FIB damage and polishing in 3D-EBSD of ceramic materials

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Outline

• Brief background to solid oxide cells
• FIB damage of strontium titanates and Y stabilised zirconia
  – Effect of FIB current
  – Effect of FIB voltage
• Automated low kV ion polishing in 3DEBSD
• Conclusion
Solid oxide cells – fuel cell or electrolyser

- Operate at high temperature
- Can be fuelled by or produce hydrocarbons
- Oxidising and reducing atmospheres
- Porous composite metal-oxide electrodes
- FOCUS: Oxygen ion conducting phases → STN & YSZ
Focused ion beam damage

*Effects of focused ion beam milling on electron backscatter diffraction patterns in strontium titanate and stabilized zirconia*, Saowadee et al.  
EBSD pattern quality degrading factors

- Surface contamination
- Surface topography
- Mechanical strain
  - Bulk – plastic deformation
  - Surface – polishing artefact
- Lower BSE – coefficient
- Surface charging
- Ion beam damage
  - Lattice damage
  - Surface amorphisation (Si is a classic example)
  - Ion implantation (Ga)

- In 3D-EBSD of ceramics surface charging and ion beam damage are limiting factors
Experimental setup

- Zeiss CrossBeam 1540XB
- NORDLYS S detector

- Pre-milling surface prepared by 2nA to a depth of 1 µm
  - Removal of polishing damage
- Six probe currents investigated
  - 0.1 – 5.0 nA
  - 30 kV
  - 0.5 µm depth
- Two voltages investigated
  - 5 kV (2.5 nA)
  - 30 kV (2.0 nA)
- Quantified in terms of band contrast and slope of indexed pixels

EBSD parameters

- 20 kV, 10 nA electron beam
- 100 x 100 x 0.1-0.4 µm maps
- WD = 15 mm
- Integration time = 24 ms (avg. 4)
- 4 x 4 pixel binning (low gain)
- 6-7 bands (Hough res. 60 x 60)
Materials

- $\text{Sr}_{0.94}\text{Ti}_{1.0}\text{Nb}_{0.1}\text{O}_3$ (STN94)
  - 2.3 μm average grain size
  - RT conductivity $\sim 1 \text{ S cm}^{-1}$
  - 10-18 nm carbon coating

- $\text{Sr}_{0.99}\text{Ti}_{1.0}\text{Nb}_{0.1}\text{O}_3$ (STN99)
  - 1.2 μm average grain size
  - RT conductivity $\sim 150 \text{ S cm}^{-1}$

- Perovskite structure

- 8% mol. $\text{Y}_2\text{O}_3$ stabilised $\text{ZrO}_2$
  - Grain size $\sim 8.9 \mu$m
  - RT conductivity $\sim 10^{-7} \text{ S cm}^{-1}$
  - 10-18 nm carbon coating

- Fluorite structure
Effect on band contrast

- General trend of decreasing band contrast with probe current
- Coated YSZ has higher band contrast than STN
- Charging prohibits EBSD on uncoated YSZ
- STN94 has higher band contrast than STN99
- Carbon coating improves STN94 pattern quality
- FIB STN surfaces have lower pattern quality than mechanical polishing
- Low kV polishing on STN94 provides optimum pattern quality
Effect on band slope

- General trend similar to band contrast
- Band slope is scaled to higher values
- Smaller relative difference between STN94 & STN 99 mechanical polishing
- Band slope appears to be a more sensitive parameter for observing ion beam influence
EBSD map comparison of 2 nA surfaces

(a) STN94
(b) coated-STN94
(c) STN99
(d) coated-YSZ

IPF (x) colouring
SRIM simulations

Ion penetration:

30 kV
• STN = 54 Å
• YSZ = 56 Å

5 kV
• STN = 19 Å
# Ion damage in STN and YSZ

<table>
<thead>
<tr>
<th></th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 kV Ga ion penetration</td>
<td>STN 4% &gt; YSZ</td>
</tr>
<tr>
<td>20 kV BSE coefficient</td>
<td>STN 8% &lt; YSZ</td>
</tr>
<tr>
<td>Hardness</td>
<td>STN 25% &lt; YSZ</td>
</tr>
<tr>
<td>Melting point</td>
<td>STN 27% &lt; YSZ</td>
</tr>
<tr>
<td>Density</td>
<td>STN 15% &lt; YSZ</td>
</tr>
</tbody>
</table>

- Marginal difference in ion penetration and BSE coefficient
- Significantly lower STN hardness and melting point
  - Suggests vulnerability to ion beam damage
  - Correlates to lower pattern quality of STN
- Density difference is accounted for in ion beam penetration simulations
Effect of FIB voltage on STN99

<table>
<thead>
<tr>
<th>FIB voltage</th>
<th>Average band contrast</th>
<th>Average band slope</th>
<th>Indexing %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 kV (2000 pA)</td>
<td>106.9</td>
<td>141.2</td>
<td>69.5%</td>
</tr>
<tr>
<td>5 kV (2500 pA)</td>
<td>207.1</td>
<td>244.8</td>
<td>91.4%</td>
</tr>
<tr>
<td>Mechanical</td>
<td>162.9</td>
<td>231.1</td>
<td>91.1%</td>
</tr>
</tbody>
</table>

(a) 30 kV

(b) 5kV

(c) Mechanical polish
(different location)
Focused ion beam polishing during 3DEBSD
3DEBSD Polishing setup
3D-EBSD example \((\text{Sr}_{0.96}\text{La}_{0.02}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3)\)

- Volume dimensions: \(X = Y = 12.6, Z = 3.0\ \mu\text{m}\)
- Resolution: \(X = Y = 0.075\ \mu\text{m}, Z = 0.1\ \mu\text{m}\)
Time

3D-EBSD+polishing

- Total time per slice: 30 minutes
- Mapping time: 23 minutes (50 ms frame time)
- FIB milling time: 6 minutes (15.9 µm$^3$)
- FIB polishing time: 1 minute

- FIB polishing adds 3.3% slice time
Conclusions

• High kV FIB milling can induce significant reduction of pattern quality in some ceramic materials
• Reducing FIB probe current can significantly improve pattern quality
• Low kV FIB polishing is the most effective way to improve pattern quality
  – Can produce higher surface quality than mechanical polishing
• For sensitive materials low kV FIB polishing provides optimum pattern quality for little increase in data acquisition time overhead

• STN in comparison to YSZ suffers greater ion beam damage
  • Low kV polishing equates STN pattern quality to YSZ

• Fully automatic 3D-EBSD with low kV FIB polishing demonstrated.
Thank you for your attention