



National Research Council

Institute of Science and Technology
for Ceramics

Faenza, Italy

Alkali Bonded SiC Based Foams

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Introduction to porous ceramics

Porous ceramics with high porosity (70-95%) are expected to be used in many technological applications such as:

structural lightened parts, insulator panels, filters and membranes, radiant burners, gas or chemical sensors, support materials for catalysis or adsorbents, because of their high gas permeability and large surface area as well as for the high temperature stability and thermal shock resistance.

“Traditional” preparations of porous ceramics:

- burnout of fugitive additives
- replica method
- foaming agent
- etc.

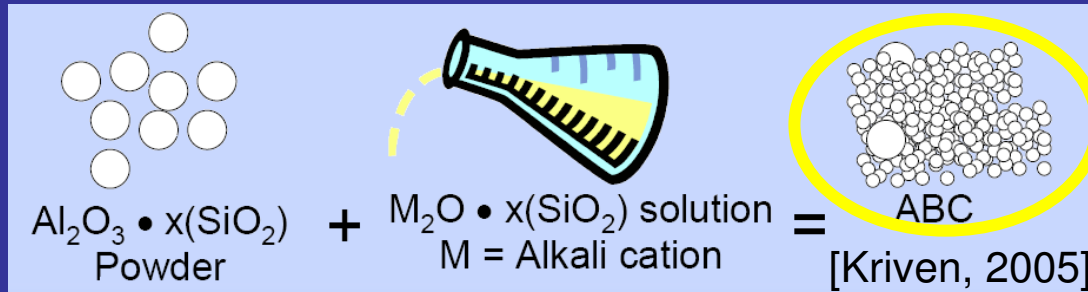
Porous ceramics are usually sintered at high temperature to reach specific mechanical and functional properties

INNOVATION: Consolidation of advanced ceramic SiC based foams by using chemically activated inorganic binders to replace the sintering step.

Among inorganic binders, **ALKALI ALUMINO SILICATE BINDERS** behave as inorganic polymers, the so called **GEOPOLYMERS** [Davidovits, 1978]

Alkali-Bonded Ceramics

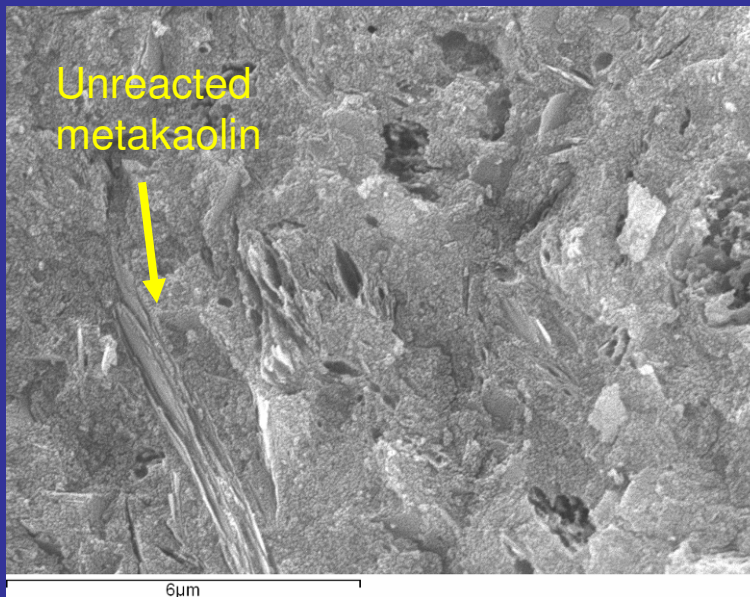
Simple processing as cements:
RT-120°C



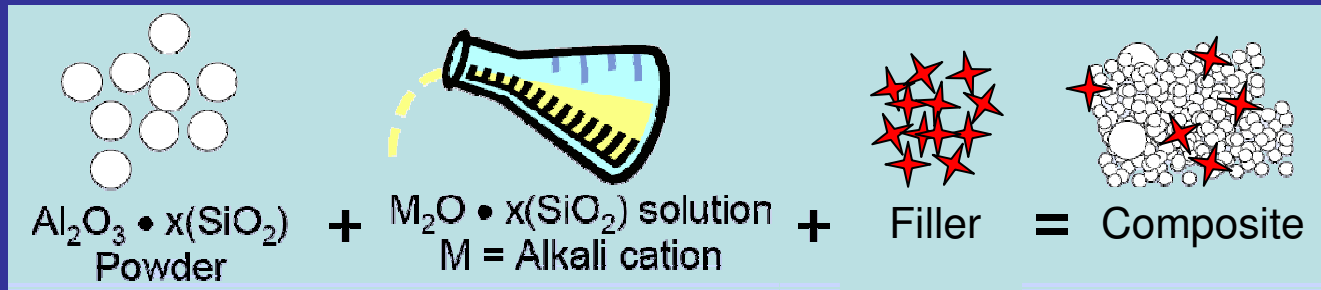
Near-net-shape:
casting in mould

Raw materials: meta-kaolin (calcined kaolin), fly ashes, natural minerals, blast-furnace slags or any source of silica and alumina
Alkaline aqueous solutions

