MSE 495 – Advanced Ceramics Technology

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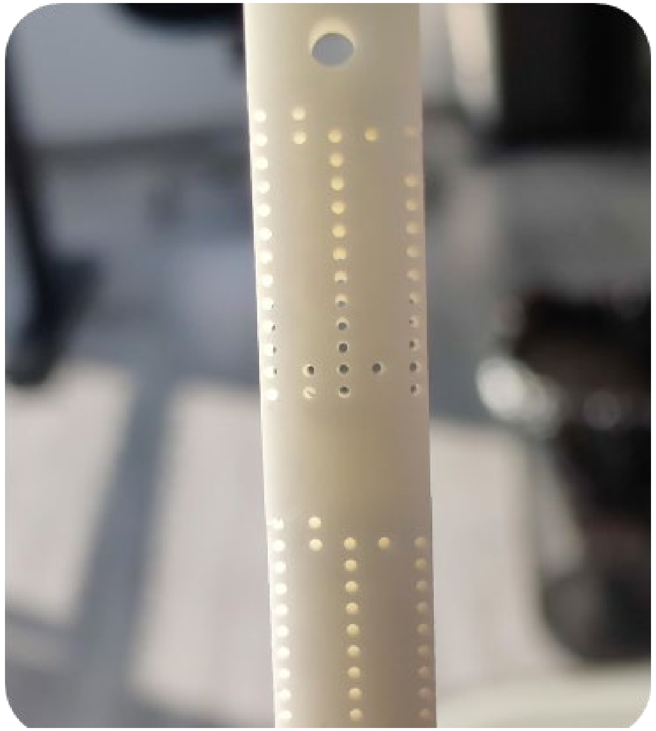
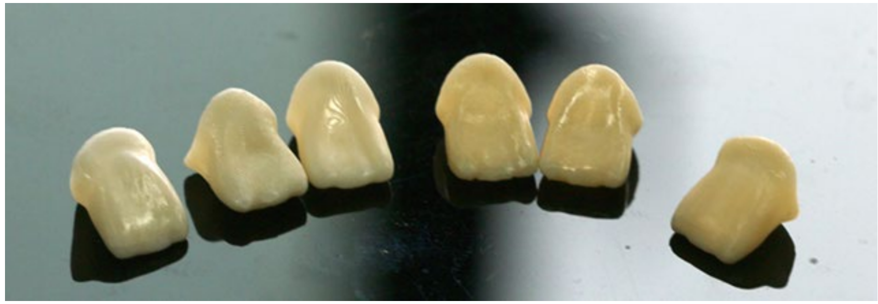
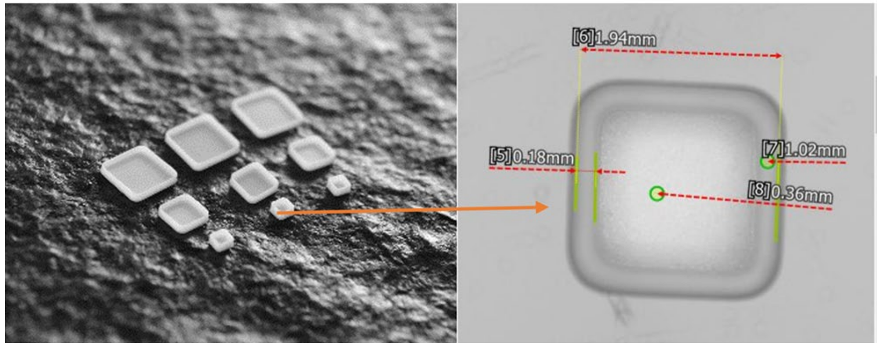
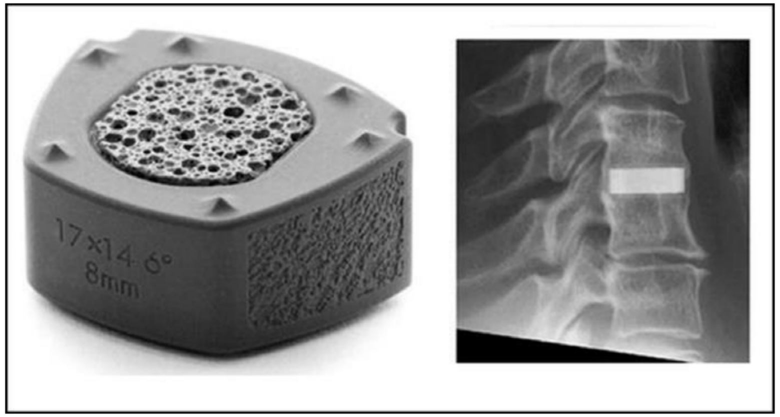
Week 6 – Non-oxide ceramics

Silicon Nitride



Silicon Nitride

Quite unique among advanced ceramics. Nearly ideal combination of properties. Composed by the most abundant terrestrial elements (N and Si), it is biocompatible and bioactive (osteoinductive and antibacterial).

