Theramin Technical Training School: Hot Isostatic Pressing

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What is Hot Isostatic Pressing?

- Hot isostatic pressing (HIPing) involves the application of temperature and pressure simultaneously to a work piece or casting. It is a processing technique particularly applied to the manufacturing industry.

- The pressure is isostatic, which ensures uniform consolidation/heat treatment of the work piece. For comparison, the products of unidirectional pressure can have non-uniform densification (for powders) due to friction forces at contact points between the sample and die.

- Under HIP environments: internal pores or defects within a solid body collapse and weld up, encapsulated powders/sintered components are densified and consolidated to give better mechanical properties.

**Applications:**
- Consolidating powders
- Diffusion bonding of different types of materials
- Removal of residual pores in sintered items
- Removal of inner defects of castings
- Rejuvenation of parts damaged by fatigue or creep
- High pressure impregnated carbonisation method
History of HIPing

- Hot Isostatic Pressing was originally designed for nuclear industry applications (under the name “gas-pressure bonding”).

- It was developed by the Battelle Memorial Institute (at the Columbus Laboratories in 1955) on behalf of the United States Atomic Energy Commission.

- The objective was to “develop a process to bond components of a small Zircaloy-clad pin-type nuclear fuel elements while maintaining strict dimensional control”

- Conventional fuel cladding fabrication methods (diffusion anneal, hot deformation) produced unsatisfactory results.

  - **Nuclear Timeline:** The Shippingport atomic power station (PA; USA) first reach criticality in 1957. The first core used “zirconium-uranium alloy, with a metallurgically bonded Zircaloy cladding layer on either side” [1]

  - Photograph showing the installation of reactor vessel at Shippingport, the first US commercial reactor [2]

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History of HIPing

- **HIP Version 1**: A 304 stainless steel tube (~3 ft./92 cm) containing the sample pin was sealed at one end and fitted with a two-way gas valve.
- Helium gas was used as the pressurising media.
- The SS tube was pressurised to 2000 psi (~14 MPa) and inserted into a furnace between 1500 to 1650 °F (843-900 °C).
- Good bonding results were observed but the temperature dwell time was between 24-36 hours.


Photograph illustrating a demonstration of the first HIP system [3]
History of HIPing

- Several ruptures of the hot-wall vessels (tubes) occurred during scale up operations.

- It was determined that the hot-wall system would therefore be limited in: size, temperature, pressure and operational lifetime.

- **HIP Version 2:** 304 stainless steel forged pressure vessel with a compressor and two single zone cartridge type furnaces. Helium gas was still used as the pressurising media.

- New capabilities: 10,000 psi (~69 MPa) and between 1500 to 1650 °F (843-900 °C).

- Very good Zircaloy bonding observed with a 6 hour dwell.

History of HIPing

- Between 1960 and 1970, Battelle Memorial Institute acquired two new HIP systems:
  - Pressure rated up to 15,000 psi (~100 MPa)
  - Pressure rated up to 50,000 psi (~345 MPa)

- Improvements were also made in the following areas: furnace design (materials and insulation), furnace electrical connections and thermocouples, (Be-Cu electrodes), pressure vessel seals and safety design.

By 1970’s, HIPs were in use by wide industrial users:

Birmingham Small Arms Group (UK), CEA (France), General Electric (Hanford Atomic Products Operations; USA), NASA Lewis Research Center (USA), Lawrence Radiation Laboratory (USA), Argonne National Laboratory (USA), Atomic Weapons Research Establishment (UK), Boeing Company and Bell Telephone Laboratories….to name a few!

Modern HIP design

Left: Photograph and schematic of HIP pressure vessel
Right: Photograph of HIP support equipment
Not shown: Argon gas manifold, user control PC, chiller

HIP control (PIC)

- Electrical connections
- Vacuum pump
- High $P$ tube to the PV
- Coolant lines
- Compressor
- Pressure vents
- Motor pump
The HIP Process

HIP Cycle:

Stage 1: Simultaneous temperature and pressure ramp (this is the most cost effective HIP cycle)

Stage 2: Hot isostatic pressing (dwell period)

Stage 3: Simultaneous ramp down and release of temperature and pressure

The example shown has a multi-stage ramp segment:

- Ramp to 400 °C @ 5 °C/min, hold for 30 min
- Ramp to 750 °C @ 5 °C/min, hold for 15 min
- Ramp to 1250 °C @ 7.5 °C/min
- Dwell for 2 hours at 1250 °C and 75 MPa
- Ramp down to 20 °C and 0 MPa
The HIP Process

Other types of HIP cycle include [5]:

**Cold-loading cycle:**
- Temperature is only applied after the pressure ramp has started.
- Temperature and pressure should reach target at the same time.
- Good for geometric control

