Imperial College London

Centre for Nuclear Engineering

CASC

Nuclear Futures Institute

PRIFYSGOL BANGOR UNIVERSITY

HOW TO MAKE A GOOD CERAMIC

BILL LEE.

Joint ICTP-IAEA International School on Nuclear Waste Actinide Immobilization.

Abdus Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, 10-14th Sept. 2018.

Basic Concept.

- Materials are manufactured to be in the solid state (or at least very viscous liquids in the case of glass).
- Their production usually involves taking solid raw materials (mineral powders) and forming a solid shaped component via intermediate solid, liquid or vapour phases.

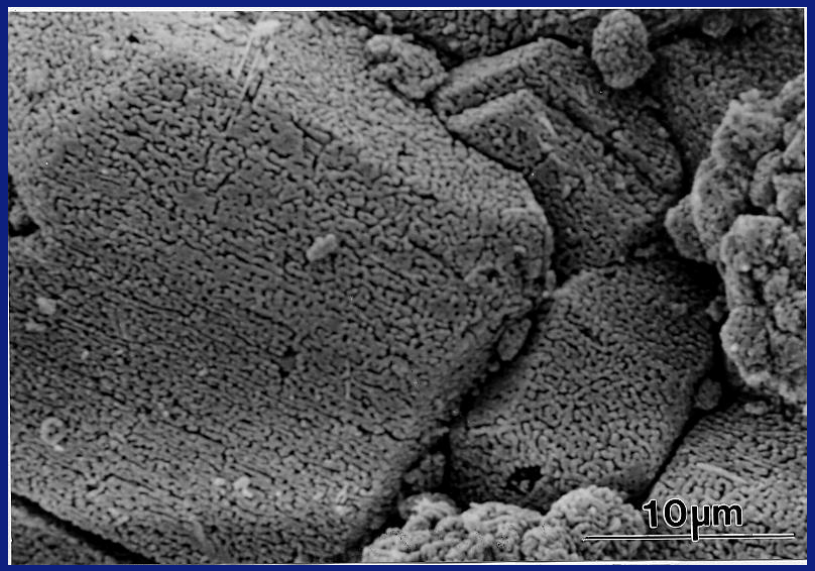
Ceramic Processing: Bulk Ceramics From Powders

Starting Powder
↓
Calcine
↓
Mill
↓
Grade particle size/size distribution
↓
Mix plus liquid additives (binders)
↓
Granulate
↓
Compact/Shape Form
↓
Dry (50% dense)
↓
Fire/Densify/Sinter (96-98% dense)
↓
Heat Treatment
↓
Machine

- Holistic approach.
- Many steps, each of which can influence properties of final product.
- Highly pure powders with small particle size (often nano) and even size distribution.
- Reduction in surface area provides driving force for densification on sintering.
- Large and controlled shrinkage on sintering.

Calcination.

- Endothermic decomposition reactions in which an oxysalt decomposes to oxide solid and gas.
- E.g. $Al(OH)_3 \rightarrow Al_2O_3 + H_2O$.
- E.g. $CaCO_3 \rightarrow CaO + CO_2$.
- Product is usually reactive and sinterable powder.



Milling.

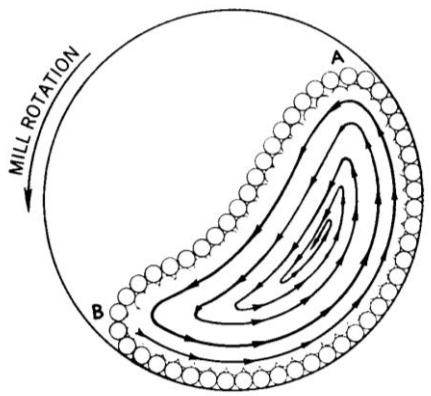


Fig. 17.4 Schematic diagram of ball mill showing media cascading from A to B and subsequent media movement.

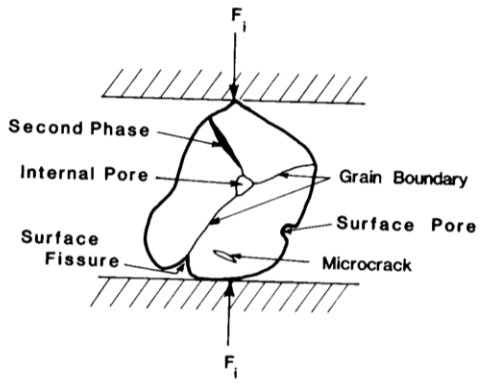


Fig. 17.9 Microstructural defects reduce the strength and grinding resistance of a particle.

- E.g. ball milling.
- Reduce particle size in controlled manner.
- Fracture of powder particles.
- Contamination from wear of media so match to product.

Granulation.

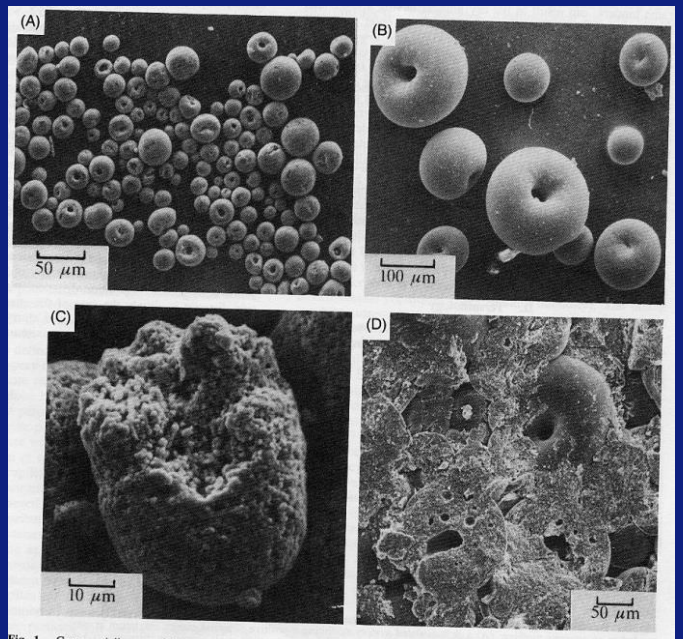


Fig. 1. Commercially spray-dried powders: (A) $MnZnFe_2O_4$; (B) Al_2O_3; (C) $MnZnFe_2O_4$; (D) fracture surface of a partially sintered compact of the Al_2O_3 in (A) showing the internal structure of the granules (Ref. 8).

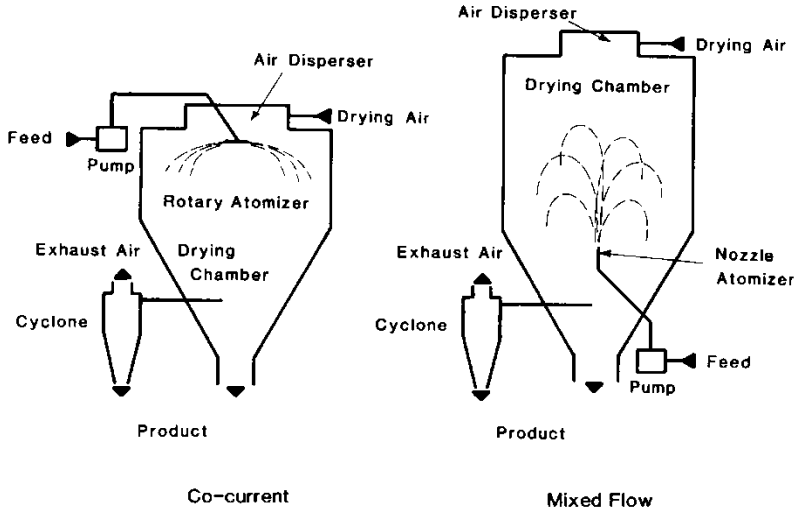


Fig. 20.5 Spray dryers: (left) cocurrent spray dryer with centrifugal atomizer, and (right) mixed-flow spray dryer with a nozzle atomizer.

- **Forming agglomerates from powder by addition of binding agent and a processing step such as spray drying.**
- **Granules (or granulates) usually made spherical to improve powder flow and packing behaviour.**

Purpose of Shape Forming.

- To get as close to final shape (not size) as possible – since machining ceramics is difficult as they are hard and it introduces surface flaws.
- To get maximum particle packing and uniformity so get minimum porosity during densification.

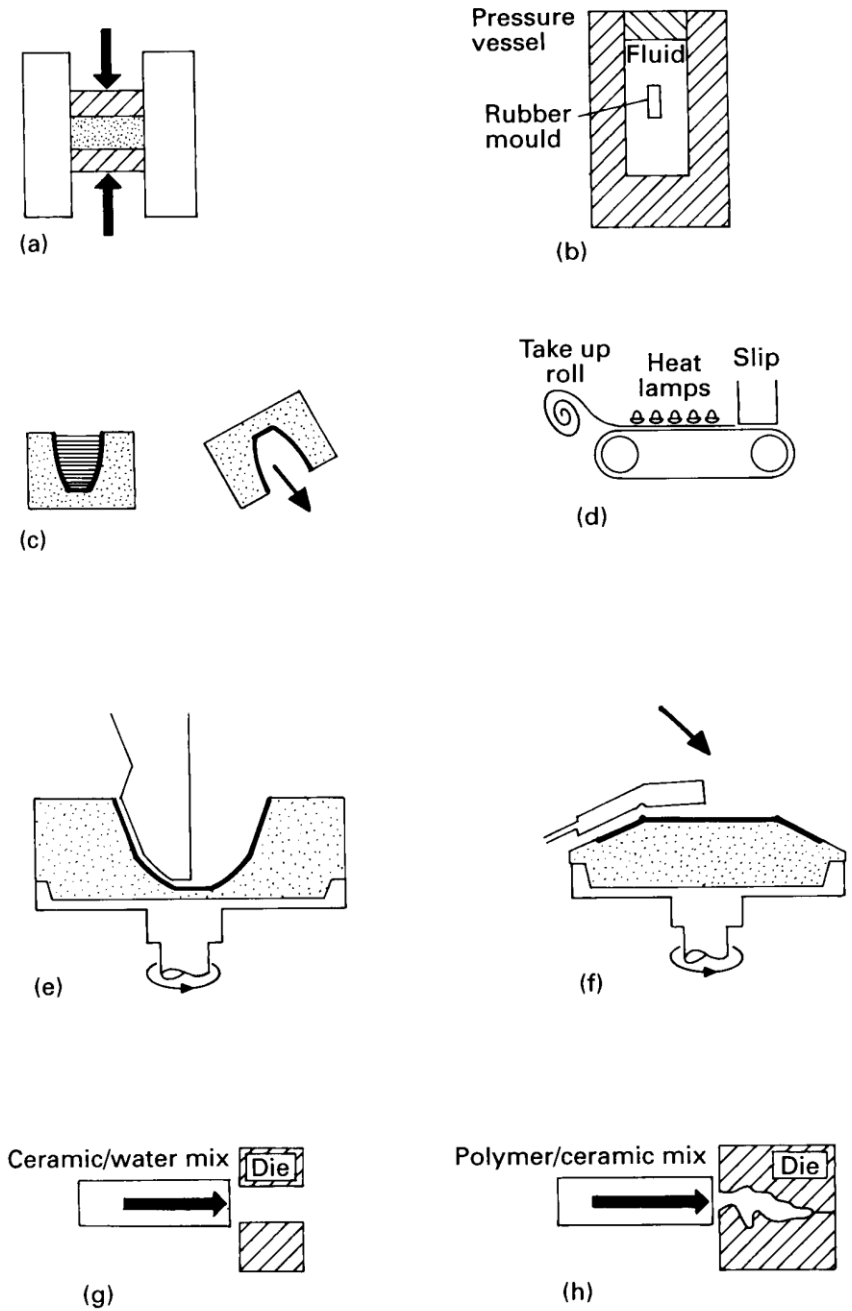


Fig. 1.26 Techniques used to form shapes from ceramic powders: (a) uniaxial pressing, (b) isostatic pressing, (c) slip casting, (d) tape casting, (e) jolleying, (f) jiggering, (g) extrusion and (h) injection moulding.