Covalent Si-N bonds, difficult to sinter but high strength, toughness, hardness.

Its properties are related to the peculiar interlocking rod-like structure of the beta modification, formed during sintering from alpha phase.

Discovered in 1857, but only between 1970-1990 was largely studied for aerospace application, industrial turbines, and piston engines.

It requires specific sintering aids and special sintering conditions, such as pressure and special atmosphere.

Si_3N_4 processing needs high purity powders (>99.95%), small crystallite size (<200nm), narrow PSD, and high fraction of alpha phase modification. It is very rare in nature (extreme stellar conditions), but it is synthetized in tons amount from several producers.

Synthesis methods:

1. Direct nitridation of Si;	COMMERCIAL
2. Carbothermal reduction of SiO_2;	COMMERCIAL (to a limited extent)
3. Diimide decomposition;	COMMERCIAL
4. Vapor phase synthesis	
5. Pyrolysis of organic compounds	

1. Direct nitridation (Solid-Vapour Reaction)

$$3Si(s) + 2N_2(g) \rightarrow Si_3N_4(s); \quad \Delta H = -750 \text{ kJ/mol}$$

Conditions: continuous rotary kilns, T ≈ 1100 °C, being exothermic temperature increases but it needs to be kept below melting temperature (≈ 1412 °C)

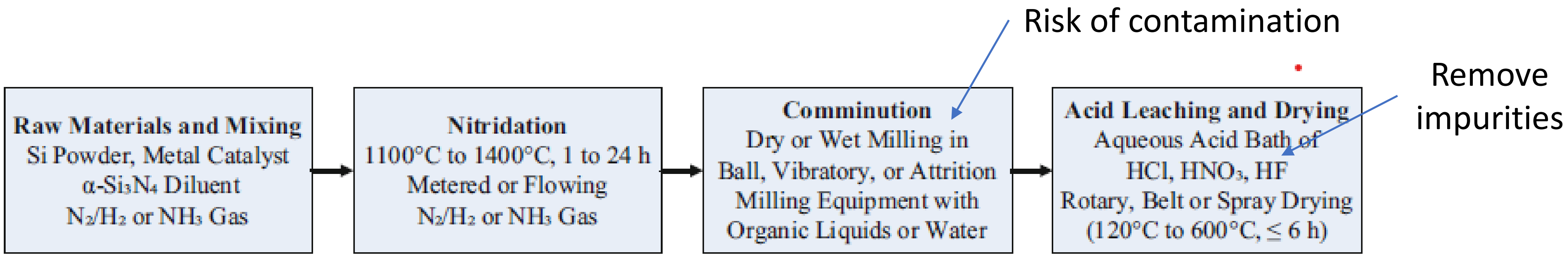


Fig. 1 Process for producing Si_3N_4 powder by the direct nitridation of silicon

Raw materials: Si high purity >99.99% with particle size <8 μm; N_2 >99.9+%

Contaminants in Si have strong influence on nitridation: Fe promoter, Al inhibiter. Oxygen needs to be completely removed (e.g. with H_2 atmosphere).

2. Carbothermal reduction

$$3SiO_2(s) + 2N_2(g) + 6C(s) \rightarrow Si_3N_4(s) + 6CO(g);$$
$$\Delta H = 1268\ \text{kJ/mol}\ [82]$$

Silica can be replaced by kaolin (silica-alumina) and produce SIAlON. Improvements were also implemented in the thermal treatment, replacing kiln oven with rotary or fluidized bed reactor.

The reactions endothermic: better temperature control can be achieved and resulting powder is less agglomerated.

Seeding with α-Si_3N_4 is also beneficial.

