Microwave Assisted Technologies for Ceramics and Chemical Processing

Shawn M. Allan*
Morgana Fall, Inessa Baranova, Dr. Holly Shulman

Ceralink Inc.
October 8, 2008, 2:00 PM

Environmentally Benign Processing II
Pittsburgh, Pennsylvania
Outline

● Background
  ● Focus on energy efficient manufacturing
  ● Technical difficulties
  ● Engineered solutions

● Case Studies
  1. Microwave Assist Technology for Nano-BaTiO$_3$ powder synthesis
  2. MAT kiln scale-up for carbon foam & ceramics
  3. Microwave Autoclave scale-up for Pt recycling from PEM fuel cells

● Summary
Materials & Energy

- Heat is ubiquitous to materials processing
- Heating processes are often bottlenecks
- Energy consumption costs, especially for ceramics, is enormous
- Energy is strategic, economic, and environmental issue
- Efficiency is critical to sustainability
- Energy consumption is directly related to pollution
Microwave Advantages

- Heat materials directly
- Energy applied in volume of product
  - Yields significant energy savings - 50% or greater
- Less dependence on thermal conductivity
- Leads to fast heating, short cycle time
  - Fine powders and grain structures
  - Fewer pollutants released from clays (e.g., HF)
- Heating can be uniform (e.g. sintering, binder burnout) or non-uniform (e.g. self limiting reaction, joining, LTCC)
## Microwaves - Dielectric Heating

### Conductivity increasing*

<table>
<thead>
<tr>
<th></th>
<th>Alumina</th>
<th>Zirconia</th>
<th>Silicon Carbide</th>
<th>Aluminum (bulk**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C 2.45 GHz</td>
<td>0.0010</td>
<td>0.015</td>
<td>0.08-1.05</td>
<td>∞</td>
</tr>
<tr>
<td>Tan δ</td>
<td>12.8</td>
<td>1.0</td>
<td>0.004 - 0.05</td>
<td>0.000001</td>
</tr>
<tr>
<td>Penetration Depth (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Magnetic field may also induce currents leading to heating
** Powder metals have measureable dielectric properties
Dielectric Property Testing

Zirconia and Alumina Insulation
Measured at 2.45 GHz

- Relates to conductivity changes
- Predicts microwave heating behavior
- Higher Tan δ → Better absorption
- Want product to preferentially absorb
- Need radiant heat at low temp
- Avoid thermal runaway at high temp
Technical Difficulties

- Material doesn’t suscept at any temperature

- Material suscepts through part of heat cycle
  - Can use susceptors for radiant heat
  - Can use MAT (microwaves + electric or gas radiant heat)

- Thermal runaway, non-uniform heating
  - Control microwave power input
  - Controlled by susceptors and/or MAT for some materials

- Equipment design, availability, and cost
Engineered Solutions

- Focus on product
  - Demonstrate feasibility
  - Scale-up plan, system mock up
  - Cost benefit / manufacturability analysis
  - Need for Teams
    - Product manufacturer
    - Equipment companies (e.g. microwaves, kiln builders)
    - Expertise in microwave + materials interactions

- Find Government support
  - Strategic products
  - Dual use equipment
  - State and Federal energy initiatives
    - DoE, NYSERDA, PEDA
1. MAT Calcination: Self Limiting Synthesis of Nano-BaTiO$_3$

Dr. Holly S. Shulman
Morgana Fall, Shawn Allan
Ceralink Inc.

Dr. Matt Creedon
Ferro Corp.

NYSERDA
Calcination and the Mixed Oxide Method

- **Perovskites**: dielectrics, ferroelectrics, piezoelectrics, sensors, transducers, capacitors, data storage elements barium titanate, strontium titanate, PZT
- Relaxors: Niobates
- Phosphors: MgWO₄, SrAl₂O₄
- Superconductors: YBCO
- Conducting ceramics: ITO
- Varistors: ZnO
- Catalysts
- Spinels, ferrites, garnets
Nanograin Ceramic Powders

Demand for smaller electronic components → need for powders with smaller grain size

Chemical Processing
- Build up from atomic scale
- High purity
- Expensive

Mixed Oxide Calcination
- Grain growth and hard agglomerates
- Addition of Impurities (due to grinding/milling)
- Energy intensive
Mixed Oxide Process for Perovskites

\[ \text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2 \]
Dielectric Properties
Tan Delta

Tan δ of TiO₂ higher than BaTiO₃ from 700–1100 °C
Microwave Heating

Microwave makes it possible to fabricate nano-barium titanate from mixed oxide calcination method