Shape Forming Techniques.

- After shape forming but before firing body is said to be green.
- Different rheology mixtures used for various shape forming operations e.g. “dry” powders, slurries, pastes and plastic bodies.

Sintering.

- Removal of pores between starting particles accompanied by shrinkage of the component combined with growth together and formation of strong bonds between adjacent particles.
- Driving force is reduction of surface area obtained by replacing a loose powder having many high energy solid-vapour interfaces with a bonded solid having fewer lower energy solid-solid interfaces.
- Therefore, desire fine starting powders (submicron size particles).
- Solid State Sintering (SSS) and Liquid Phase Sintering (LPS), <20% liquid.
- Usually aim in structural ceramics for as high a density as possible.

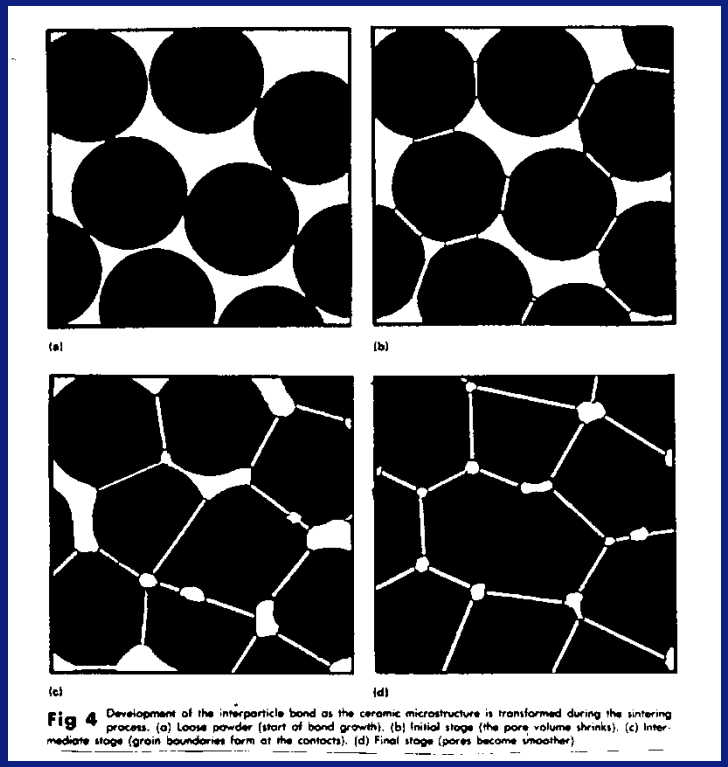


Fig 4 Development of the interparticle bond as the ceramic microstructure is transformed during the sintering process. (a) Loose powder (start of bond growth). (b) Initial stage (the pore volume shrinks). (c) Intermediate stage (grain boundaries form at the contacts). (d) Final stage (pores become smoother)

Ceramic Densification Processes.

- **SSS Solid State Sintering:**
  Only solid involved in mass transport.

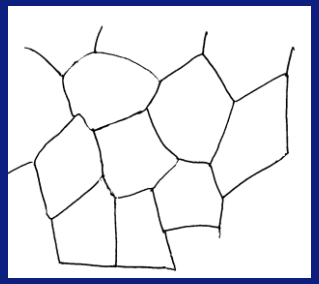
- **LPS Liquid Phase Sintering:**
  Less than 15vol% of ceramic becomes liquid.

- **VGS Viscous Glass Sintering:**
  All ceramic becomes liquid. Viscous flow.

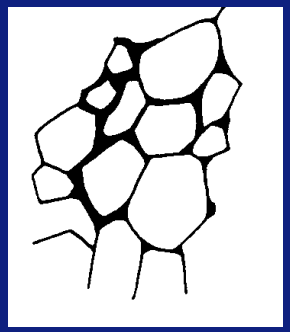
- **VCS Viscous Composite Sintering:**
  > 15vol% but < 60vol% of ceramic becomes liquid. Common in clay-derived ceramics.

Relation Between Ceramic Microstructure and Densification Process.

- **Solid State Sintered.**
  Typically single phase, clean grain boundaries.



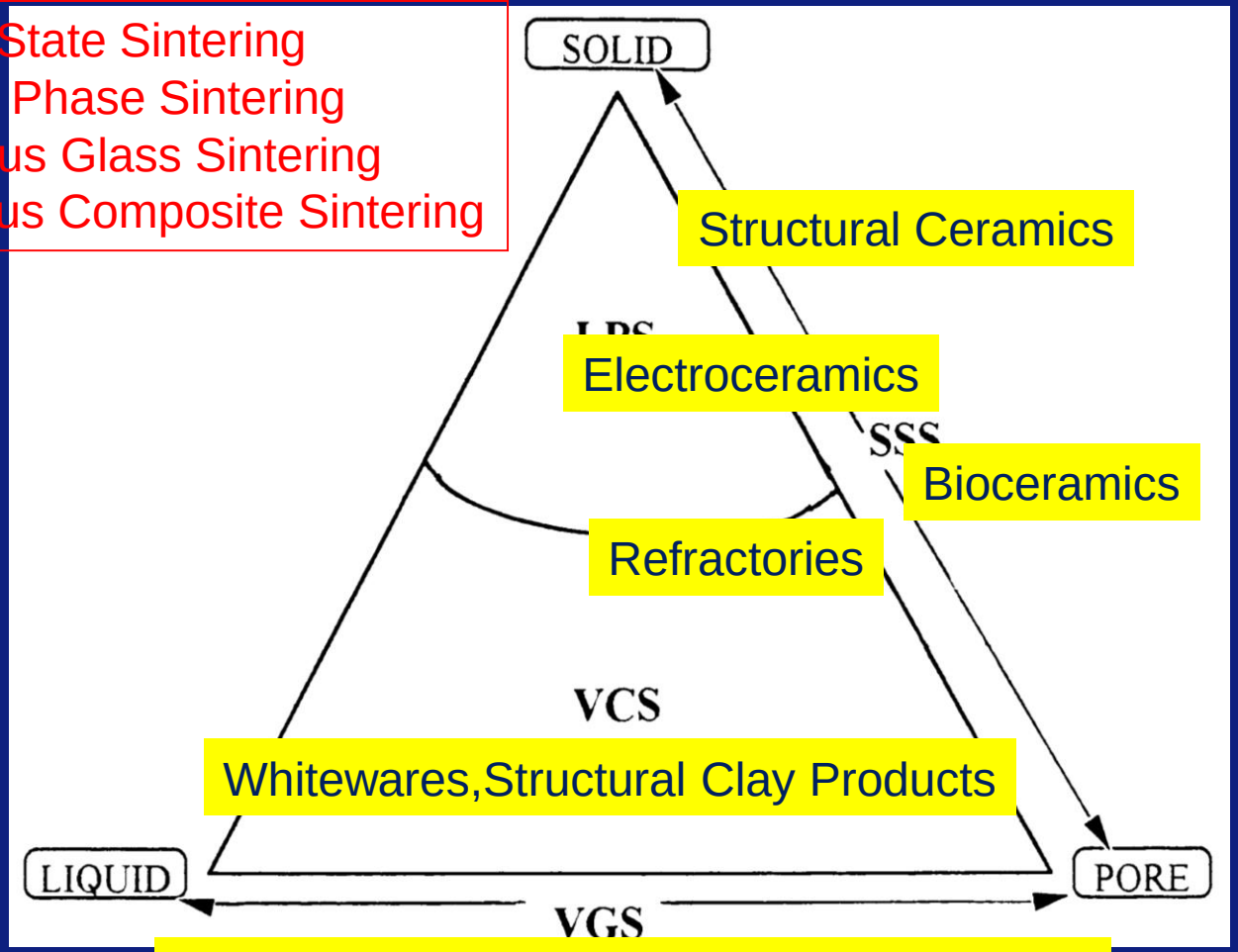
- **Liquid Phase Sintered.**
  Second phase at grain boundaries, often glassy.



- **Vitreous or Viscous Composite Sintered.**
  Multiphase grain and bond system.

Relation Between Ceramic Type and Densification Process.

SSS Solid State Sintering
LPS Liquid Phase Sintering
VGS Viscous Glass Sintering
VCS Viscous Composite Sintering



Structural Ceramics

Electroceramics

Bioceramics

Refractories

Whitewares,Structural Clay Products

Glasses, Glass Ceramics, Glazes, Enamels

Importance of Wetting and Capillary Forces in Ceramic/Glass Processing.

- Provide a mechanism for migration of liquid.
- Movement of liquid helps e.g.
  - to hold together wet powder agglomerates, rearrangement of particles during mixing,
  - removal of water in drying and slip casting,
  - glazing of ceramics,
  - corrosive attack of refractory linings by molten liquids (glasses and metals),
  - densification during LPS (alumina spark plug),
  - spreading of molten glass on liquid Sn (float glass).

Glass/Ceramic/Cement Wasteforms

Ceramics | Cements

Solid State or Liquid Phase Sintered

- Pressureless Sintered or Hot Pressed.
- Single phase e.g. zircon or multiphase e.g. Synroc.

Room Temp. Hydration

- OPC-based Composites or Alternates e.g. CSA.
- Multiphase.

Glass Composite Materials

Vitrified or Viscous Composite Sintered

- Glass Ceramics.
- Crystal-containing Melted Wasteforms (cold or hot crucible).
- Crystal Waste Encapsulated in Glass Matrix.

Glasses

Vitrified

- R7T7.
- Magnox
- RBMK.

Categories of Wasteform.