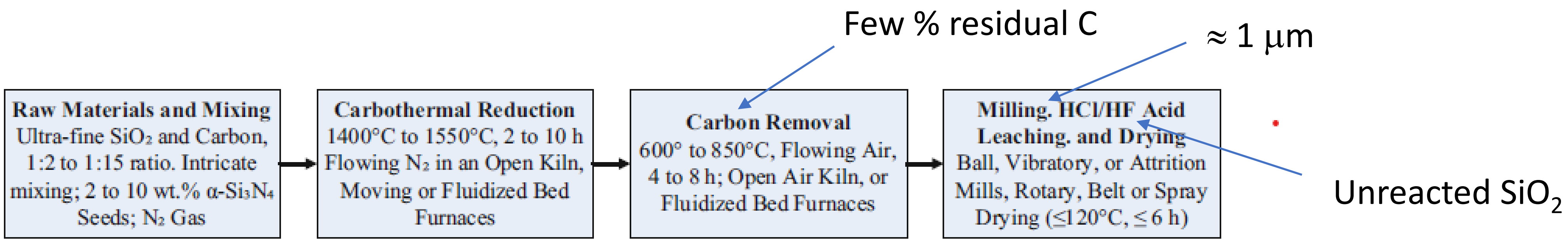


Fig. 2 Process for producing α-Si_3N_4 powder by carbothermal reduction of silica (SiO_2)

α-Si_3N_4 content > 95%, submicron particle size, purity >97% (mainly residual oxygen and C contamination).
Raw materials: fume silica (>99.97%, 10-150 nm), activated carbon (>99.95%, 10-20 nm), mixing ratio 4-5:1 (C:SiO_2), N_2 large excess (>99.95%). Despite large progress, this process have shown limited economic success respect to direct nitridation and diimide decomposition.

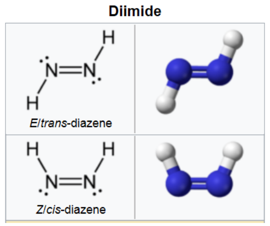
[82] Weimer, A.W.; Eisman, G.A.; Susnitzky, D.W.; Beaman, D.R.; McCoy, J.W. Mechanism and Kinetics of the Carbothermal Nitridation Synthesis of α-Silicon Nitride. J. Am. Ceram. Soc. 1997, 80, 2853–2863, https://doi.org/10.1111/j.1151-2916.1997.tb03203.x.

3. Diimide decomposition

Si diimide

$$SiCl_4 + 6NH_3 \rightarrow Si(NH)_2 + 4NH_4Cl; \quad \Delta H_{298} = -676.0 \text{ kJ/mol} \quad [108]$$

$$3Si(NH)_2 \rightarrow Si_3N_4 + 2NH_3; \quad \Delta H_{298} = 230.8 \text{ kJ/mol} \quad [118]$$



Very old known process, but commercially developed only in 1970-1990. It is a two-steps reaction. First, diimide is formed. $SiCl_4$ and NH_3 (liquid) reaction is exothermic and not easy to control. The process improved by dissolving the chemicals in an organic solvent at low T (e.g., -50, -80 °C). At that conditions, NH_4Cl is soluble (in liquid ammonia) into the solvent mixture (hexane and liquid ammonia are not soluble into each other) and the solid diimide is separated by filtration. The rection mainly occurs at the interface of the two liquid phases.

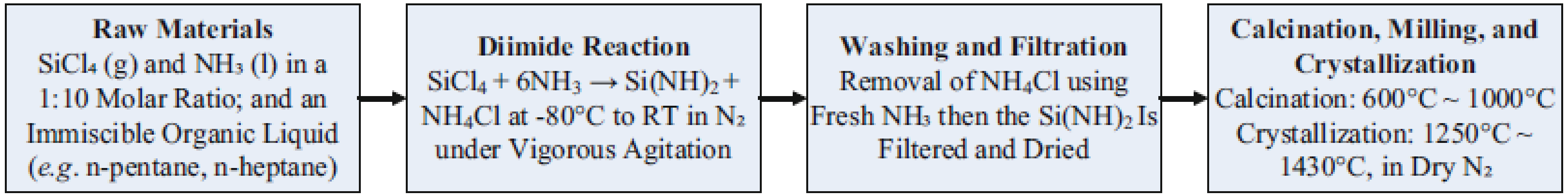


Fig. 3 Process for producing α-Si_3N_4 powder using silicon diimide decomposition

In the second step, the diimide is calcined under dry N_2 and then milled. The resulting material is amorphous which then crystalizes to α-Si_3N_4 at higher T. This method provide materials at high purity, quality and reproducibility used for MedTech applications.