**Hot-loading cycle:**
- Pressure is only applied after the temperature has reached the target temperature.
- Ideal for glass encapsulated products (early pressure will crack the glass containment)

**Pressure-loading cycle:**
- Temperature is only applied after pressure reaches the target.
- Allows use of lower temperatures (e.g. for powder recrystallisation)

The HIP work piece

- Closed porosity materials: No additional containment required (e.g. castings)

- Open porosity materials: Need to be vacuum sealed in a canister/capsule.
  - Typically fabricated using metals, glass or ceramic
  - This process also removes water vapour and air than could lead to oxide formation and affect the sintering process
  - After HIPing, the canister/capsule is removed from by machining to leave the HIPed product

- **Note:** In nuclear applications, the canister would be form part of the overall waste package (multi-barrier approach)
The University of Sheffield currently are the only site in the UK with the capability for processing radioactive waste forms by HIP! More information coming later...

Advantages of HIPing
(with regards to nuclear waste immobilisation)

✓ No volatile off gas during process
✓ 100% waste loading possible
✓ Hermetically sealed: minimised secondary wastes
✓ Conditioned waste volume minimised
✓ One process for multiple waste streams
✓ Batch process: flexibility and accountability
✓ Range of processing conditions
✓ Up to 60% volume reduction

Photographs of the University of Sheffield HIP with an example of a HIP canister A) pre and B) post processing

N.B. Images not to scale!
HIP for nuclear waste immobilisation - Synroc

- Australian Science and Technology Organisation (ANSTO) developed a group of synthetic rock "synroc" based on calcium titanates as hosts for immobilising nuclear fuel reprocessing waste.

- Synroc-C is the most studied variant of the synroc group. The phase assemblage is typically a combination of: rutile, hollandite, perovskite and zirconolite. The composition is shown in Table 1.

- Synroc-C can incorporate up to 35 wt. % solids waste without changing the phase assemblage.

Table 1: SYNROC-C composition [6]

<table>
<thead>
<tr>
<th>Phase (nominal composition)</th>
<th>wt%</th>
<th>Radionuclides in lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollandite</td>
<td>30</td>
<td>Cs, Rb</td>
</tr>
<tr>
<td>Ba(Al,Ti)$_2$Ti$<em>5$O$</em>{14}$</td>
<td>30</td>
<td>RE, An</td>
</tr>
<tr>
<td>Zirconolite</td>
<td>30</td>
<td>Rate An</td>
</tr>
<tr>
<td>CaZrTi$_2$O$_7$</td>
<td>20</td>
<td>Sr, RE, An</td>
</tr>
<tr>
<td>Perovskite</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Ti oxides (TiO$_2$, Ti$<em>n$O$</em>{2n-1}$)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Alloy phases</td>
<td>5</td>
<td>Tc, Pd, Rh, Ru, etc.</td>
</tr>
</tbody>
</table>

RE, An = rare earths and actinides respectively

HIP processing of Synroc

## Types of Synroc

<table>
<thead>
<tr>
<th>Waste</th>
<th>TiO$_2$</th>
<th>ZrO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>BaO</th>
<th>CaO</th>
<th>K$_2$O/Na$_2$O</th>
<th>SiO$_2$</th>
<th>UO$_2$</th>
<th>Other</th>
<th>Mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reprocessed SNF</td>
<td>33.0</td>
<td>10.0</td>
<td>16.0</td>
<td>-</td>
<td>17.0</td>
<td>6.0</td>
<td>5.0</td>
<td>13.0</td>
<td>-</td>
<td></td>
<td>HPZFKL</td>
</tr>
<tr>
<td>Synroc-B</td>
<td>-</td>
<td>60.3</td>
<td>10.8</td>
<td>6.3</td>
<td>-</td>
<td>6.4</td>
<td>16.2</td>
<td>-</td>
<td>-</td>
<td></td>
<td>HPZ</td>
</tr>
<tr>
<td>Reprocessed SNF</td>
<td>57.0</td>
<td>5.4</td>
<td>4.3</td>
<td>-</td>
<td>4.4</td>
<td>8.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>HPZR</td>
</tr>
<tr>
<td>Defence waste</td>
<td>18.8</td>
<td>6.6</td>
<td>18.6</td>
<td>23.8</td>
<td>-</td>
<td>1.8</td>
<td>3.6</td>
<td>7.2</td>
<td>2.1</td>
<td>17.5</td>
<td>PZNS</td>
</tr>
<tr>
<td>Reprocessed SNF</td>
<td>87.8</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>RZPH</td>
</tr>
<tr>
<td>SNF</td>
<td>37.7</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>1.2</td>
<td>10.4</td>
<td>-</td>
<td>-</td>
<td>49.7</td>
<td>0.2</td>
<td>PyR</td>
</tr>
</tbody>
</table>