Microstructures developed from metakaolin



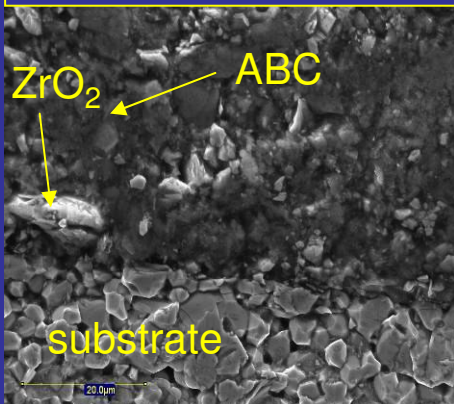
Alkali Bonded Ceramic Materials



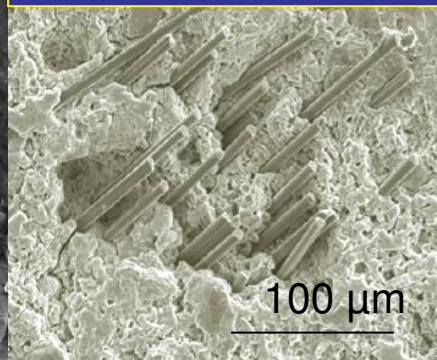
Nano-precipitates acts as a glue sticking together unreacted Al-Si source materials and fillers (powder or fibres)

ABC materials are **COMPOSITES: the filler functionalizes the materials**

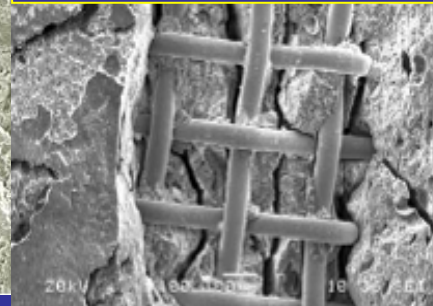
Ceramic powders:
refractoriness, CTE



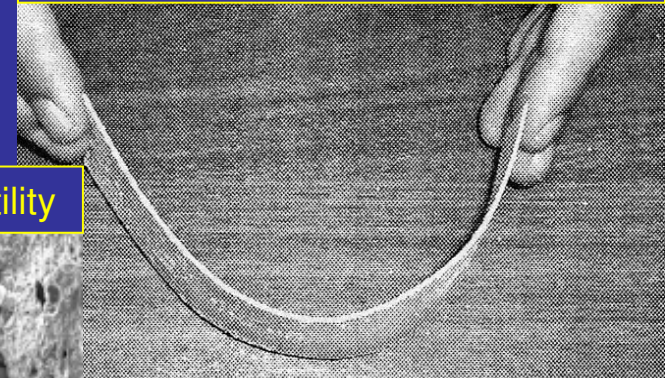
Fibers (carbon, glass):
mechanical properties, heat transfer



Metal cages \Rightarrow ductility



Organics (CMC, PEG): flexibility



Alkali Bonded SiC Based Foams preparation

RAW MATERIALS

SiC powders - 90 wt% of the foams:

- α -SiC grade 100F, SIKA TECH, Saint-Gobain, s.s.a.: 0.58 m²/g.
- β -SiC grade BF 12, H.C. Starck, s.s.a.: 11.6 m²/g.

Calcined kaolin at 750 °C (metakaolin), grade BS4, AGS Mineraux, s.s.a.: 30 m²/g

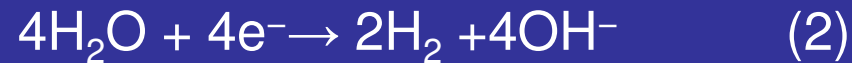
KOH/K₂SiO₃ aqueous solution with SiO₂:K₂O=2 and H₂O:K₂O=23, pH=12