- Selective heating - heat reactants, not final product
- Fast Heating - less time for grain growth
- Lower process temperature - lower kinetics for grain growth
- Enhanced reactions - More complete reactions in less time

*Dielectric Properties* show pre-cursor powders heat better compared to final product → self limiting reaction
Microwave Assist Technology

Solution: Use Microwave Assist Technology (MAT) to improve traditional calcination method

- Combination of radiant heat (gas or electric) with microwave energy
- Balance microwave heat with radiant heat
- Patented Technology
- Simultaneously apply both microwave and radiant
MAT Results
Microwave Drives Reaction Faster
850 °C Calcining Temperature

Microwave power off

BaTiO$_3$
BaCO$_3$
BaCO$_3$  Dwell Time

23
35
45
60
MAT Results
Microwave Drives Reaction Faster
850 °C Calcining Temperature

Microwave power off

Microwave power on
MAT Results

Conventional calcining
850 °C, 35 min dwell
Incomplete calcine
12% BaCO₃ present
SSA = 7.44 m²/g
Dₛ = 134 nm

MAT calcining
850 °C, 35 min dwell
Fully reacted BaTiO₃
SSA = 5.85 m²/g
Dₛ = 170 nm

Conventional calcining
1000 °C, 3 hour dwell
Fully reacted BaTiO₃
SSA = 2.30 m²/g
Dₛ = 550 nm
MAT Results
Energy Consumption

Parameters
MAT: 850 °C, 35 minute dwell
Conventional: 1000 °C, 3 hr dwell
MAT Results

Reproducibility 19 runs, 800 °C, 60 min dwell
Avg. surface area = 7.6 m²/g → particle size 130 nm
range ±25 nm

- **Cp** = 1.33
  - Want Cp to be 1.33 or higher

- **Cpk** = 1.23
  - A process with Cpk over 1 is a capable process.
  - The closer Cpk is to Cp, the better

- Specification 170 nm
- MLCC thickness 1.0 micron
Summary
Microwave Assist Technology

Microwave Assist Technology provides:

- Rapid calcining
- Energy savings
- Lower kiln temperature
- Enhanced reactions
- Selective and self limiting heating
- Finer grains
- Applicability to wide range of materials
2. MAT Firing: Carbon Foam & Bulk Ceramics

Dr. Holly S. Shulman
Morgana Fall, Shawn Allan
Ceralink Inc.

Dr. Drew Spradling
Touchstone Research Laboratory

United States Department of Defense
NYSERDA
Carbon Foam Firing Challenges

- **Strategic Material**
  - Mold for C-C composites
  - Lightning Protection

- **Problem**
  - Large cross-sections
  - Highly insulating, unusual expansion properties
  - Inert atmosphere
  - Maximum process temperature of 1050 °C

  **Slow, Energy Intensive Firing Cycles → 7 days!!**

- **Solution**
  - Carbon is effective susceptor in microwave field
  - Increase heating uniformity → faster heating
  - Use MAT (microwave + electric kiln design)
Proof of Concept

- Carbon self heats in microwave
  - Problem → inverse temp profile with pure microwave
  - Carbolite burnout furnace
  - Modified by Ceralink to accept microwaves
  - Allowed firing in 1/10 time

![Diagram of microwave heating system with labels: Microwave inlet, Gas inlet, Carbon Material, Electric heating elements.]
- MAT 1/10\textsuperscript{th} of firing time for small brick
- Anticipate a small sample contribution to fast firing
- Predict large scale time/energy reduction of 50%
MAT Pilot Scale-up

TEAM Approach
- C-FOAM Manufacturer – Touchstone Research Laboratory
- Kiln construction – Harrop Industries
- Microwave equipment supplier – Thermex Thermatron
- MAT design, systems integration, license – Ceralink Inc.
- Support – United States Department of Defense

Specifications:
- Elevator Design
- 3ft x 3ft x 3ft workspace
- Inert atmosphere
- 1620 °C Capability
- 915 MHz, Two port

Commissioned: November 2007
Bulk Ceramic Firing
Alumina/SiC Composites

Material suscepts well
Achieved higher density
Improved product uniformity over Conventional and MAT lab kiln
80% process time reduction

Blasch Precision Ceramics
Albany, New York

Ceralink has exclusive license in North America to use and sublicense MAT
Cycle Time and Energy Savings
Alumina/SiC

- 80% energy savings
- Similar or better properties
- Faster turn-around time
- Less product in process
Porcelain Insulators
Alumina Replaced Porcelain

- Feasibility testing showed:
  - Time and energy savings
  - 45 hrs conventional firing → 10 hrs MAT firing
  - Full size insulator → 10” core, 72” tall
  - Used dielectrics & porcelain science to work out MAT process
3. Microwave Autoclave for Polymer Fuel Cell Reclamation

Shawn Allan, Morgana Fall, Dr. Holly S. Shulman
Ceralink Inc.