- H – hollandite $(\text{Ba}, \text{Cs}, \text{Rb})_x(\text{Ti}, \text{Al}, \text{Mg}, \text{Fe})_8\text{O}_{16}$
- P – perovskite $(\text{Ca}, \text{Ln}, \text{Sr}, \text{Ba}, \text{Act})(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb})_8\text{O}_{3}$
- Py – pyrochlor $(\text{Ca}, \text{Act}, \text{Ln})(\text{Zr}, \text{Hf}, \text{Act})(\text{Ti}, \text{Nb}, \text{Fe}, \text{Al})_2\text{O}_{7}$
- Z – zirconolite $(\text{Ca}, \text{Act}, \text{Ln})(\text{Zr}, \text{Hf}, \text{Act})(\text{Ti}, \text{Nb}, \text{Fe}, \text{Al})_2\text{O}_{7}$
- F – Ba-felspar $\text{BaAl}_2\text{Si}_2\text{O}_8$
- K – kalsilite $(\text{K}, \text{Cs})\text{AlSiO}_4$
- L – Leusite $(\text{K}, \text{Cs})\text{AlSi}_2\text{O}_6$
- R – Rutile TiO$_2$
- N – Nepheline NaAlSiO$_4$
- S – Spinel $(\text{Fe}, \text{Mn}, \text{Ni})_2(\text{Ti}, \text{Al})\text{O}_4$

Durability of Synroc

Case Study 1: Plutonium immobilisation

The management and safe storage of separatedPuO$_2$ is the subject of international scrutiny and concern

Baseline strategy:

- Plutonium is considered a zero asset waste
- Storage planned until 2120 at Sellafield, materials assumed to remain in place after this date.
- No costs are currently included in the baseline plan beyond 2120.
- Plan does not include all infrastructure required to maintain storage beyond 2120.
- PuO$_2$ is not considered a passive form for long term storage.
- A proportion of the stockpile will need to be converted to passive form before 2120.

Challenges to the baseline strategy:

- Management arrangements for plutonium storage are not optimised.
- Requirements for long term safe storage and secure storage are not fully developed.
- Final treatment and disposal route and costs, require definition.
Case Study 1: Plutonium immobilisation

- Upon completion of fuel reprocessing, the UK will have a stockpile >140t of PuO$_2$
- Dual track strategy of immobilisation and reuse by MOX fabrication for LWR
- MOX challenges:
  - Not all Pu will be suitable (Am-241 ingrowth)
  - Industrial scale MOX fabrication difficult
- Pu wasteform required to immobilise wastes for over 100,000 years until the radiotoxicity returns to natural uranium levels
- **Hot isostatic pressing** identified as possible thermal treatment route for PuO$_2$ wastes.

**Advantages of HIPing Pu:**

- Uniform incorporation of radionuclides
- Batch process (inventory control)
- No off-gas production
- No secondary wastes produced
- Hermetically sealed wasteform
- Up to 60% volume reduction
- Significant cost saving
Case Study 1: Plutonium immobilisation

Zirconolite glass/ceramic host

- CaZrTi$_2$O$_7$: high durability and radiation tolerance
- Natural mineral analogues (predict long term behaviour)
- Readily incorporates actinides and rare earths
- Full ceramic suitable for high Pu residues, glass-ceramics suitable for low Pu residues
**Case Study 2: Active HIPing (Magnox sludge)**

**Magnesium Borosilicate Glass**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mg(OH)$_2$ (g)</th>
<th>Mg (g)</th>
<th>H$_3$BO$_3$ (g)</th>
<th>SiO$_2$ (g)</th>
<th>U$_3$O$_8$ (g)</th>
<th>Waste loading (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBS-M (U) (high)</td>
<td>4.694</td>
<td>2.816</td>
<td>12.208</td>
<td>6.040</td>
<td>18.820</td>
<td>59.1</td>
</tr>
<tr>
<td>MBS-C (U) (low)</td>
<td>18.109</td>
<td>1.132</td>
<td>22.200</td>
<td>10.983</td>
<td>3.801</td>
<td>41.0</td>
</tr>
</tbody>
</table>

Images of MBS-M (U) and MBS-C (U) at 200 µm scale.
Case Study 2: Active HIPing (Magnox sludge)

- Crystalline phases are predominantly quartz, uranium oxides and suanite (a magnesium borate – $\text{Mg}_2\text{B}_2\text{O}_5$). No unreacted Mg metal detected
- Bulk quartz appears largely unreacted, key binder is likely a magnesium borate
- Further characterisation required to confirm assignments and UOx composition (by oxidation state).