>
<td>Not given</td>
<td>Not given (near theoretical value)</td>
<td>J. Lu, Appl. Phys. Lett., 81, 4324-6 (2002).</td>
</tr>
<tr>
<td>3 at.% Nd:Lu$_2$O$_3$</td>
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<tr>
<td>5 at.% Eu:Lu$_2$O$_3$</td>
<td>VS+ HIP</td>
<td>1873-1923 K for 2h 2123 K, 200 MPa for 4 h</td>
<td>&gt;10 μm</td>
<td>Not given (high) (1.6-1.7 mm)</td>
<td>Z.M. Seeley, Opt. Mater., 33, 1721-6 (2011).</td>
</tr>
<tr>
<td>10 at.% Yb:Lu$_2$O$_3$</td>
<td>HP + HIP</td>
<td>1873 K for 2h 1873 K, 200 MPa for 2 h</td>
<td>20–50 μm</td>
<td>~80% (3 mm)</td>
<td>J. Sanghera, Opt. mater., 33, 675-4 (2011).</td>
</tr>
<tr>
<td>5 at.% Yb:Lu$_2$O$_3$</td>
<td>NPS(H$_2$)</td>
<td>1953 K for 45 h</td>
<td>Not given</td>
<td>48% (1 mm)</td>
<td>H.J. Zhang, Opt. Mater., In press.</td>
</tr>
<tr>
<td>Lu$_2$O$_3$</td>
<td>SPS</td>
<td>1723 K, 100 MPa for 2.7 ks</td>
<td>0.91 μm</td>
<td>71.4 % (1 mm)</td>
<td>This work</td>
</tr>
</tbody>
</table>

VS: vacuum sintering, HP: hot pressing, NPS(H$_2$): pressureless sintering in H$_2$, HIP: hot isostatic pressing
Transmittance of LuAG after Annealing

- Transparent LuAG was obtained at a relative low sintering temperature of 1723 K.

Effect of $T_{SPS}$ on Microstructure and Transmittance of Lu$_2$Ti$_2$O$_7$

- The transmittance was 57 and 74% at a wavelength of 550 and 2000 nm, respectively.

Journal of the American Ceramic Society, 94(2011) 3851. An, Ito, Goto
Effect of $T_{\text{SPS}}$ on Transmittance of Lu$_3$NbO$_7$

- Transmittance increased with increasing $T_{\text{SPS}}$ from 1573 K (a) to 1773 K (d).
- It became opaque at $T_{\text{SPS}}$ 1823 K (e).

Effect of Annealing on Transmittance of Lu$_3$NbO$_7$

- The rim part became transparent at 1023 K (a).
- The whole part became transparent at 1123-1323 K (b-c).
- It became opaque at 1423 K.
**Transparent Lu-based Oxide by SPS**

<table>
<thead>
<tr>
<th>Lu₂O₃</th>
<th>Lu₂Ti₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>S transparent</td>
<td>S transparent</td>
</tr>
<tr>
<td>S transparent</td>
<td>S transparent</td>
</tr>
<tr>
<td>SPS transparent</td>
<td>SPS transparent</td>
</tr>
</tbody>
</table>

Lu₂O₃  : Lu₂Ti₂O₇

As-sintered          After annealing          After annealing

**LuAG**

<table>
<thead>
<tr>
<th>Lu₃NbO₇</th>
<th>Lu₃Hf₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>S transparent cer</td>
<td>S transparent cer</td>
</tr>
<tr>
<td>S transparent cer</td>
<td>S transparent cer</td>
</tr>
</tbody>
</table>

As-sintered          After annealing

The text is 30 mm below the specimens.

All the specimens are around 10 mm in diameter with 1 mm thickness.

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**Carbide-Boride Eutectic Composites**

- **Carbides:** B₄C, TiC, SiC, ZrC, etc.
- **Borides:** TiB₂, ZrB₂, etc.

- **Advantages**
  - High temperature structural materials
  - Ultrahigh melting point and high hardness
  - Poor machining performance

- **Self-assembled composites**
- Eutectic or peritectic reaction

- **Preparation methods**
  - Floating zone melting
  - Arc melting

**Eutectic composites**

- B₄C-TiB₂
- B₄C-SiC
- B₄C-TiB₂-SiC
- TiC-TiB₂
- TiC-SiC
- TiC-TiB₂-SiC
- ZrC-TiB₂
- ZrC-ZrB₂
- SiC-ZrB₂
Phase Diagram of TiC-TiB₂-SiC Ternary System

- Eutectic composites in TiC-TiB₂-SiC system were prepared by arc-melting.