Dr. Lawrence Shore
BASF Catalysts LLC

United States Department of Energy
Polymer Fuel Cells

5 layer Membrane Electrode Assembly

- Gas Diffusion Layer
- Anode Catalyst Layer
- Nafion® Membrane
- Cathode Catalyst Layer
- Gas Diffusion Layer

Recycling Project Goals:
- Digest platinum catalyst into solution
- Avoid burning Nafion membrane
Precious Metal Recovery
Microwave Digestion

- Ceralink assisted BASF → $5 mil from DOE to develop a method for precious metal recovery from used fuel cell membranes.

- Current method is ashing:
  - Fluoropolymer + flame → HF → costly environmental problem
  - And… Platinum → $511 /m²
  - Nafion® → $2,400 /m²

- Microwave digestion → up to 99% Pt recovery
  - Improved yield
  - Avoid HF generation
  - Easier to manage by-products
  - Simultaneous recovery of metal and polymer

- Uses for recycled Nafion®
Microwave Autoclaves

- Short cycle times → Quick process development
- Accelerated reactions (microwave superheating)
- Safety: no physical contact with heat source
- Allows high T-P research without exhaustive materials search
- Significantly lower cost vs. specialty alloy autoclaves
- Cold walls – less system corrosion
Lab Scale Research

- Highly corrosive reagents
  - Concentrated HCl, Cl₂, Aqua Regia
  - Easier to neutralize waste acids & emissions
  - Lab scale containment – PTFE vessels

- Adjust reagent combinations for desired effects
  - Digest platinum and carbon (1)
  - Only digest platinum (2)

- 100-200 °C, 10-50 atm, 10-30 minutes

- Versus bench top 70 °C stir plate reaction → Improved yield (up to 50%)
- **Up to 99% Pt recovery in Microwave Vessels**
Microwave vs. Benchtop

Stir plate ~70 °C
1 atm
stirred

Microwave ~200 °C
20-40 atm
30 minute soak
no agitation

Effects →
Temperature,
Pressure,
Stirring,
Containment
Scale-up Challenges

- Identifying critical process component
  - Microwave, Stirring, Containment, or … ?

- Materials selection for larger vessels
  → up to **600L**

- Reactor design for special environment

- Microwave integration

- Volumetric scaling of high pressure process
Microwave Autoclave Prototype Team

- Autoclave Engineers is a division of Snap-Tite Corp
  - specializes in ASTM standard high pressure vessels
- Microwave Materials Technology (MMT)
  - microwave equipment expert
- Ceralink
  - design, team coordination, testing
- BASF (Engelhard)
  - end user
Prototype Microwave Autoclave

- 1 kW, 2.45 GHz microwave power
- 200 °C at 50 atm
- Working volume of 2-5 L
- Integrated computer control
- PTFE inner vessel, 316 SS outer vessel
- Titanium plumbing
- Two reagent metering ports
- Temperature and pressure monitoring
Ongoing Outcomes
BASF Microwave Autoclave

- Successful lab demonstration of platinum and Nafion® recovery
- A patent applied for PEM recovery process
- New microwave autoclave designed and built for process scale up
- Titanium autoclave built to study high P-T without microwave
  - Aqua regia and wet Cl₂ resistant without use of Teflon liner
  - Microwave autoclave used for extensive corrosion testing
- BASF designing pilot plant facility
- HF emissions from PEM fuel cell recycling will be avoided
Commercialization
Microwave Heating Technology

Barriers
• Need for demonstration
• Need for specific commercial design
• Need for manufacturability and cost benefit analyses
• Need for funding, government & industry support
Summary

- Microwave heating comprises highly efficient process technologies.
- Feasibility, cost benefit, and environmental analyses are essential.
- Broad feasibility has been demonstrated.
- Landscape changing as energy costs rise, need for solutions.
- Multidisciplinary teams are needed to bridge the gap for the commercialization of new microwave processes.
Acknowledgments

New York State Energy Research and Development Authority

United States Department of Defense - Dr. Doug Deason at SMDC under a Phase II & Phase III SBIR contract

United States Department of Energy

Come learn more about Ceralink and Energy Efficient Microwave Heating Technologies from our partners at the Expo:

Thermex Thermatron
Harrop Industries
Carbolite