Distilled water

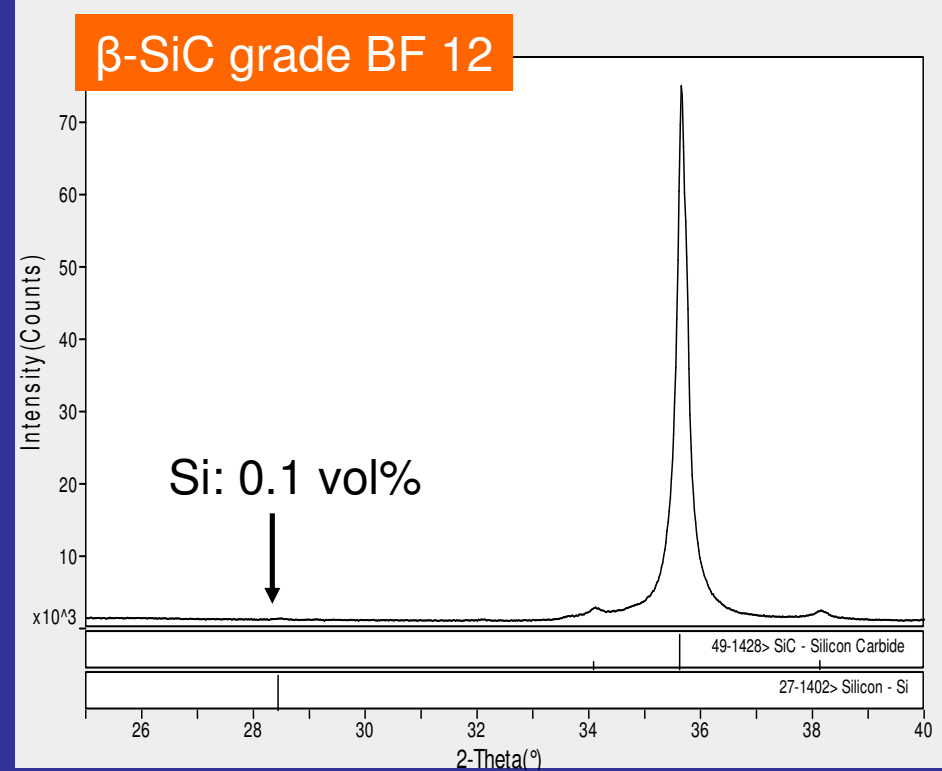
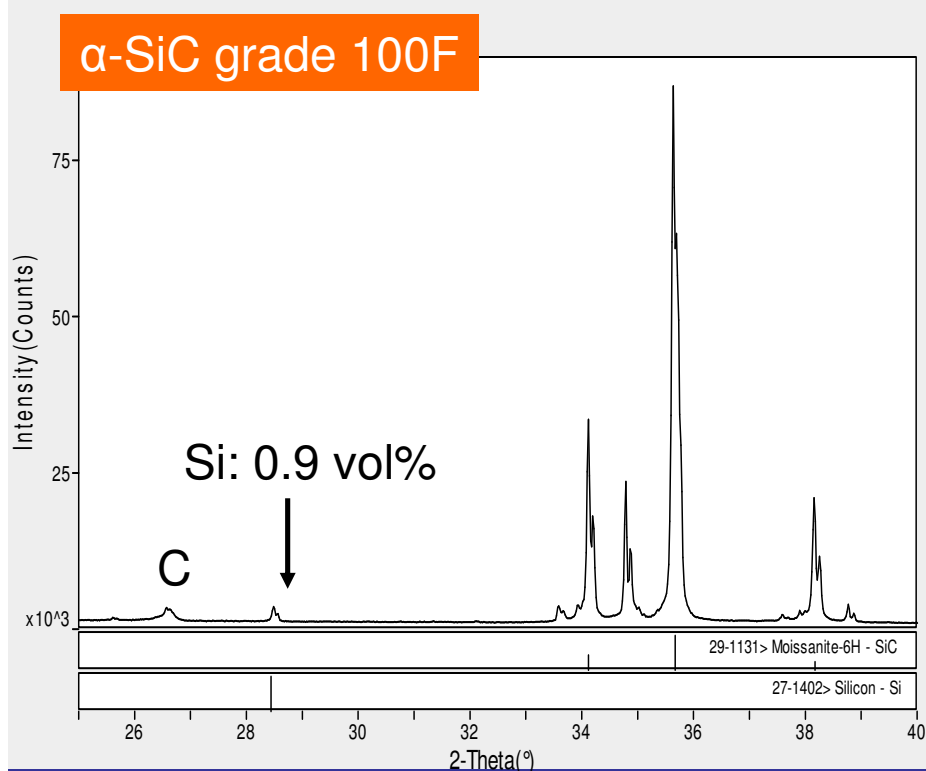