- Glasses (covered by Florence Bart).
- Glass Composite Materials (GCM's):
  1. Glass ceramics.
  2. Crystal-containing glasses from process.
  3. Crystalline waste encapsulated in melt which solidifies to glass.
- Ceramic wasteforms:
  1. Single phase: e.g. $ZrSiO_4$, ZrO_2
  2. Multiphase: e.g. Synroc.

Advanced Wasteforms: Glass Composite Materials (GCMs)

Mixed Glass and Crystal Wasteforms.

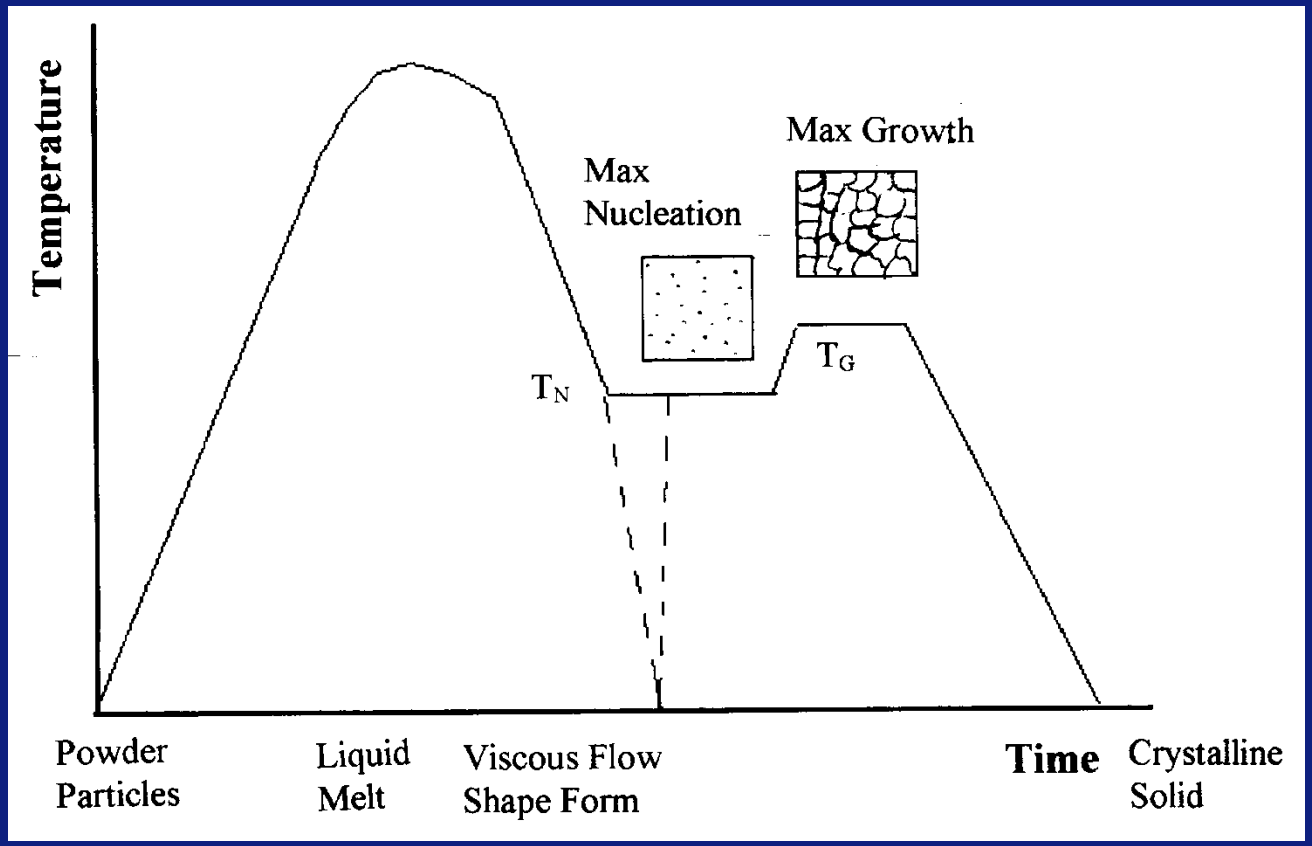
1. **Glass ceramics, glass crystallised on cooling or in separate heat treatment step e.g. zirconolite-based for separated long-lived actinides.**
2. **Glassy wasteforms in which crystals form on processing e.g. French U/Mo glasses via Cold Crucible Melter.**
3. **Crystalline waste encapsulated in melt which solidifies to glass (e.g. Joule Heater In-Can Vitrification).**

1. Glass Ceramic Processing & Crystallisation.

- Viscous Glass Sintering, crystallise on cooling (via hold) or in separate operation.
- Bulk and surface crystallisation.
- Bulk or pressed powder (surface nucleation).
- Nucleating agent to encourage heterogeneous nucleation and fine microstructure.
- Frequently form metastable phases which transform to thermodynamically-stable phases on heat treatment.

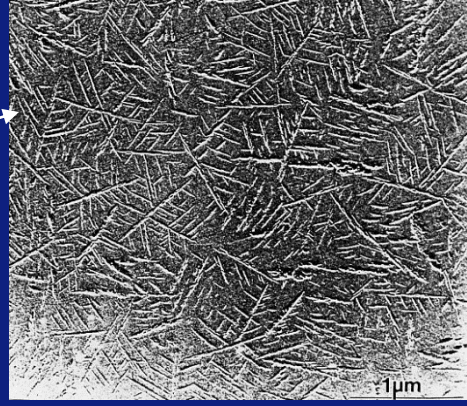
Glass Ceramic Processing.

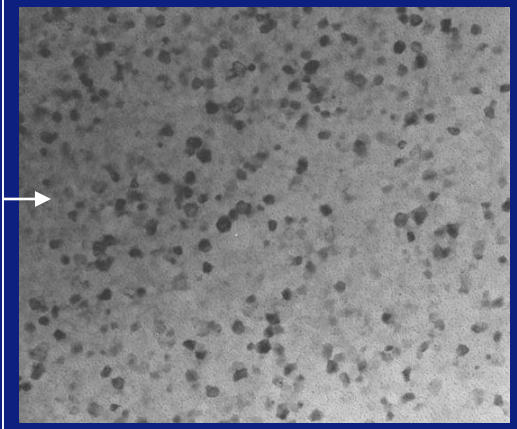
- Often two step heat treatment.
- Can hold on cooling from melt, *controlled* cooling.

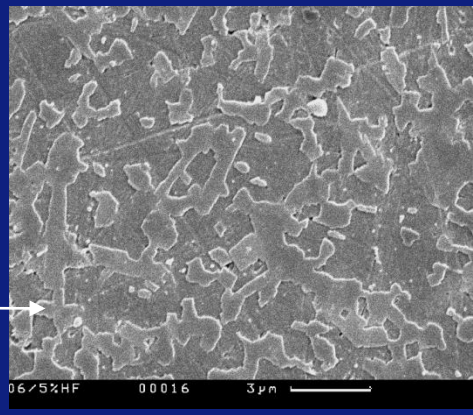


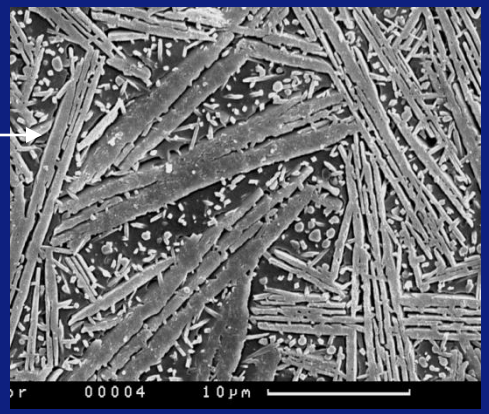
Glass Ceramic Microstructures.

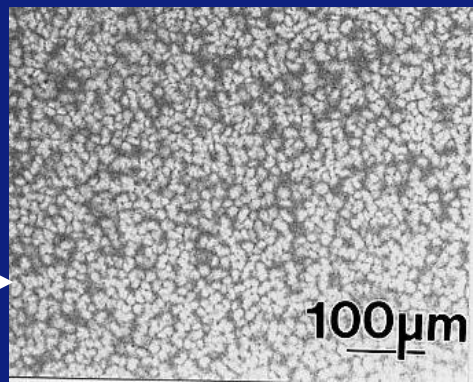
- Dendritic.
- Ultra-fine Grained.
- Coast and Island.
- House of Cards.
- Spherulitic.





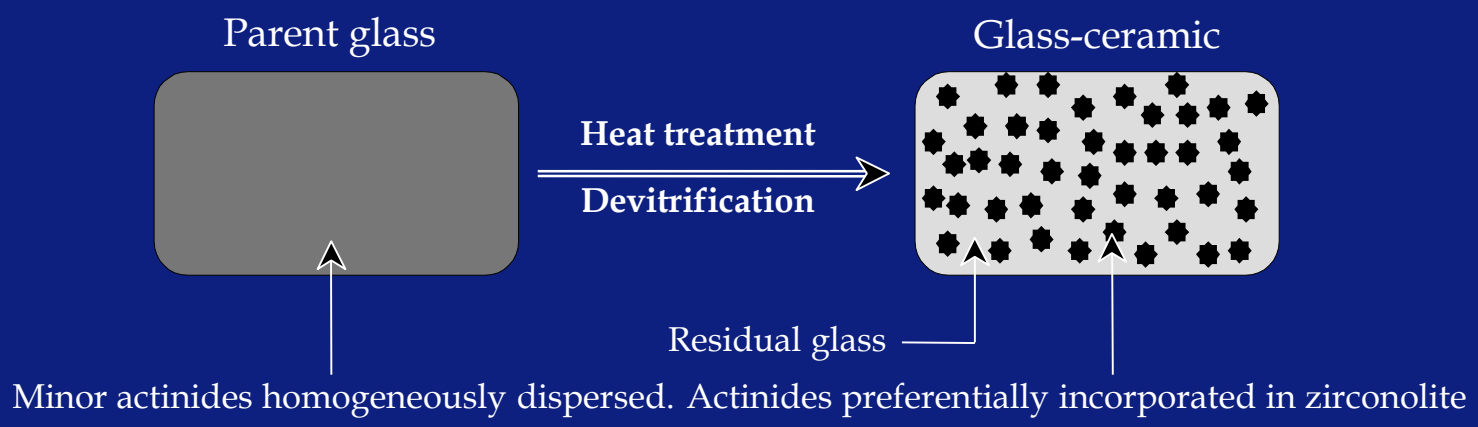






GCM's: Glass Ceramics.