Oxidation Protection System of Shuttle

- Nose Cap, Chin Panel, and Seals
- Forward External Tank Attachment "Arrowhead" Plate
- Wing Leading Edge Panels and Seals
Active Oxidation and Bubble Formation at High-Temperature

Properties of ZrB₂-SiC Composites

- ZrB₂-SiC is an eutectic system.
- Eutectic composition is not clear.
- Thermal and electrical properties: No report
- Mechanical properties

<table>
<thead>
<tr>
<th>SiC content (vol%)</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Strength (MPa)</th>
<th>Toughness (MPa m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>489</td>
<td>23 ± 0.9</td>
<td>565 ± 53</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>10</td>
<td>450</td>
<td>24 ± 0.9</td>
<td>713 ± 48</td>
<td>4.1 ± 0.3</td>
</tr>
<tr>
<td>20</td>
<td>466</td>
<td>24 ± 2.8</td>
<td>1023 ± 94</td>
<td>4.4 ± 9.2</td>
</tr>
<tr>
<td>30</td>
<td>484</td>
<td>24 ± 0.7</td>
<td>1089 ± 152</td>
<td>5.3 ± 0.5</td>
</tr>
</tbody>
</table>

Microstructure of ZrB₂-SiC Composites

- ZrB₂-SiC composites
- ZrB₂: gray
- SiC: black
- 40ZrB₂-60SiC (mol%)
- Uniform microstructure

Sintering of ZrB₂-SiC Composites During SPS

- Shrinkage completion temperature increased with increasing SiC content.
- Shrinkage of 80 mass% SiC started at 2113 K and displacement continued after holding at 2273 K.
- Shrinkage of composites containing 20-60 mass% SiC completed within 60 s at 2273 K.
- Addition of SiC up to 80 mass% improved densification of ZrB₂.
Relative Density of ZrB₂-SiC Composites

0-100 mass% SiC, 2073-2173 K, 300 s and 2273-2373 K, 180 s

- The addition of 20-60 mass% SiC resulted in an increase in relative density at 2173 K.
- 99.9% relative density was obtained for the 20-60 mass% SiC composites at 2273 and 2373 K for 180 s.

Fracture Toughness of ZrB₂-SiC Composites

0-100 mass% SiC, 2173 K, 300 s and 2273-2373 K, 180 s

- Kᵣ of ZrB₂-SiC composites decreased with increasing sintering temperature.
- Maximum Kᵣ was obtained for ZrB₂-SiC composites containing 50 mass% SiC for all sintering temperatures.
- When SiC content exceeded 50 mass%, Kᵣ of ZrB₂-SiC composites started to decrease.
**Microstructure of ZrB₂-SiC Composites**

40 mass% SiC, 2173 K-300 s, 2373 K-180 s

- At 2173 and 2273 K, microstructures comprise equiaxed ZrB₂ and α-SiC grains.
- Elongated α-SiC grains formed at 2313 K and irregular texture composed of ZrB₂ and fine α-SiC grains were observed at 2373 K.

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**Melting Point of ZrB₂-SiC Eutectic Composites**

- Spark plasma sintering
- Heating to be melted
- Melting point: 2570 K

- Eutectic composition:
  - 41.5ZrB₂-58.5SiC (mol%)  
  - Eutectic melting point:
    - 2570 K
Local Structure of ZrB$_2$-SiC Eutectic Composites

Eutectic Temperature 2570 K
Sintering Temperature 2373 K

Cutting Tools

- Chip
- Drill
- Milling cutter
- Endmill

Requirements:
- High hardness
- High toughness
- High thermal stability

Harsh environment at the chip edge
Cubic Boron Nitride (cBN)

- Non-sinterability
- Transformation to hBN at high temperature

Fabrication of cBN Cutting Tools

Ultra-high pressure (>5GPa) sintering of cBN or hBN with binders such as metal Al and TiC

Moderate pressure (<100 MPa) hot-pressing

More practical applications
Microstructure of Al₂O₃-cBN Composite

- **20vol% cBN, 1573-1873K, 600s**

  - **1573K**
    - Sharp edged well adhered cBN particles at 1573K.
  - **1673K**
    - A small amount of voids and cracks around cBN particles at 1673K.
  - **1773K**
    - Phase transformation of cBN to hBN at 1773-1873K.