Foming agent: Si⁰

Redox reaction with H₂ evolution



Si⁰ traces are intrinsically contained in all SiC powders

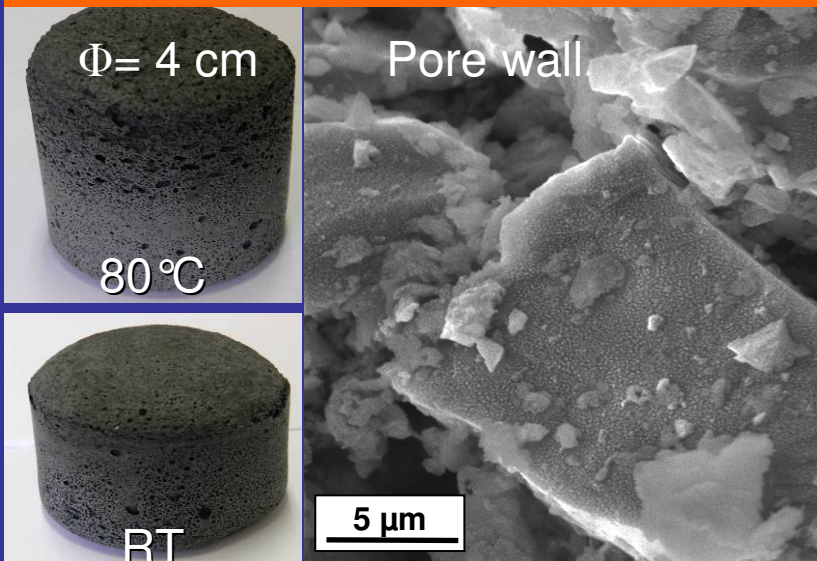


Alkali Bonded SiC 90 wt% Based Foams

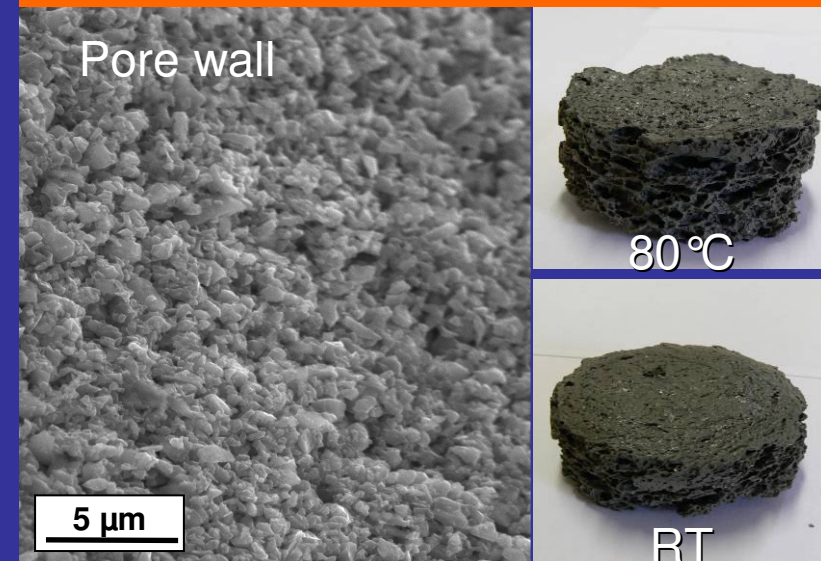


Gas evolution leads to foamed macro-structures, i.e. inorganic *in situ* foam formation, when the viscosity of the composite slurries increases contemporary and the material consequently consolidates.

α -SiC grade 100F, s.s.a.: 0.58 m²/g



β -SiC grade BF 12, s.s.a.: 11.6 m²/g



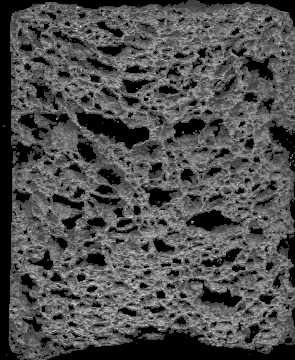
Foaming versus process temperature

α -SiC grade 100F, 0.9 vol SiC

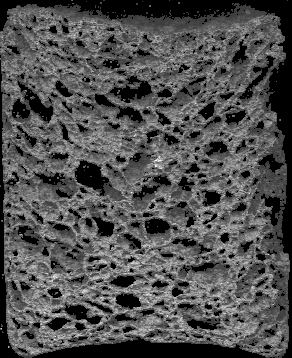
4 cm



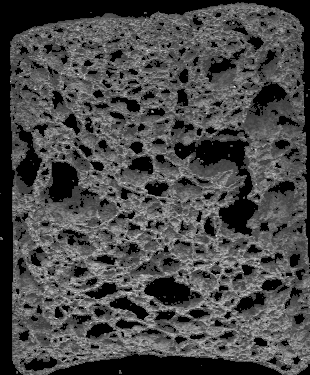
RT, $\Delta V = +100\%$
 $d \sim 0.65 \text{ g/cm}^3$, porosity: 78%



40°C, $\Delta V = +150\%$
 $d \sim 0.55 \text{ g/cm}^3$, porosity: 80%



60°C, $\Delta V = +150\%$
 $d \sim 0.50 \text{ g/cm}^3$, porosity: 83%



80°C, $\Delta V = +150\%$
 $d \sim 0.50 \text{ g/cm}^3$, porosity: 83%



Foaming is thermodynamically favoured by increasing the process temperature:

RT, $\Delta G: -359.4 \text{ KJ}$

40°C, $\Delta G: -361.6 \text{ KJ}$

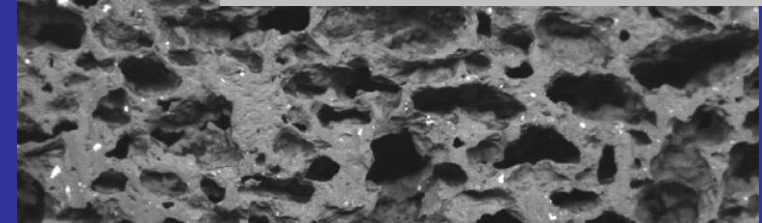
60°C, $\Delta G: -364.2 \text{ KJ}$

80°C, $\Delta G: -366.6 \text{ KJ}$

β -SiC grade BF 12, 0.1 vol% SiC

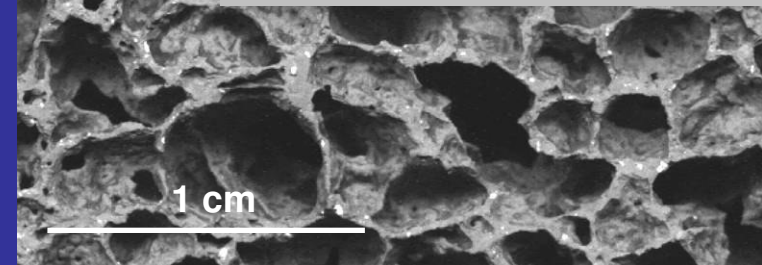
RT

$\Delta V = +50\%$
 $d \sim 0.49 \text{ g/cm}^3$, porosity: 84%



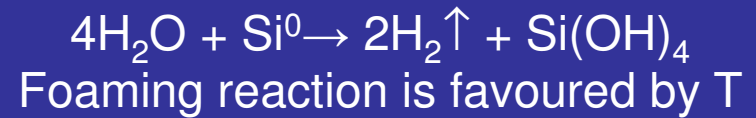
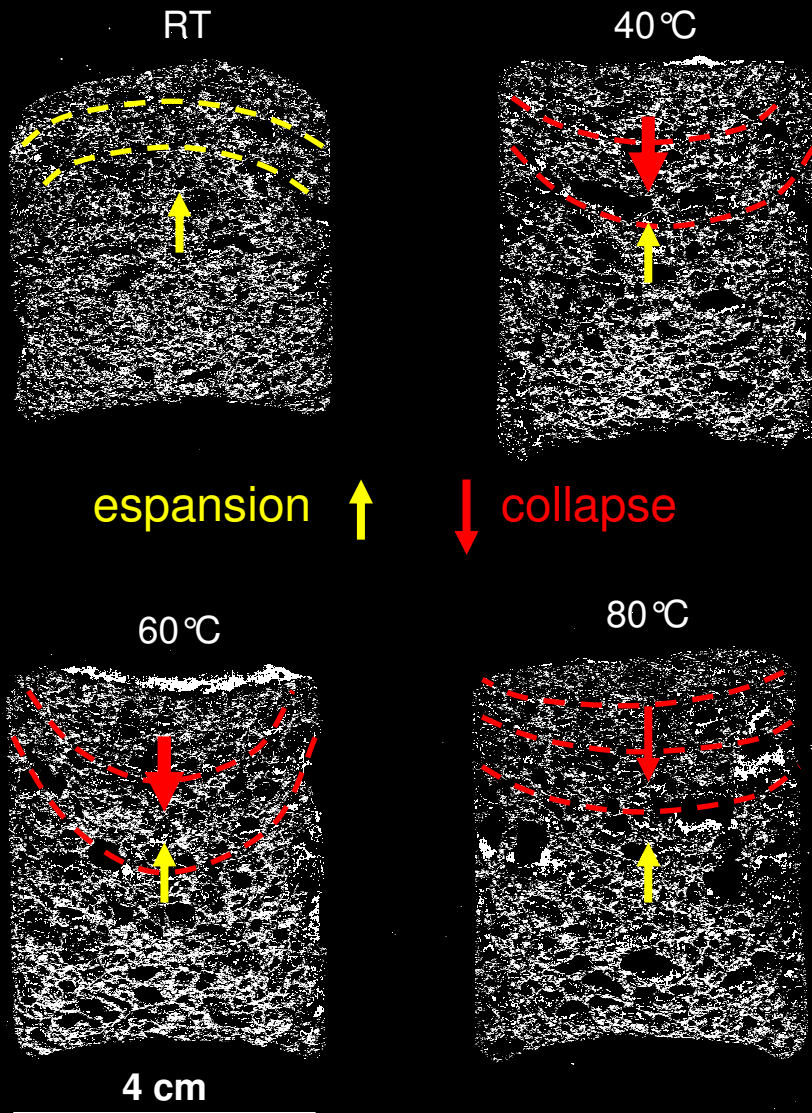
80°C

$\Delta V = +100\%$
 $d \sim 0.40 \text{ g/cm}^3$, porosity: 87%



Foaming: thermodynamic and viscosity effects

Image analysis of the ultra-macro-pores shape and direction



Viscosity decreased with T



Structure collapse occurred when the gas pressure exceeded the strength of the pore walls

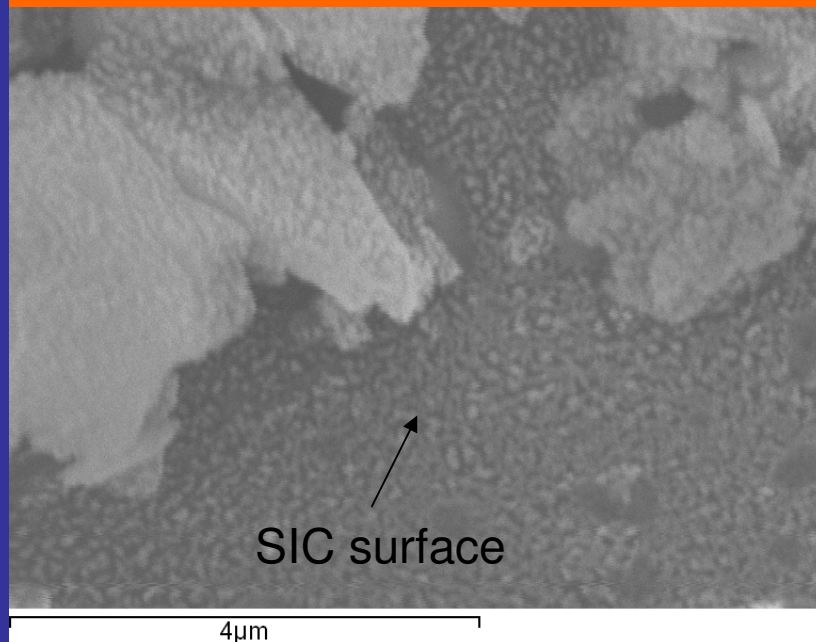
RT: volume expansion due to the low gas pressure

