Synthesis of Ultrafine/Nanocrystalline Ti-Si-C Powder through Na-Reduction of Liquid Chlorides

Ø 70-200nm

SEM micrograph of c-SiC powder

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Financed through: The National Graduate School of Space Technology
At room temperature under flowing argon, SiC and TiC/Ti/Ti5Si3 amorphous precursor powders, were synthesised through solid Na-particles reduction of liquid chlorides. The NaCl side-product was separated from the precursor at T=1000°C to the cooler region of an alumina tube while the ceramic powder remained in the graphite crucible used. At this temperature the TiC/Ti/Ti5Si3 powder was crystallised, while the SiC precursor remained amorphous. After T=1300°C kept for 2h and 15-24h respectively TiC/Ti/Ti5Si3-> TiC/Ti and the amorphous SiC powder was crystallised. The crystalline phases were confirmed by x-ray diffraction. The particle sizes of the 1300°C crystallised powders were estimated by SEM micrographs to be 70-1000nm and 70-200nm for the TiC/Ti and SiC respectively. The impurities was estimated to be less than 1 and 5 atomic % respectively when analysed by energy dispersive x-rays.

**Keywords:** EDX, SEM, XRD, ultrafine/nanocrystalline powder
Introduction Na-reduction of liquid chlorides

- **UF/NC powders** Particles Ø less than 1μm and 100nm respectively [1]
  - **NC**- high strength, increased damage resistance [2]

- **High pressure synthesis** >>1 atm
  - **NC**, 25-60nm, Ti5Si3 and TiSi2 Tc~650°C, *Na, Mg, Zn, Al reductants* [3]
  - **UF/NC**, 5-3000nm, *Si* Tc~ 350°C *using Na* [5]

- **Atmospheric pressure synthesis**
  - **UF/NC ?**, "varying"?, TiC/SiC, Tc~ 1500°C, *Na reductant* [4]

- **Applications**
  - **TiC/SiC**- TiC-particles in SiC matrix improves fracture toughness [11]
  - **SiC**- heating element for tube furnaces, furnace-crucibles
  - **TiC**- Wear resistance tools, aerospace materials [10]
  - **TiSi2**- diffusion barrier in 250nm size range
**EXPERIMENTAL** Set-up, chemicals, tube-furnace, crucible etc

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Amounts (mmol) TiCl4/SiCl4/CCl4/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>0/100/40/240</td>
</tr>
<tr>
<td>TiC/Ti/Ti5Si3</td>
<td>60/100/40/240</td>
</tr>
</tbody>
</table>

- Nonpolar tetrachlorides dissolve in nonpolar hydrocarbon solvents, n-heptane, toluene
- Na-particles Ø <100µm
- SiCl4 and CCl4 volatile
- Air and moisture sensitive chemicals
- The amount of nonpolar hydrocarbon solvents toluene and n-heptane is 136 and 545 mmol respectively
RESULTS Reaction formulas times and temperatures

**h-Ti5Si3** = hexagonal-Ti5Si3
**c-TiC** = cubic-TiC similarly for Ti and SiC
"SiC" = amorphous-SiC similarly for "TiC" and "Ti5Si3"

**TiC/Ti/Ti5Si3**

*Reduction Synthesis:*
\[ 6\text{TiCl}_4(\text{l}) + 10\text{SiCl}_4(\text{l}) + 4\text{CCl}_4(\text{l}) + 24\text{Na}(\text{s}) \rightarrow x\text{TiC} + y\text{Ti5Si3} + z\text{Ti} + 24\text{NaCl}, \quad T=25^\circ \text{C}, \text{tr}=48\text{h} \]

*NaCl Separation & Crystallisation 1:*
\[ x\text{TiC} + y\text{Ti5Si3} + z\text{Ti} + 24\text{NaCl} \rightarrow \text{c-TiC}(\text{s}) + \text{h-Ti5Si3}(\text{s}) + \text{c-Ti}(\text{s}), \quad T=1000^\circ \text{C}, \text{tr}=48\text{h} \]

*Crystallisation 2:*
\[ \rightarrow \text{c-TiC}(\text{s}) + \text{h-Ti5Si3}(\text{s}) + \text{c-Ti}(\text{s}), \quad T=1100^\circ \text{C}, \text{tr}=2\text{h} \]

*Crystallisation 3:*
\[ \rightarrow \text{c-TiC}(\text{s}) + \text{c-Ti5Si3}(\text{s}) + \text{c-Ti}(\text{s}), \quad T=1200^\circ \text{C}, \text{tr}=2\text{h} \]

*Crystallisation 4:*
\[ \rightarrow \text{c-TiC}(\text{s}) + \text{c-Ti}(\text{s}), \quad T=1300^\circ \text{C}, \text{tr}=2\text{h} \]

**SiC**

*Reduction Synthesis:*
\[ 10\text{SiCl}_4(\text{l}) + 4\text{CCl}_4(\text{l}) + 24\text{Na} \rightarrow 4\text{SiC}(\text{s}) + 24\text{NaCl}(\text{s}) + 6\text{SiCl}_4(\text{g}) \rightarrow 4\text{SiC}(\text{s}) + 24\text{NaCl}(\text{s}), \quad T=25^\circ \text{C}, \text{tr}=48\text{h} \]