XRD Profiles of Al₂O₃-cBN Composites

- **20vol% cBN, 1573-1873K, 600s**
- **0-50vol% cBN, 1473-1673K, 600s**

  - **1573K**
    - A slight transformation to hBN at 1673K.
  - **1673K**
    - Density of more than 98% at 1573-1673K (10-20vol% cBN).
Vickers Hardness of Al₂O₃-cBN Composite

0-30vol% cBN, 1473-1873K, 600s

- The highest hardness of 26 GPa at 1573K (20vol% cBN)

Strategy to Consolidate cBN Powder

- Modification of Powder Surface (Coating)
  - Fluidized bed CVD (FBCVD)
- Rotary CVD
- Nano-particle/Nano-film Coating on Powders
  - Ni, SiO₂ Coating on cBN Powder
- Consolidation of cBN-base Composites by SPS
CVD Coating of Particle/Film on Powder

Fluidized bed CVD

Most frequently employed CVD technique for deposits on powders

Surface Modification of cBN Powder by Rotary CVD

Surface modification of powder
Nano-particle on powder
Accelerate sintering (SPS)
High performance materials
New functional materials

Schematic of RCVD system
Cross section of reactor
Morphology of SiO$_2$-coated SiC Powder

- Amorphous SiO$_2$ was uniformly coated on SiC particles, and the nano-layer thickness of the a-SiO$_2$ ranged from 60 to 80 nm at deposition time of 7.2 ks.
- The SiO$_2$ mass content in the SiC/SiO$_2$ powder was estimated at 22 mass% by mass gain after RCVD.

Polished surface morphology of sintered body

- Compared with monolithic SiC, SiO$_2$ prevented the grain growth of SiC.
- At 2023 K, SiO$_2$ reacted with SiC, and Si was produced.
SEM images of Ni Precipitated TiC, TiCN Powder

<table>
<thead>
<tr>
<th>Ni precipitated TiC powder</th>
<th>Ni precipitated TiCN powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{O_2} = 160$ Pa</td>
<td>$P_{O_2} = 160$ Pa</td>
</tr>
<tr>
<td>500 nm</td>
<td>500 nm</td>
</tr>
</tbody>
</table>

Precipitated phase
- $P_{O_2} = 0$ Pa: single phase Ni
- $P_{O_2} = 80$~$160$ Pa: Ni + NiO
- $P_{O_2} = 240$ Pa: NiO + TiO$_2$

Microstructure
- Ni or NiO nanoparticle about 20~100 nm in diameter was precipitated.
  - Ni nanoparticles were uniformly precipitated.

Sintering Behavior of Ni Nano-Particle Precipitated TiCN

- Shrinkage at a low temperature region

$0.56$~$0.68 \times T_m$(Ni)
TEM Images of cBN/SiO₂ Powder

- cBN
  - Naked cBN
- cBN/SiO₂-1:
  - Isolated islands
- cBN/SiO₂-2:
  - Continuous SiO₂ layer
- cBN/SiO₂-3:
  - Island+layer

\[ R_s: \]
1: \(5.56 \times 10^{-9}\) m³ s⁻¹
2: \(11.11 \times 10^{-9}\) m³ s⁻¹
3: \(16.67 \times 10^{-9}\) m³ s⁻¹

XRD Patterns of SiO₂-cBN Composites

- 50 vol% cBN/SiO₂ composites
  - Phase transformation of cBN to hBN occurred at 1973 K.
DENSITY OF SiO$_2$-cBN COMPOSITES

- SiO$_2$-(40-50) vol% cBN/SiO$_2$ composites was almost fully densified.

Ni content in cBN: 1.6 mass%

HARDNESS OF VARIOUS SiO$_2$-cBN COMPOSITES

- Hardness increased by coating Ni and SiO$_2$ on cBN powder.

- The highest hardness was 14.5 GPa (50 vol% cBN/SiO$_2$).

Ni content in cBN: 1.6 mass%
## Summary

- **SPS (Spark Plasma Sintering)**  
  - Spark? Plasma? Unknown
- **ECAS (Electric Current Activated/Assisted Sintering)**  
  - Mass Transport by Electric Filed? Unknown

## Effects of SPS

- Non-Sinterable Refractory Material, Easy-to-decompose Materials in a short time (within a few minutes)
- Meta-stable or Non-stable Materials are sinterable.
  - ✓ Excess surface energy (Stress on the surface, Defects…)
  - ✓ Re-arrangement and desification before neck growth

## Future Study

- ✓ Sintering Mechanism
- ✓ Non-sinterable Material ➞ Surface Modification of Powder