40°-60 °C: collapse because high H₂ pressure and low viscosity

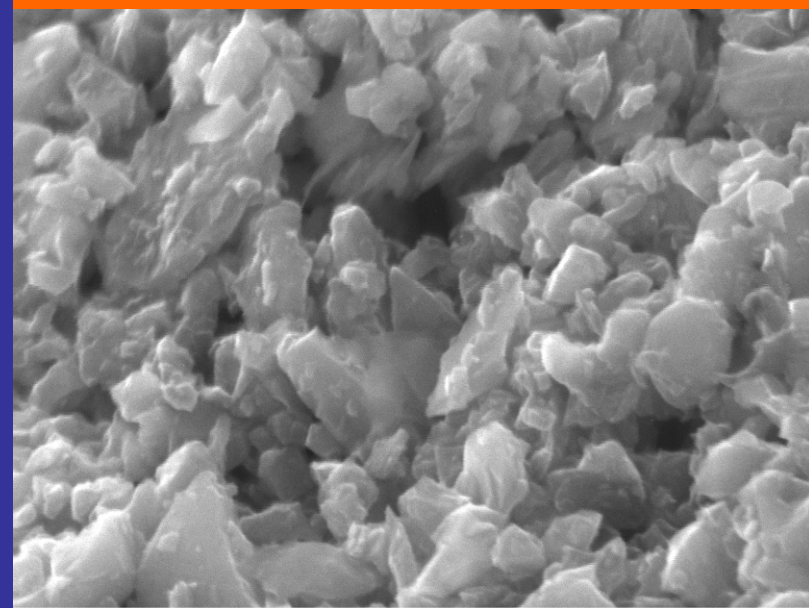
80 °C: optimal setting for geopolymer with viscosity increase that limited the structural collapse under high H₂ pressure

Micro- and nano-structure

α -SiC grade 100F, s.s.a.: 0.58 m²/g



β -SiC grade BF 12, s.s.a.: 11.6 m²/g

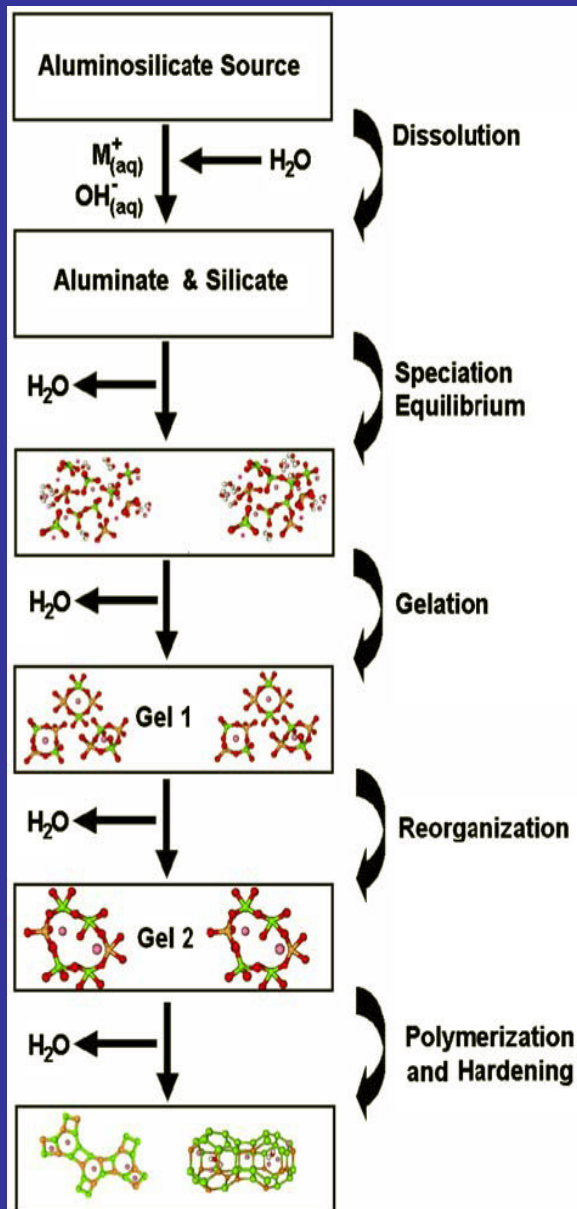


The microstructures β -SiC and α -SiC foams are very different

The surface of the α -SiC big particles is covered by geopolymeric nanoprecipitate of 60 nm and almost fully geopolymerized metakaolin particles.

In β -SiC foams, small grains constitute uniform and compact pore walls, where the binder is almost not visible