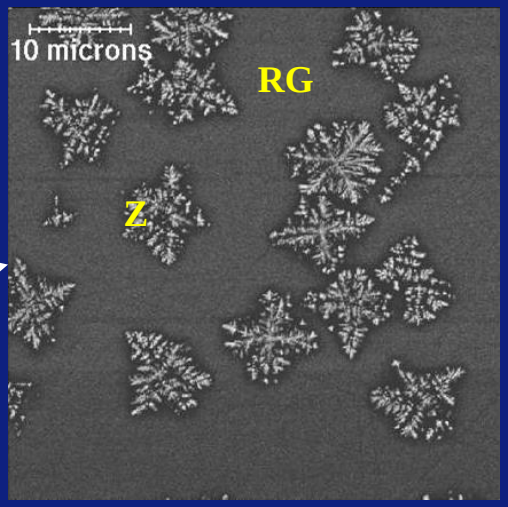
- Desirable to separate very long lived actinides from waste and incorporate into more durable and smaller volume form.
- E.g. zirconolite-based ($CaZr_xTi_{3-x}O_7$, $0.8 \leq x \leq 1.37$) glass ceramics in calcium aluminosilicate (CAS) glass.

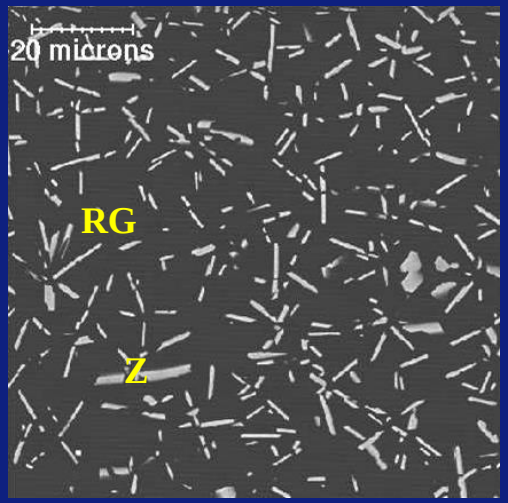


⇒ Double barrier of containment (crystals + residual glass)

Actinide-incorporating Zirconolite Glass Ceramics.

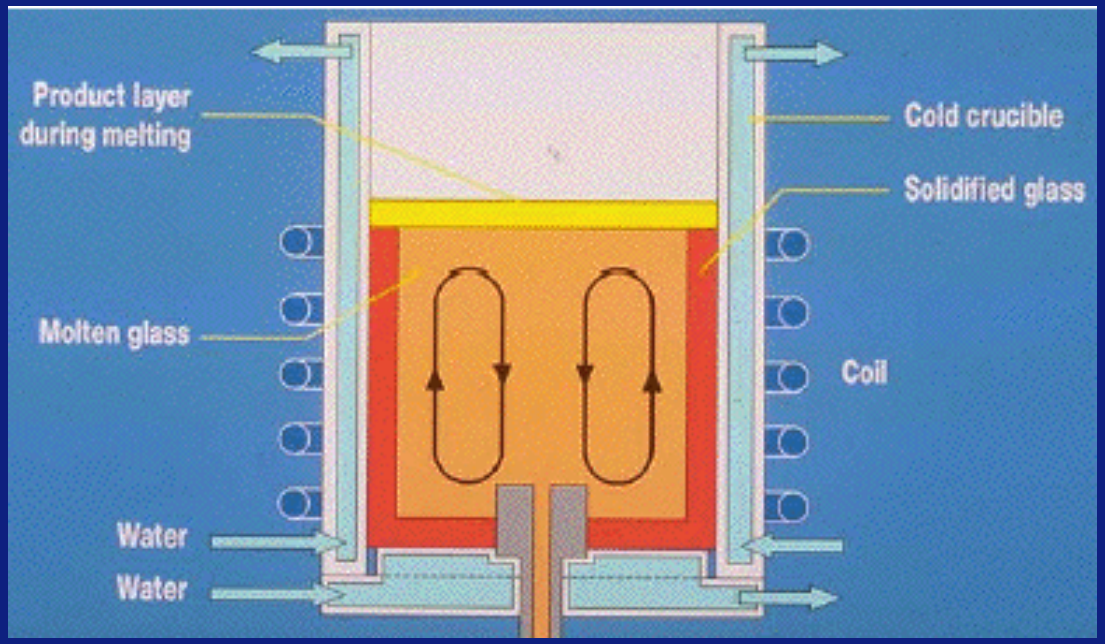
- T_m 1550-1650°C.
- T_c 950°C bulk nucleation metastable fluorite-structured zirconolite dendrites (Z) in residual glass (RG).
- T_c 1050°C elongated zirconolite (Z).
- Nd (simulant actinide) only in zirconolite crystals.





2. GCMs in which crystals form on Cold Crucible Melting.

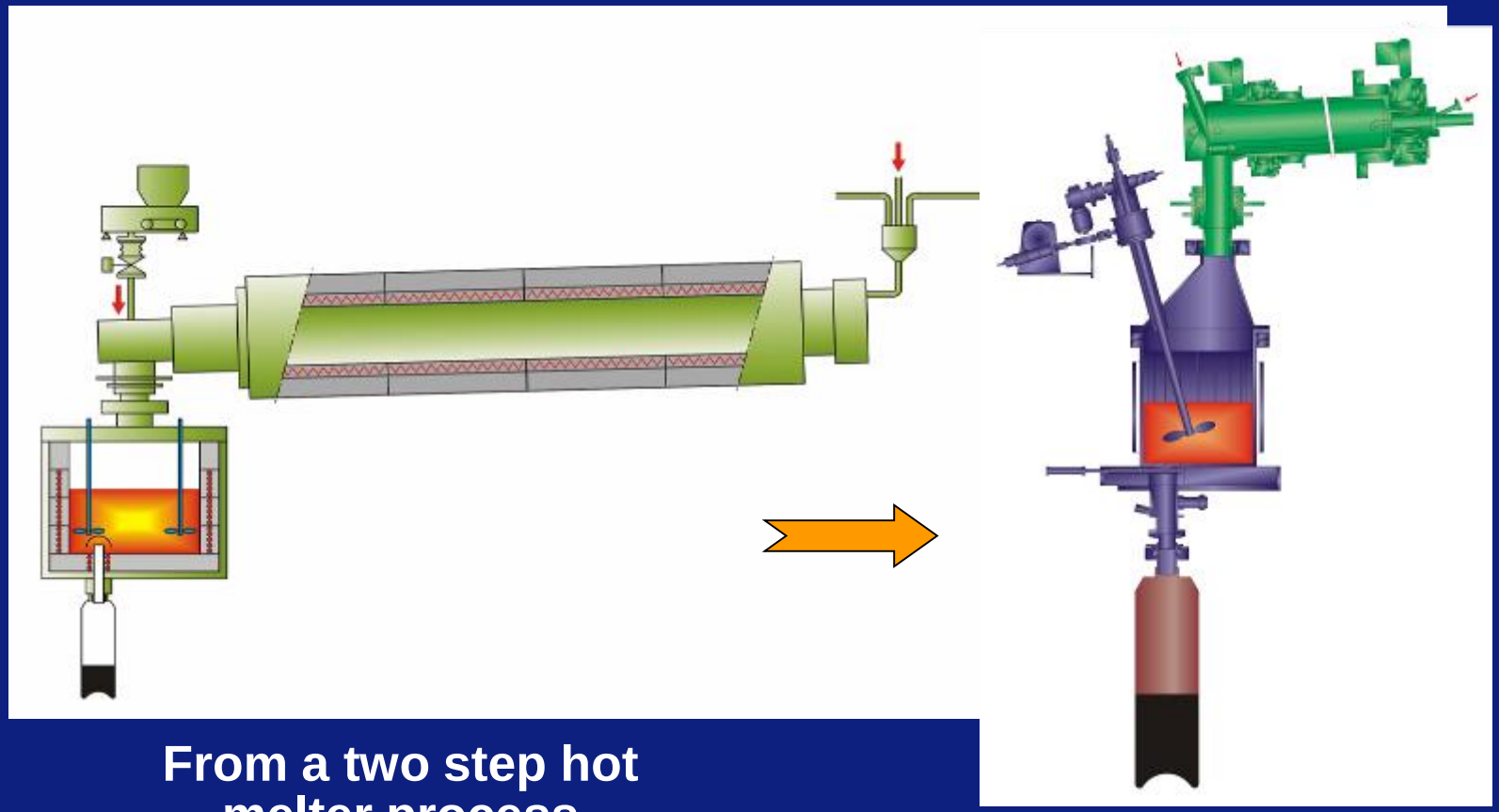
- Small batch-type melters.
- Can go to higher temperatures than standard induction melters so good for refractory wastes.
- No contamination of refractory lining.



Cold Crucible Induction Melter at La Hague, France

- CEA have U/Mo/P-rich waste from gas cooled reactors.
- High Mo and P melt is corrosive and requires high temperature (1250ºC) glass formulation to incorporate enough Mo (12wt%) so cannot use two stage hot crucible.
- Developed CCM in which waste and CaO-ZrO_2 enriched alumino-borosilicate glass additives melted by direct high frequency induction.
- Greater waste loading and glass throughput due to higher melting temperature.
- Greater flexibility in feed stream variability acceptance due to high temperatures and mechanical stirring in melter.
- CCM installed early 2010 in existing vitrification hot cell.

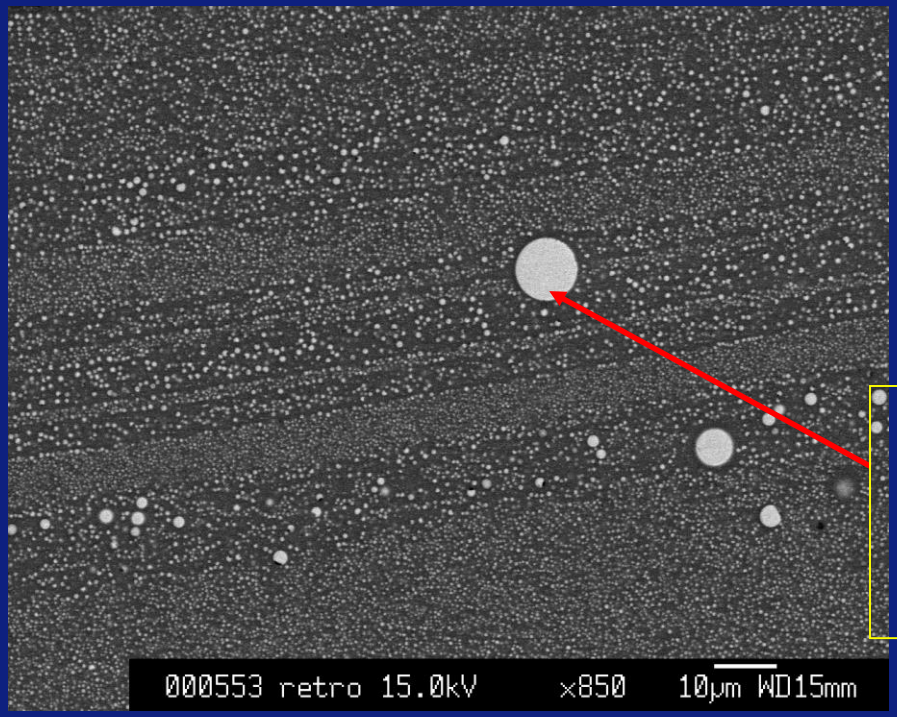
Major On-line Developments
The Cold Crucible Induction Melter