[108] Crosbie, G.M.; Predmesky, R.L.; Nicholson, J.M.; Stiles, E.D. Prepilot Scale Synthesis of Silicon Nitride under Pressure. Am. Ceram. Soc. Bull. 1989, 68, 1010–1014.
[118] NIST-JANAF Thermochemical Tables. https://janaf.nist.gov/ 2023

Comparison of commercial materials

Table 1 Chemical and physical properties of commercially available Si_3N_4 powders

Powder production process	Direct nitridation of silicon				Diimide decomposition	Carbothermal reduction of silica
Manufacturer	Höganäs[a]	Vesta[b]	Denka[c]	AlzChem[d]	Ube[e]	Toshiba[f]
Trade name	M11 HP	P95H	SN-9FWS	Silzot HQ[Plus]	SN-E10	A-200
% N	≥38.5	NR	NR	>38.7	>38.0	37.5
% α-Si_3N_4	≥90.0	>91.0	≥91.0	≥95.0	>95%	98.0
Impurities wt.%						
C	<0.30	<0.50	<0.10	<0.20	<0.10	0.90
O	<2.0	<1.50	<0.80	<0.60	<2.00	2.00
Al	<0.005	<0.08	<0.09	<0.07	0.0001	0.20
Ca	<0.001	<0.02	<0.10	<0.03	<0.0001	0.01
Fe	<0.001	<0.06	<0.018	<0.03	<0.001	0.007
Si	NR	<0.2	NR	<0.02		NR
Cl	NR	<0.002	NR	<0.02	<0.01	NR
Physical properties						
Surface area (m^2/g)	9.0–12.0	10.0–12.0	11	NR	9.0–13.0	NR
Particle size (d_{50} µm)	0.7–0.9	0.9	0.7	1.9	0.6	0.9

Sources: [a]hoganas.com/en; [b]Vesta Si Europe AB, Ljungaverk, Sweden; [c]denka.co.jp/eng/; [d]alzchem.com/en/; [e]ube.com/contents/en/; [f]Lange et al. Ref. [38]

The produced materials are all very similar and in principle all suitable for applications in MedTech. Sometimes the material selection is a matter of regulatory affairs, traceability, supply chain, and conservative approaches.

Source: Silicon Nitride Bioceramics, Springer, 2024 https://doi.org/10.1007/978-3-031-67047-3

Silicon nitride and ceramic processing

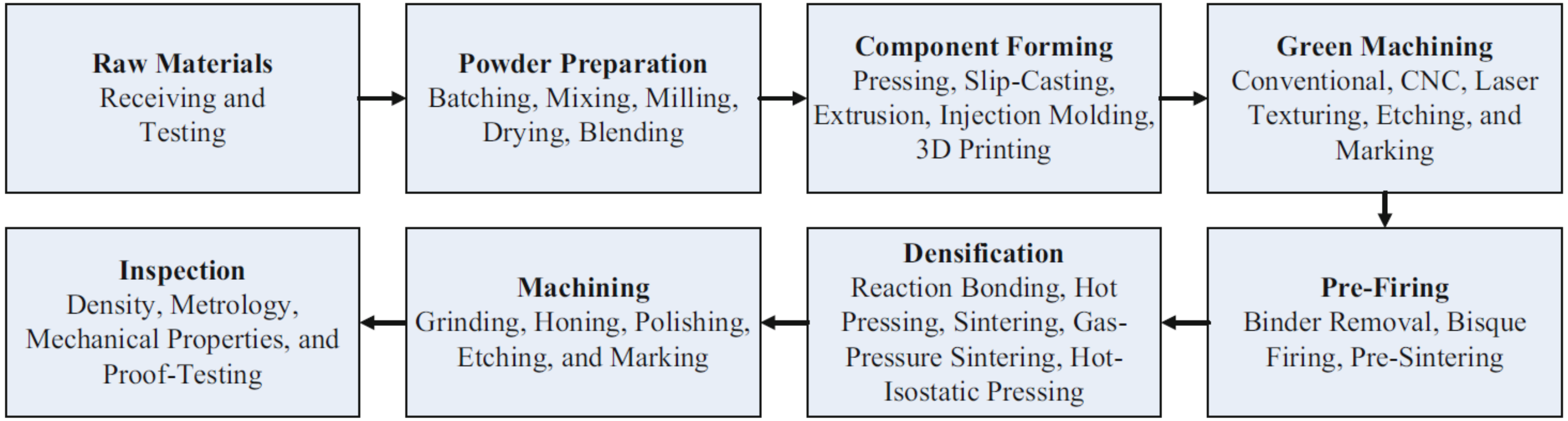


Fig. 4 Processing of silicon nitride bioceramics

See the entire course, nothing new!

Almost all methods make use of sintering aids. The most common are MgO, CaO, Y_2O_3, and Al_2O_3 in the amount up to 10wt%. Their working principle is the formation of a liquid phase at high T (liquid phase sintering, see Dr. M. Stuer slides) and promoter for β-Si_3N_4 formation. High amount of Al_2O_3 can be used to yielding SiAlON, which is a common MedTech ceramics.