*NaCl Separation:*
\[ 4\text{SiC}(\text{s}) + 24\text{NaCl}(\text{s}) \rightarrow 4\text{SiC}(\text{s}), \quad T=1000^\circ \text{C}, \text{tr}=48\text{h} \]

*Crystallisation:*
\[ 4\text{SiC}(\text{s}) \rightarrow 4 \text{c-SiC}(\text{s}), \quad T=1300^\circ \text{C}, \text{tr}=15-24\text{h} \]
RESULTS TiC/Ti/Ti5Si3 - Reduction Synthesis

Reaction: \(6\text{TiCl}_4(l) + 10\text{SiCl}_4(l) + 4\text{CCl}_4(l) + 24\text{Na(s)} \rightarrow x\text{“TiC”} + y\text{“Ti5Si3”} + z\text{“Ti”} + 24\text{NaCl}\)

\[T = 25^\circ C, \ tr = 48h\]

- N-heptane and Na in toluene added through center neck
- N-heptane diluted TiCl4, SiCl4 and CCl4 60
- 100mmol and 40mmol respectively added dropwise through dropping funnel
- Stirring Varied 250-750rpm
RESULTS TiC/Ti/Ti5Si3- NaCl-Separation and crystallisation

Determination of NaCl-separation T:

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Atomic % Na+Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>8.3</td>
</tr>
<tr>
<td>950</td>
<td>3.1</td>
</tr>
<tr>
<td>1000</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

EDX-analysis on the powder that remained in the graphite crucible after 48h of heat-treatment.
RESULTS TiC/Ti/Ti5Si3- Crystallisation 1100°C, 1200°C, 1300°C

- T=1300°C
- T=1200°C
- T=1100°C

Element | Atomic %
--- | ---
C | 8.73
O | 5.97
Si | 0.49
Ti | 92.79

Element | Atomic %
--- | ---
C | 9.13
O | 5.97
Si | 0.49
Ti | 84.43

Element | Atomic %
--- | ---
C | 10.57
O | 5.33
Na | 0.36
Si | 0.82
Ti | 79.91

Ø 70-1000nm
RESULTS SiC- Reduction Synthesis

 Reaction:

\[10\text{SiCl}_4(\ell)+4\text{CCl}_4(\ell)+24\text{Na} \rightarrow 4\text{"SiC"}(s)+24\text{NaCl}(s)+6\text{SiCl}_4(g)\rightarrow 4\text{"SiC"}(s)+24\text{NaCl}(s)\]

T=25°C, tr=48h

- N-heptane and Na in toluene added through center neck
- N-heptane diluted SiCl4 and CCl4 100mmol and 40mmol
  Respectively added dropwise through dropping funnel
- Stirring Varied 250-750rpm
RESULTS SiC- NaCl Separation and Crystallisation

**NaCl Separation:**

$4\text{"SiC"}(s) + 24\text{NaCl}(s) \rightarrow 4\text{"SiC"}(s)$, $T=1000^\circ\text{C}$, $tr=48\text{h}$

**Crystallisation:**

$4\text{"SiC"}(s) \rightarrow 4\text{c-SiC}(s)$, $T=1300^\circ\text{C}$, $tr=15-24\text{h}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>43.4</td>
</tr>
<tr>
<td>O</td>
<td>31.2</td>
</tr>
<tr>
<td>Na</td>
<td>9</td>
</tr>
<tr>
<td>Si</td>
<td>13.3</td>
</tr>
<tr>
<td>Cl</td>
<td>3.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
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</tr>
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<tbody>
<tr>
<td>Si</td>
<td>44.7</td>
</tr>
<tr>
<td>C</td>
<td>50.9</td>
</tr>
<tr>
<td>Impurities (Cl, Ca, Ti)</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Ø 70-200nm
# RESULTS

Summary on 1300°C crystallised phases

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>TiCl4/SiCl4/CCl4/Na</th>
<th>XRD Phases</th>
<th>EDX Ti/ Si/ C/Impurities</th>
<th>SEM Ø</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>0/100/40/240</td>
<td>SiC</td>
<td>2.6/ 44.7/ 50.9/ 1.8</td>
<td>70-200nm</td>
</tr>
<tr>
<td>TiC/Ti/Ti5Si3</td>
<td>60/100/40/240</td>
<td>TiC/Ti</td>
<td>92.7/0.5/6.7/0</td>
<td>70-1000nm</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Ultrafine/nanocrystalline powders of TiC/Ti and SiC has been synthesised at T=1300 °C from an amorphous precursor. The amorphous precursors were synthesised at room temperature through solid Na-particles reduction of liquid chlorides. The crystallised TiC/Ti and the SiC powder was confirmed by x-ray diffraction and impurities was estimated to be less than 1 and 5 atomic % respectively when analysed by energy dispersive x-rays.
QUESTIONS?

Thanks for your attention!
REFERENCES