From a two step hot melter process

To a two step cold crucible melter process

U/Mo Wasteform Microstructure

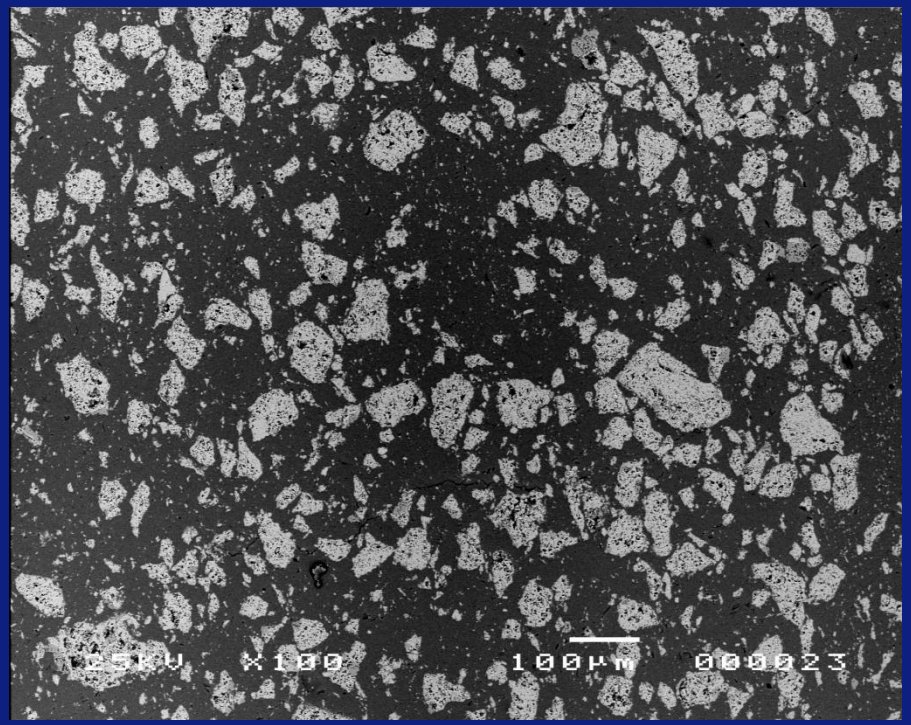


µ-spheres enriched in Mo, P, Ca.

- **Liquid-liquid phase separation leads to crystallisation of water soluble molybdate microspheres isolated in R7T7 type glass matrix.**

Courtesy T. Advocat, CEA Marcoule, France.

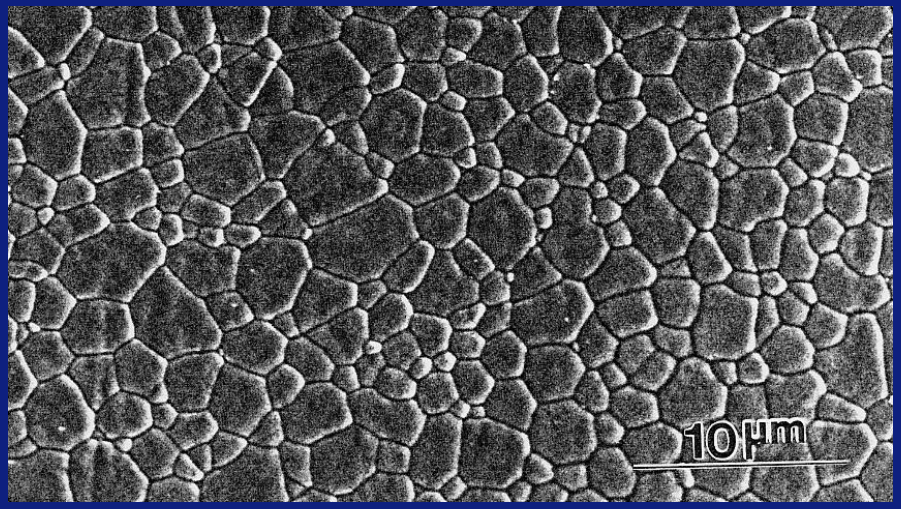
3. Novel Wasteforms: Glass Composite Materials (GCMs) from Thermal Technologies

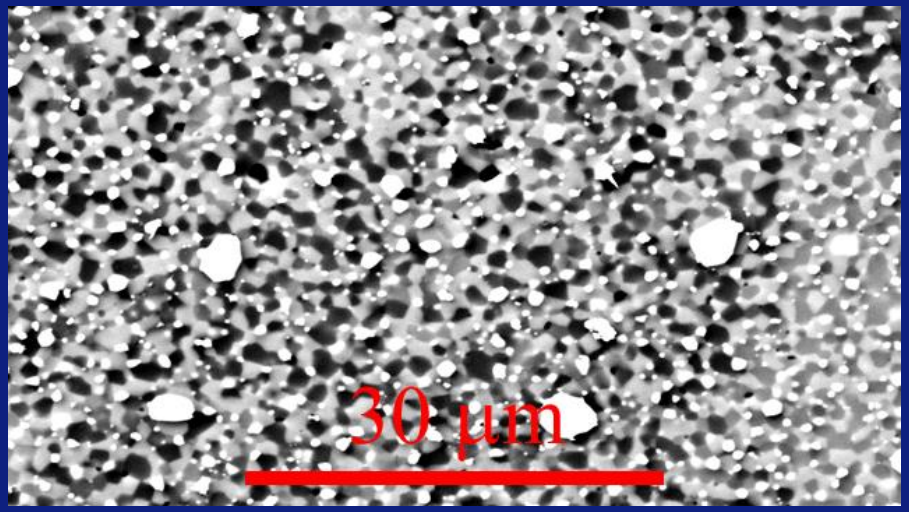


- Mixed crystal and glass wasteforms
- Refractory crystals encapsulated in glass matrix with which they do not react. By hot pressing 30 vol% $La_2Zr_2O_7$ pyrochlore in Pb silicate glass.
- Crystalline waste encapsulated in melt which solidifies to glass (e.g. Joule Heater In-Can Vitrification).

Ceramic Wasteforms.

- **Desire durable, high-density, solid solution ceramics made by firing pressed powders and powdered waste at high temperature.**



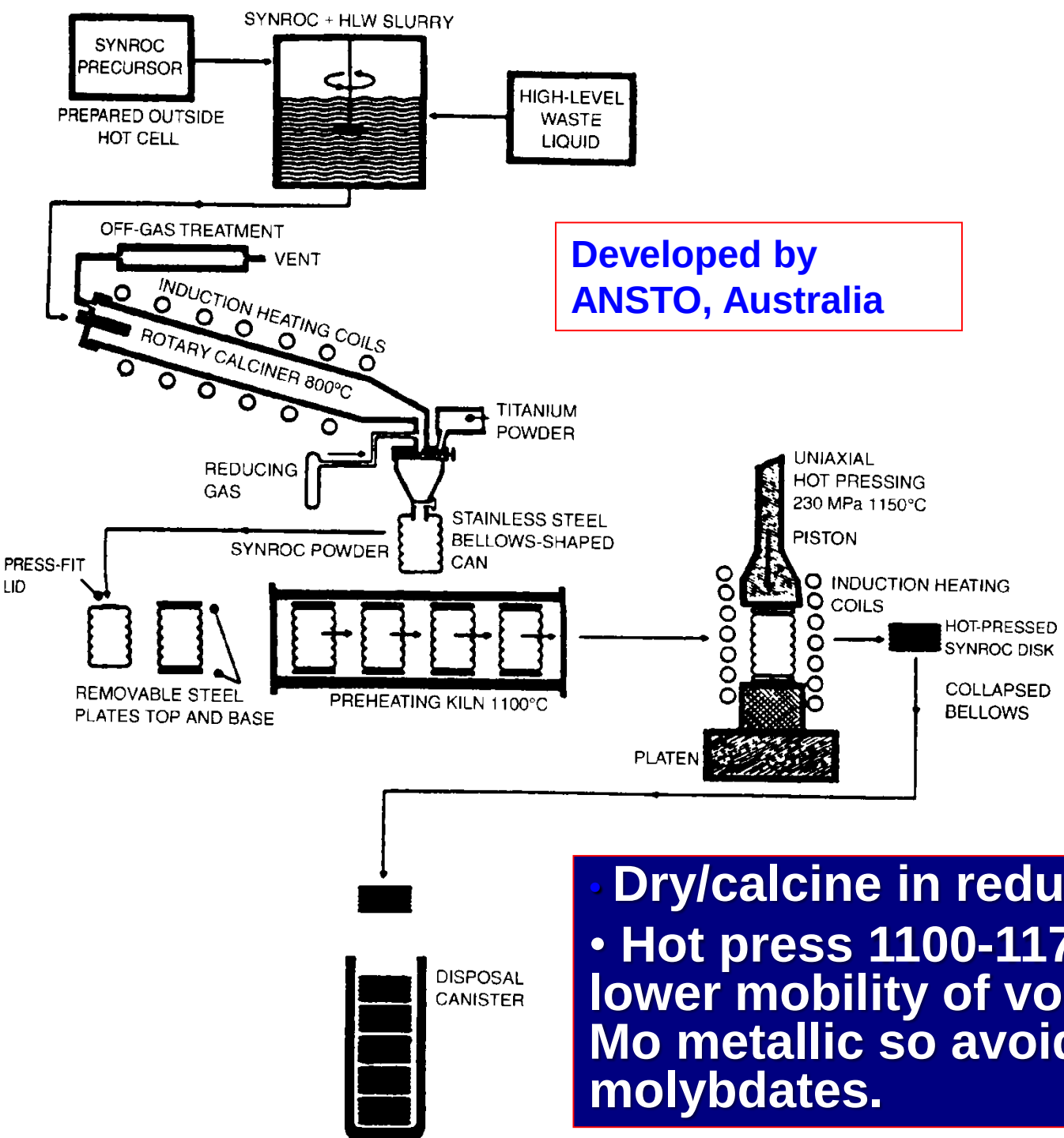


- ***Single-phase*** **zirconia $(Zr,Gd,An)O_2$ or pyrochlore.**

An = (U, Pu, Np, Am and Cm)

- ***Multi-phase*** **ceramics such as hot pressed titanate/zirconates like Synroc better for immobilising multi-valent actinides.**

Synroc Process.