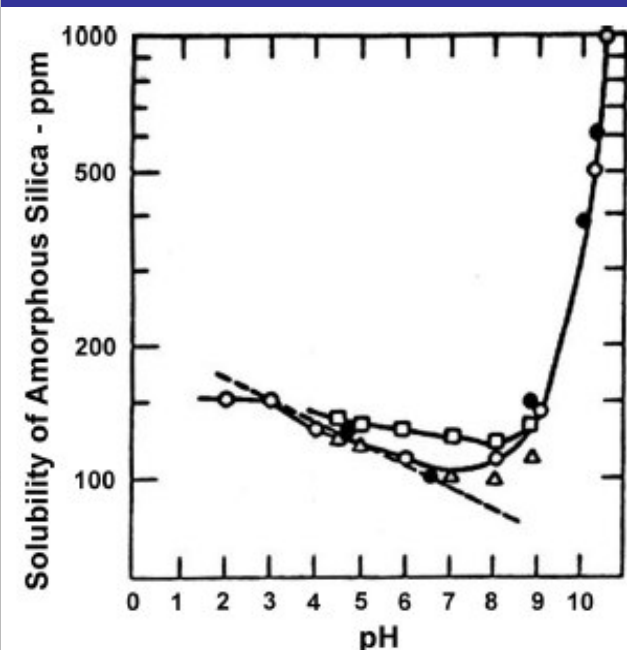
Geopolymerization mechanism



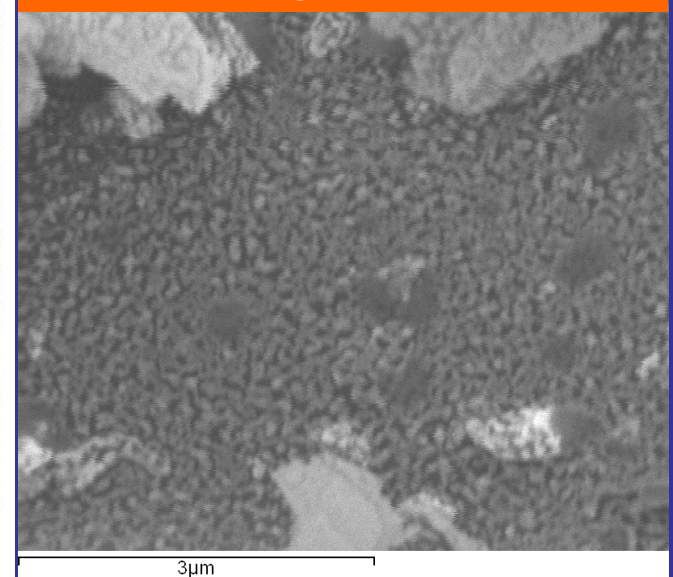
During alkaline hydrolysis the aluminosilicate source is dissolved giving distinct aluminate and silicate species.

The surface of SiC grains is always covered by an oxygen rich layer similar to the amorphous silica. Silica can readily be dissolved in alkaline media at $pH > 10$ to form $Si(OH)_4$ monomer, too.

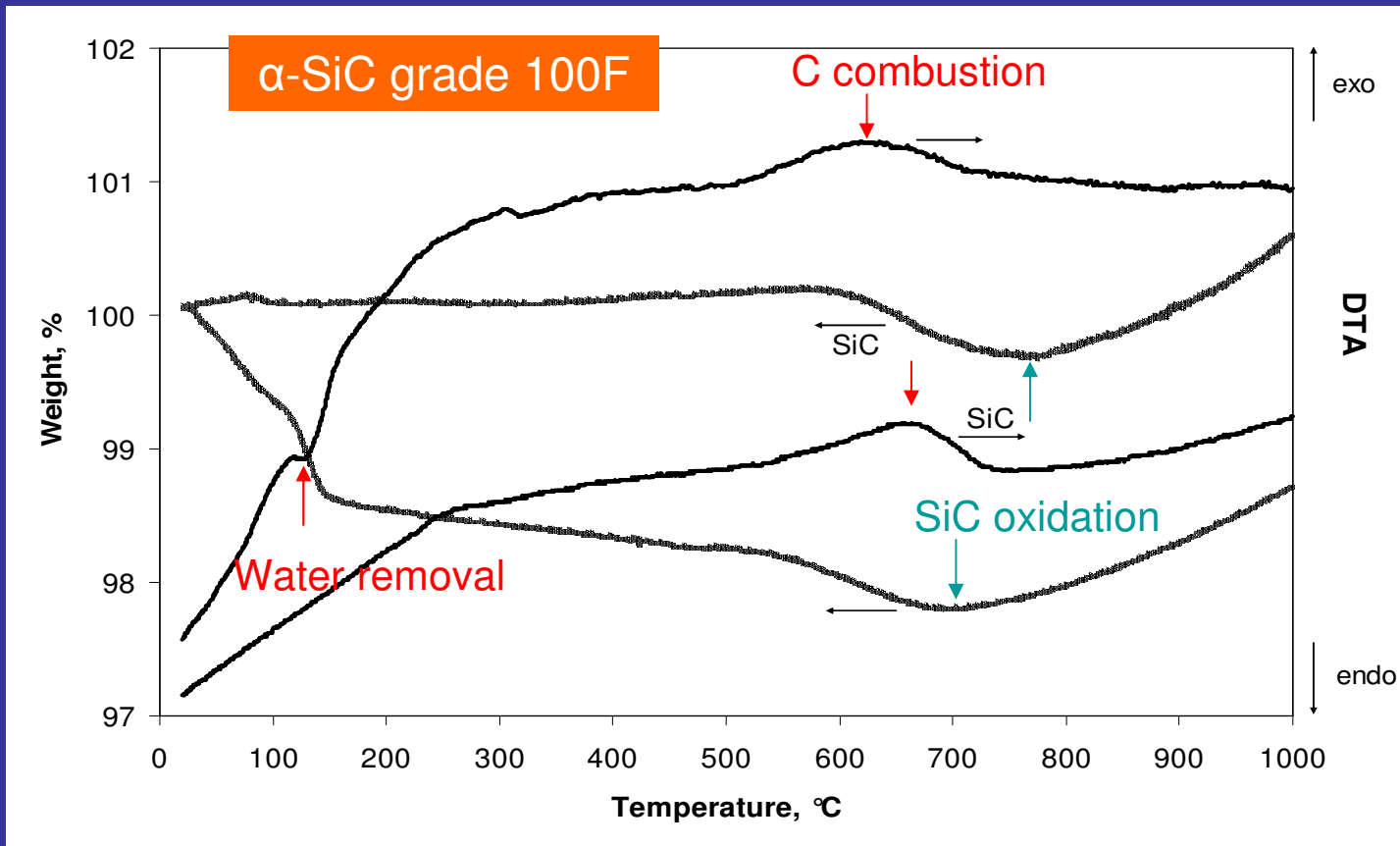
The surface of SiC particles participates to the geopolymeric process and geopolymeric nano-precipitates easily formed on SiC surface.