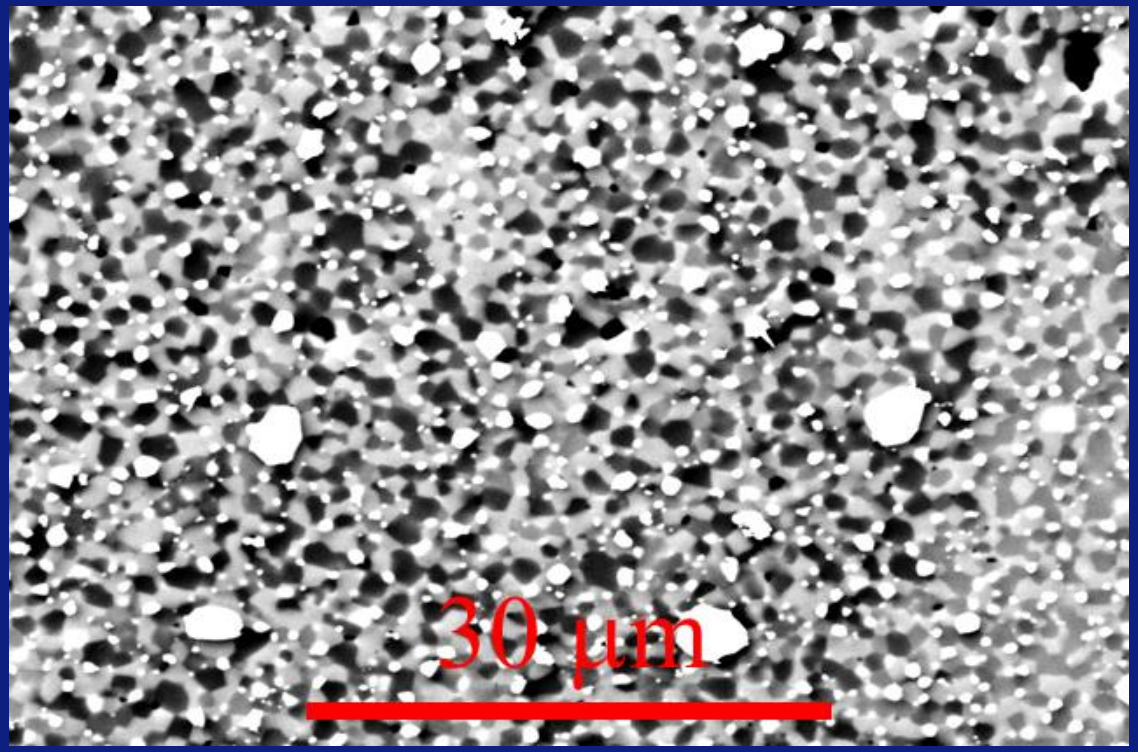


Developed by ANSTO, Australia

- **Relatively simple chemical route involving Ti and Zr alkoxide hydrolysis in presence of NaOH**

- **Dry/calcine in reducing conditions.**
- **Hot press 1100-1170°C + 2 wt% Ti to lower mobility of volatiles and keep Mo metallic so avoid water soluble molybdates.**

Multiphase Ceramics.

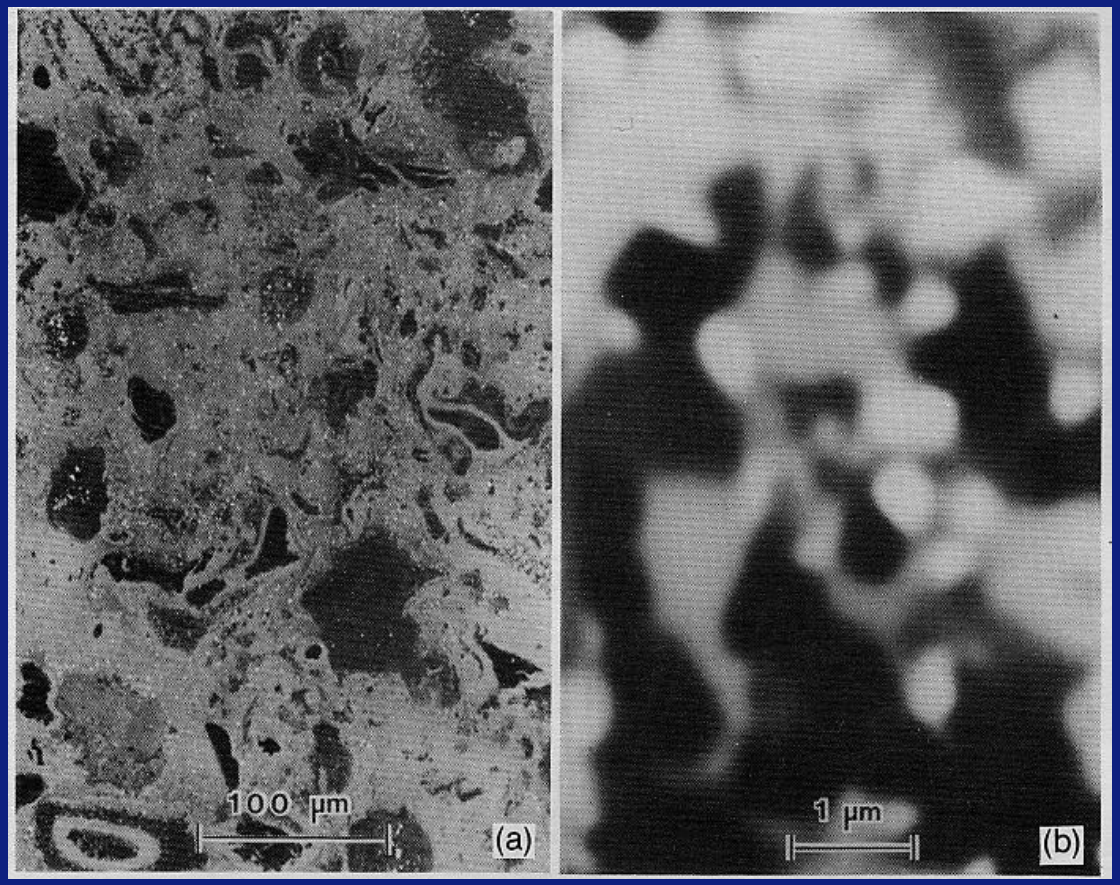


- **Typically consist of fine grains of up to 6 phase types: fluorite derivatives (zirconolite, $CaZrTi_2O_7$), perovskites ($CaTiO_3$), rutile (TiO_2), hollandites ($BaAl_2Ti_6O_{16}$), magnetoplumbite($Sr_{0.6}Fe_2O_3$), β-alumina types and alloys.**

Synroc Formulations.

- Different radionuclides in each phase e.g. Pu in zirconolite, Cs in hollandite.
- Various formulations designed to accommodate wastes containing many different radionuclides via different proportions of these phases.
- E.g. Synroc C with 20% waste is 30% zirconolite, 30% hollandite, 20% perovskite, 10% rutile, <5% magnetoplumbite and <5% alloy.

Synroc C Microstructure: SEM.



10wt% waste loading.

BSE images.

- Inhomogeneous at 100µm scale.
- 4 grey levels at 1µm scale.

Synroc C Microstructure: TEM.

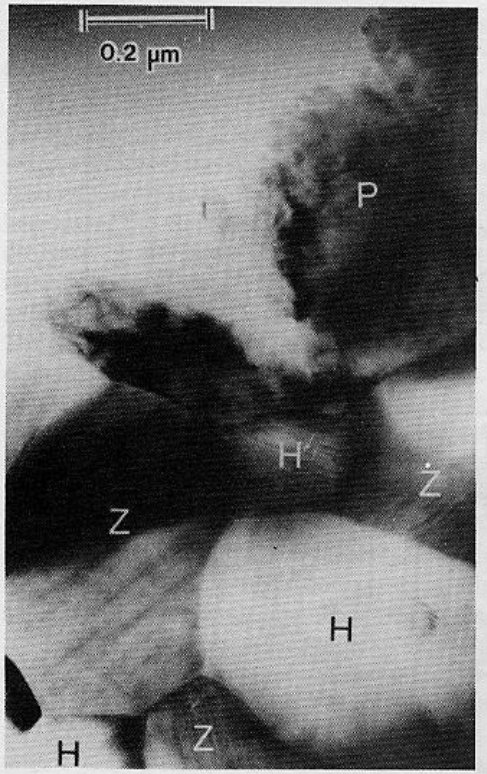


Fig. 4. Bright-field transmission electron micrograph of Synroc C. Hollandite-type crystals (*H*) have moire fringes or modulations; zirconolite crystals (*Z*) are banded due to polysynthetic twinning; perovskite crystals (*P*) are mottled.

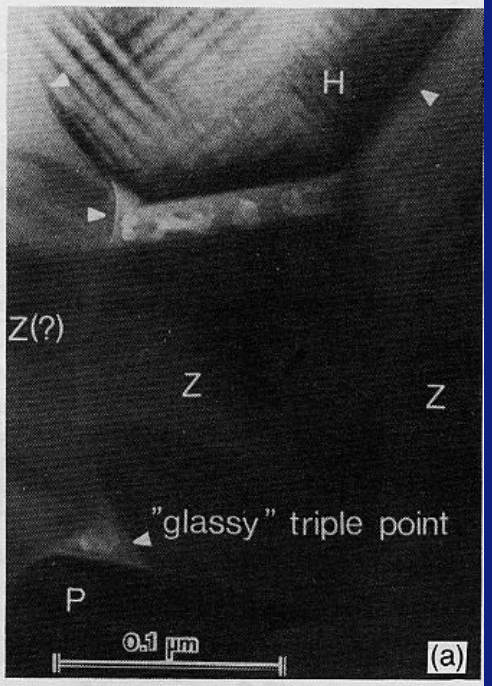


Fig. 6. (*a*) Bright-field image of Synroc C, sh "glassy" triple point, and (center) band of mat region. (*b*) Lattice image of semicoherent grai granular film is apparent.

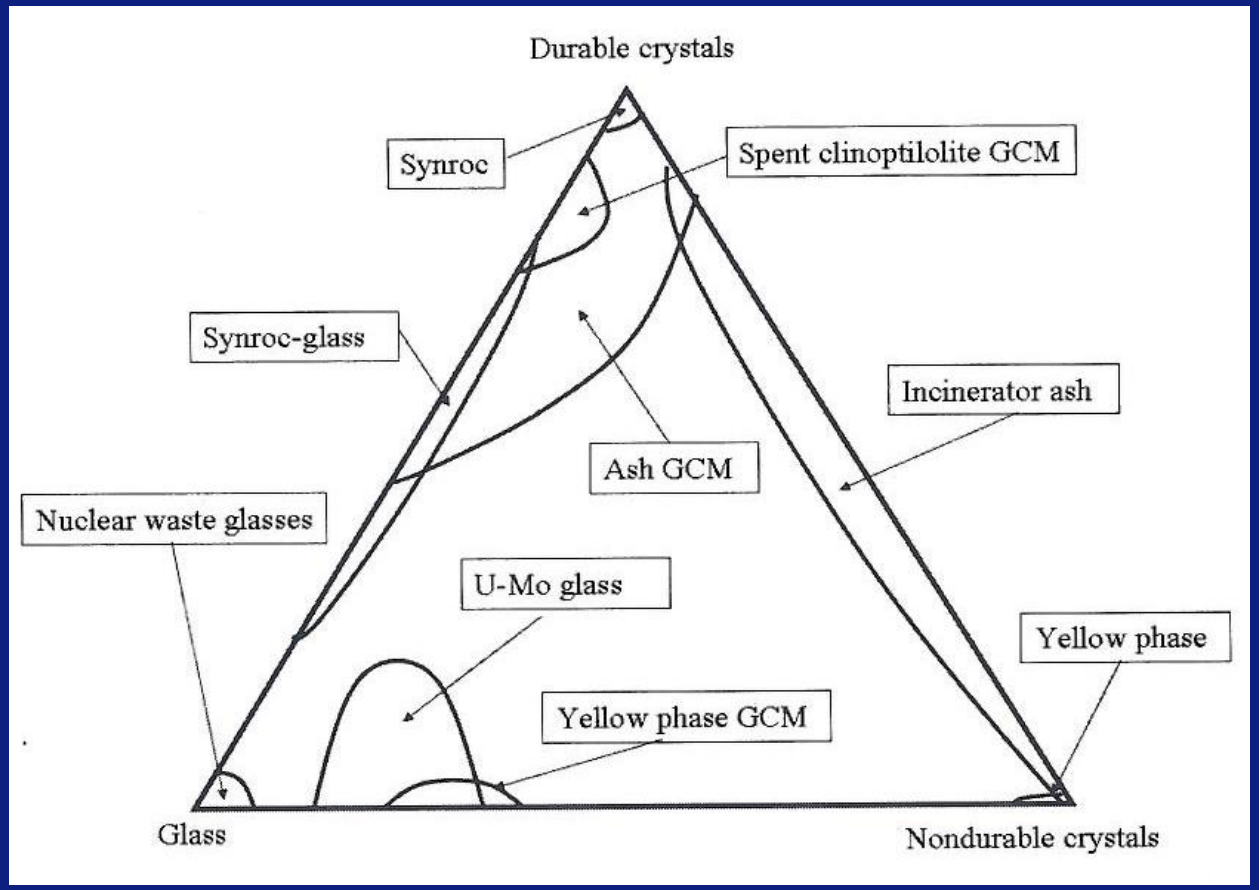
- **Waste incorporation often accompanied by structural modification e.g. via planar defects: twins or crystallographic shear planes.**
- **Glassy phase suggests liquid phase sintering.**
- **Heterogeneous glass location and composition?**

Synroc + Complex Waste Stream/Processing Contaminants.

- Incorporation of common waste stream impurities individually stabilises new phases e.g. monazite $CePO_4$ (P_2O_5), pseudobrookite $MgTi_2O_5$ (MgO) and pollucite $CsAlSi_2O_6$ (SiO_2).
- Adding impurities simultaneously leads to formation of soluble glassy phase containing active species.

Overview of Glass, GCM and Ceramic Wasteforms.

- Avoid bottom RH corner.
- Keep non-durable phases isolated in microstructure.
- Recent trend to GCM's with adequate durability.



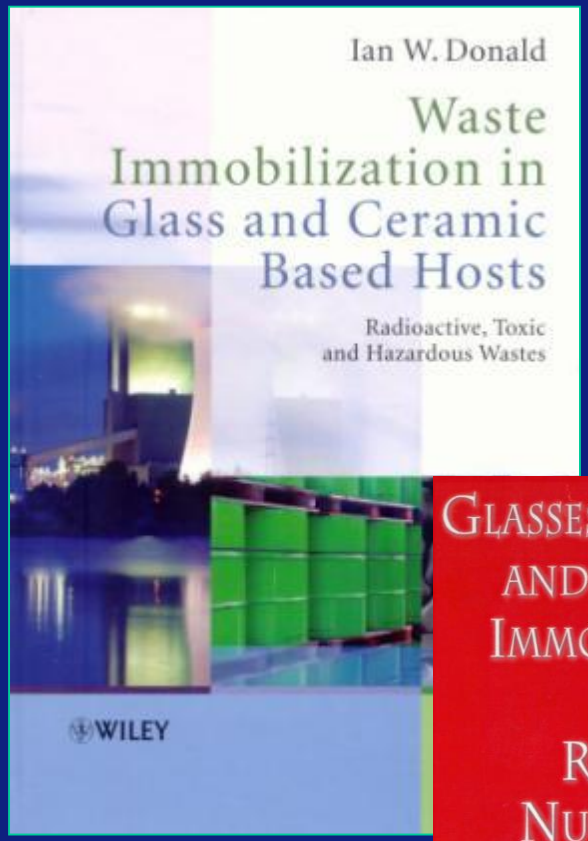
MI Ojovan and WE Lee, "Glassy Wasteforms for Nuclear Waste Immobilisation," Met and Mats. Trans. 42A 837-851 (2011).

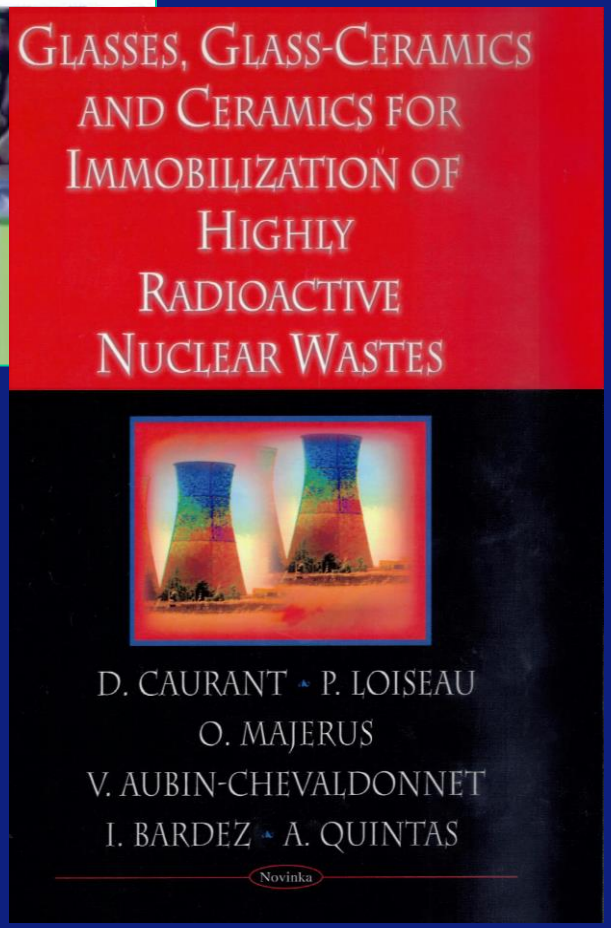
Conclusions.

- Many different hosts used for immobilising radioactive wastes ranging from cements to “fully” amorphous glasses and “fully” crystalline ceramics.
- Glass Composite Materials such as Pu-containing zirconolite glass ceramics suitable for some difficult wastes.
- Range of ceramics being examined including single-phase zircon for Pu and multiphase Synroc for more complex waste streams.

Conclusions.

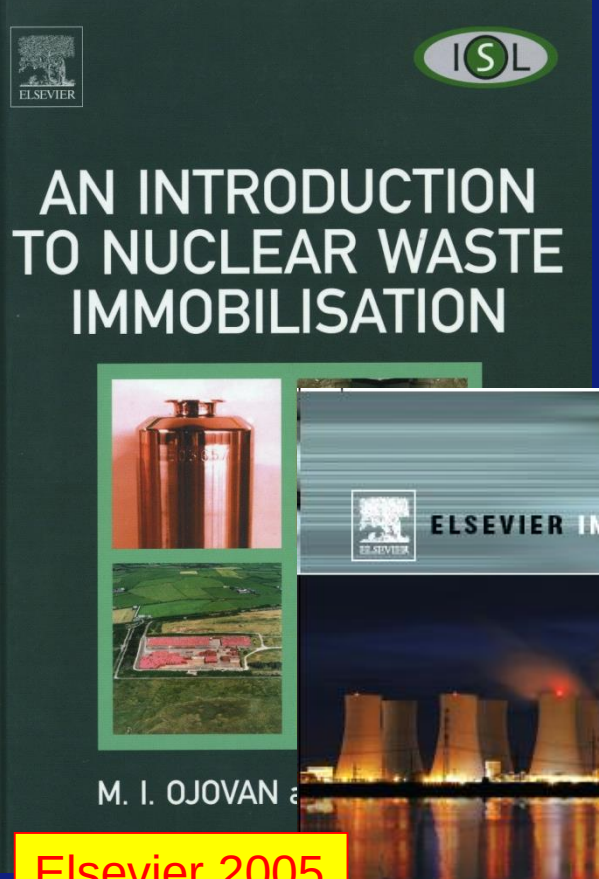
Glasses are currently used for immobilisation of HLW, ILW and LLW providing reliable immobilisation of radionuclides.



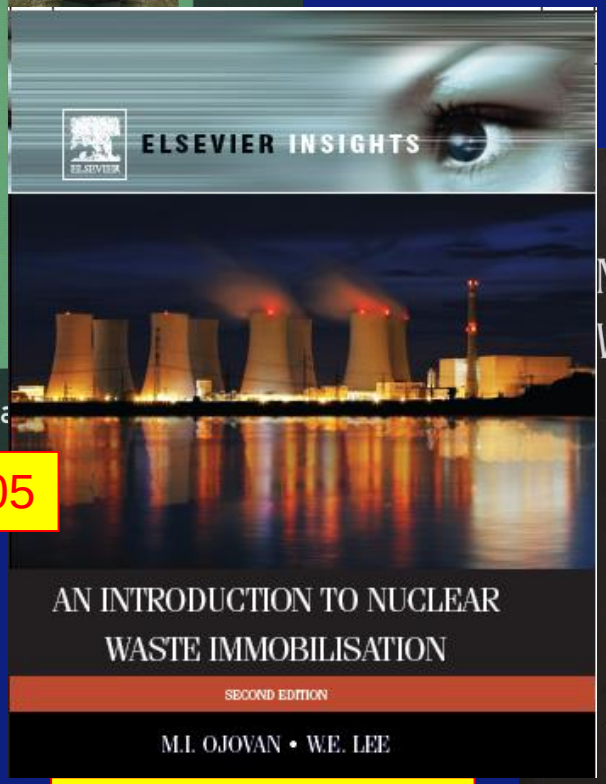


New developments include glass composite materials (GCM) - durable and flexible wasteforms for a wide range of radionuclides and toxic components.