α -SiC grade 100F



Oxidation: non-isothermal STA in air

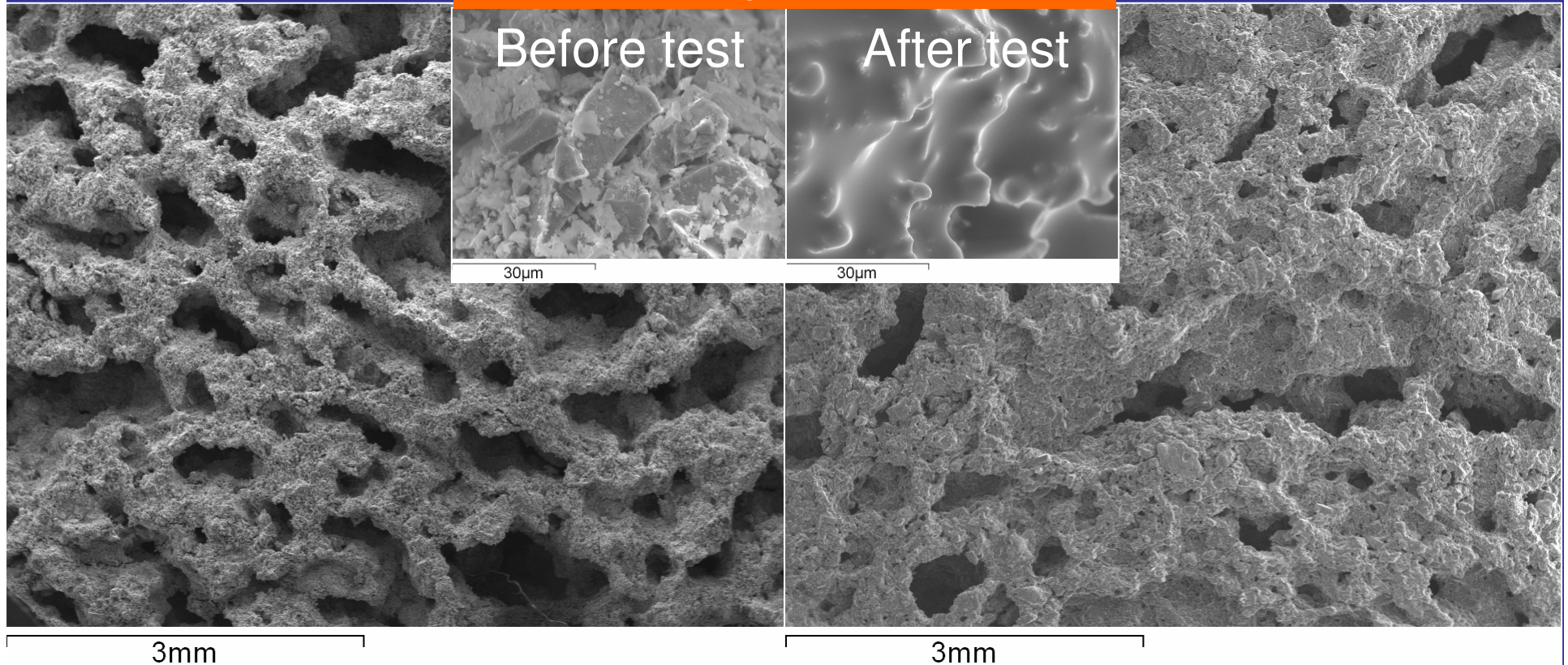


No weight change has been registered for SiC powder up to 600 $^{\circ}\text{C}$, where a weight loss of 1% may be related to residual carbon combustion (exothermic peak).

The SiC-based foam shows a weight loss due to water removal (endothermic peak ~ 130 $^{\circ}\text{C}$). The oxidation starts at lower temperature because the silica layer, that is usually present on the SiC surface is leached by the $\text{KOH}/\text{K}_2\text{SiO}_3$ solution at $\text{pH}=12$.

Preliminary tests of long term oxidation: 100 h at 1200 °C

α -SiC grade 100F



- the weight gain (+7%) related to the oxidation of SiC is half of the pure SiC powder
- Macro-porosity remains the same and the shrinkage is close to zero because of the expansion due to SiC oxidation
- Micro and nano-porosity disappear because of protective glass layer formation (SiO_2 from SiC oxidation + leucite $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ from geopolymer transformation)

Summary

INNOVATION: Consolidation of SiC based foams by using alkali activated inorganic binders (geopolymers) to replace the sintering step.

Si⁰ foaming agent is intrinsically contained in all SiC powders.

Thermodynamic and viscosity conditions influence the foaming structures since collapse occurs when the gas pressure exceed the strength of the pore walls.

The surface of SiC particles participates to geopolymerization as it is covered by amorphous silica and geopolymeric nano-precipitates easily formed on SiC surface.

The oxidation start at lower temperature because SiC surface is depleted of amorphous silica.

The linear shrinkage is close to zero after long term oxidation at 1200 °C and micro- and nano-porosity disappear because of protective glass formation.

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