- **For more information see these books!**



Elsevier 2005



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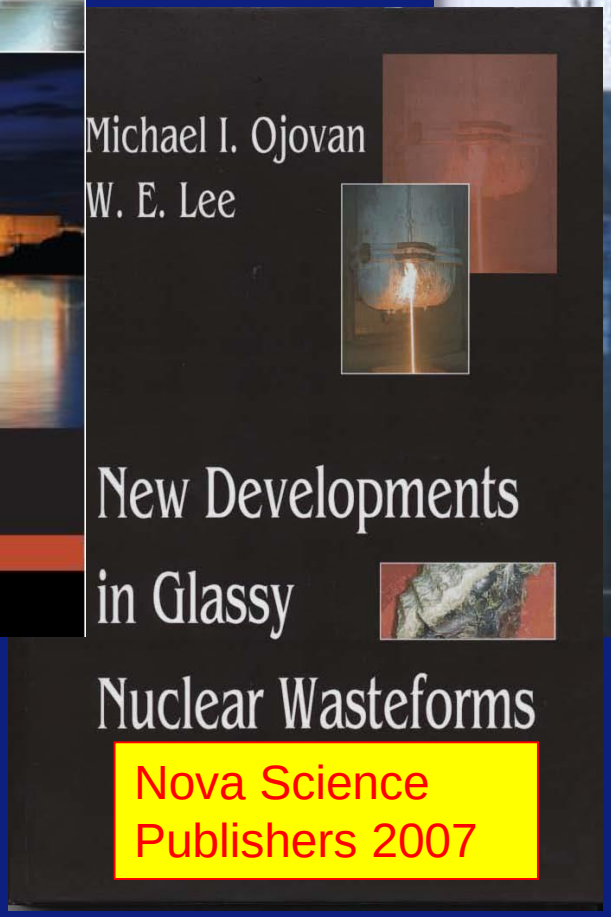

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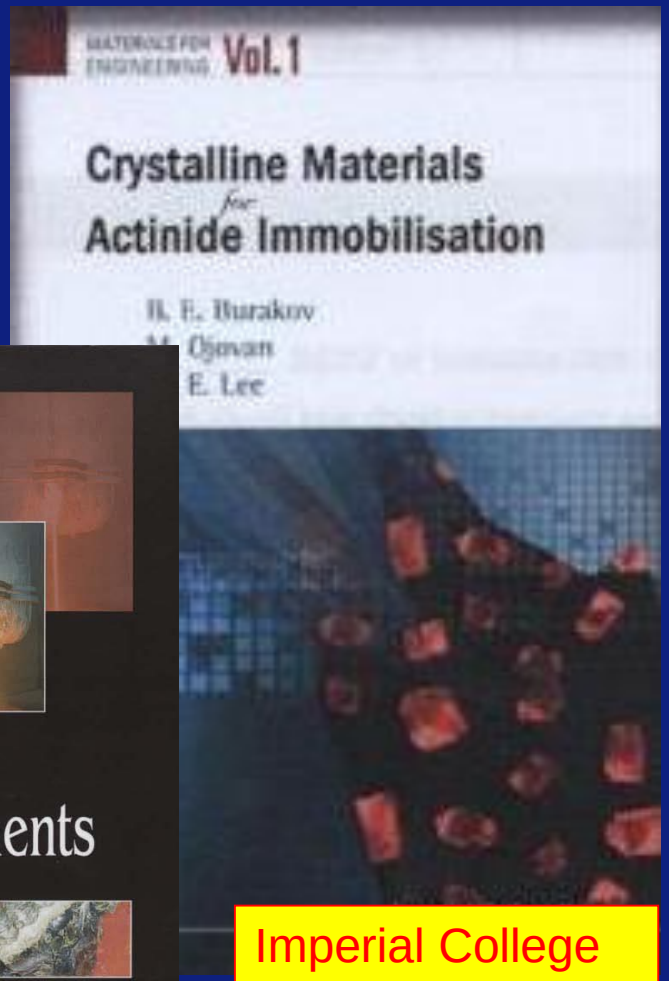

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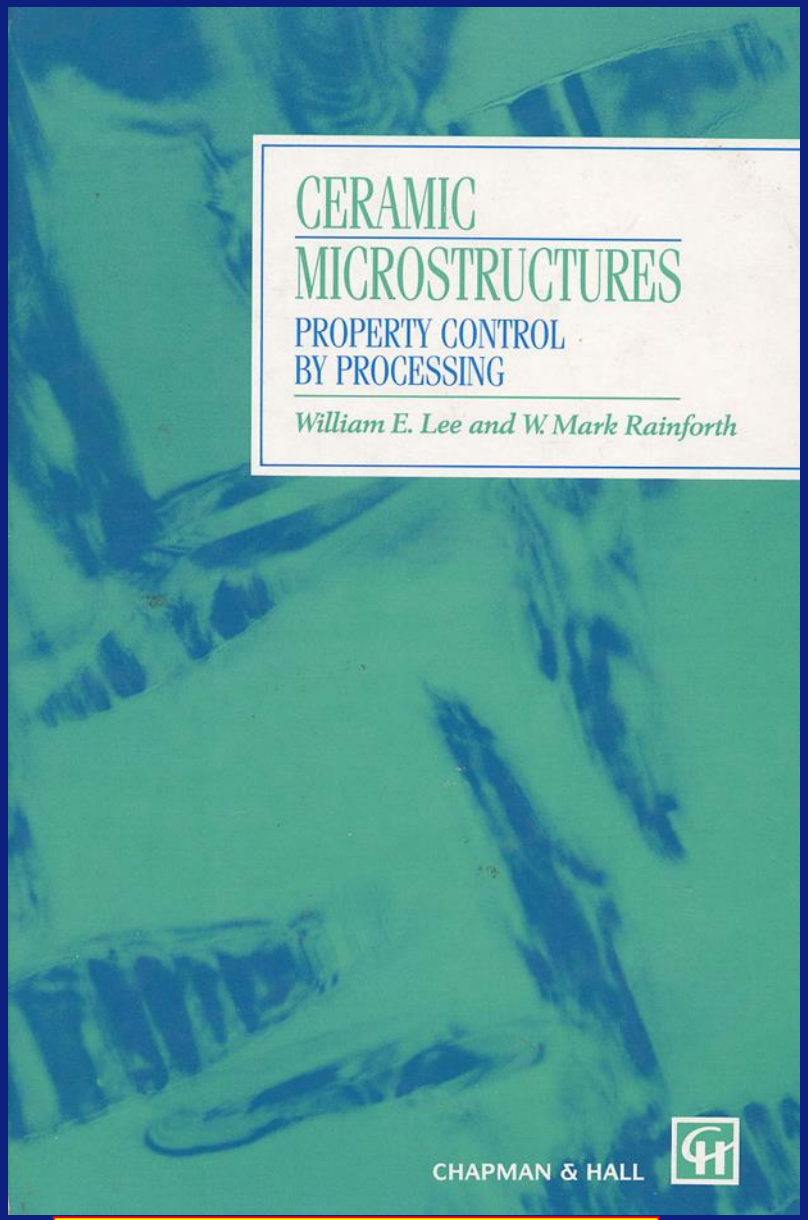

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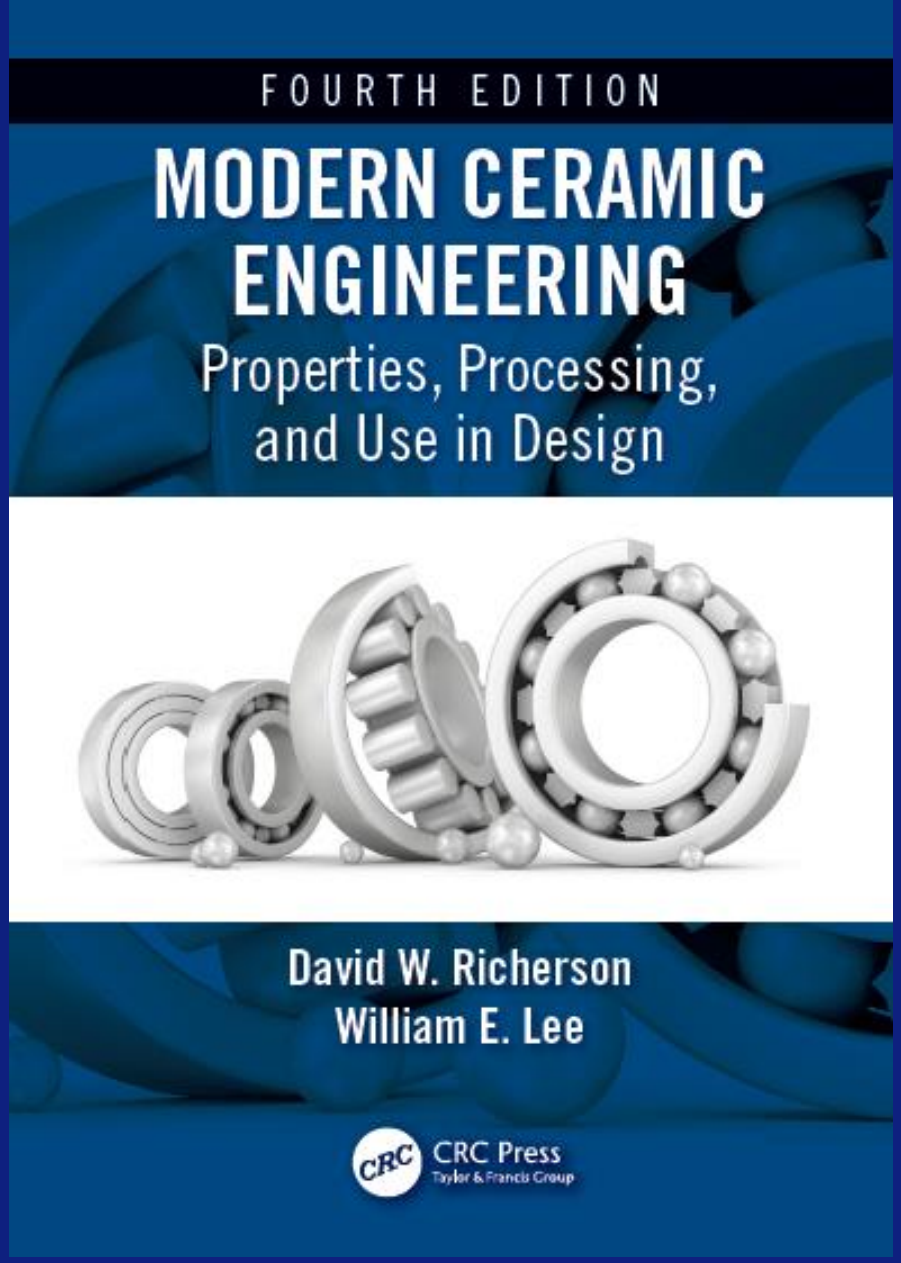

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