

ZrC_{1-x} as a Factor in the Disposal of Spent Gen IV VHTR Fuel

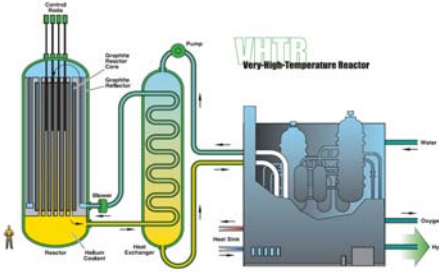
H.F. Jackson, W.E. Lee, D.C. Parfitt, R.W. Grimes

Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

Generation IV and the Very High Temperature Reactor

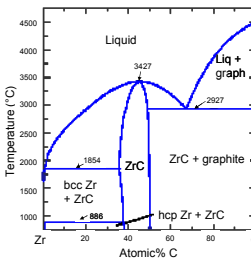
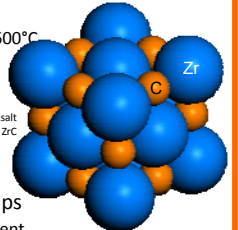
Generation IV: An international collaboration to develop next generation nuclear energy systems, with goals of sustainability, safety, economy, and proliferation resistance.

Very High Temperature Gas-Cooled Reactor (VHTR): Capable of producing heat and hydrogen, with a helium coolant outlet temperature of at least 1000°C. Nominal fuel temperatures will exceed 1250°C.



ZrC will replace/supplement SiC in VHTR TRISO fuel

- ZrC melts at 3500°C, SiC decomposes above 1800°C
- ZrC better retains fission products, especially at T > 1600°C
- SiC corroded by fission product Pd and leaks Ag-110m
- Migration of UO₂ kernel under thermal gradient ("amoeba effect") found to be inhibited by ZrC



ZrC Knowledge Gaps

- Process development and fuel performance is less well understood than for SiC
- "Amoeba effect" - what happens when ZrC-UO₂ interact?
- Wide range of nonstoichiometry (ZrC_{1-x}) with what effect on properties?
- How is phase equilibria in TRISO affected by ZrC component?

TRISO Waste Disposal Options

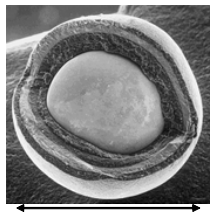
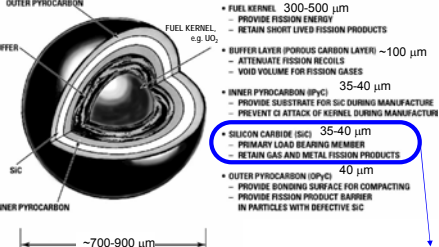
While the ceramic layers themselves in TRISO are intrinsic barriers to radionuclide release, long-term performance of the coatings under potentially corrosive disposal conditions, especially for ZrC-based TRISO, has not been established.

Fuel pebbles/compacts may be temporarily stored in surface facilities before direct disposal in geological repository. Fuel may be reprocessed to remove the graphite matrix to minimise waste volume and recover actinide materials. Vitrification of TRISO particles is also under investigation.

"Solutions to adequate waste management will be developed." Gen IV International Forum webpage on VHTR reactor

TRISO: Tri-Structural Isotropic Coated Particle Fuel

Current design:



The multilayered TRISO fuel form retains fission products for all foreseeable conditions. However, SiC performance is limited at VHTR operating temperatures.

Thousands of TRISO particles are pressed into tennis-ball sized pebbles or compacts.

Desirable properties for fission product retention layer:

- Dimensional stability under irradiation
- High thermal conductivity
- Refractoriness: high strength at high temperature
- Chemical inertness

Methodology

This work will investigate non-stoichiometry of ZrC and its effects on material properties.

Synthesis and processing of ZrC_{1-x}, x = 0.02 to 0.5

- ZrO₂ + 3C → 2ZrC_(s) carbothermal reduction of powders
- Pressureless sintering, hot isostatic pressing



Synthesis in Ar-atmosphere graphite tube furnace

Characterisation

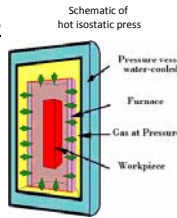
- **Chemical:** composition, phases
- **Microstructural:** grain morphology, porosity, defects
- **Thermal:** thermal expansion, thermal conductivity
- **Mechanical:** strength, hardness, creep

First principles quantum mechanical modelling of ZrC using CASTEP

Uses density functional theory to calculate total energy of crystal.

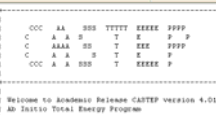
From there, we may predict:

- Defect-free ZrC lattice vs. non-stoichiometric ZrC lattice
- Mechanism of defect accommodation
- Defect structures and ordering
- Material properties such as lattice parameter, bulk modulus, elastic constants
- Accommodation of U and fission products in ZrC lattice



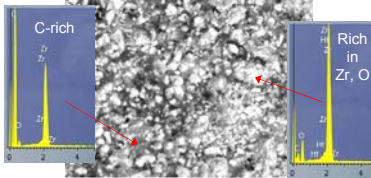
Thermodynamic calculations using Gibbs Energy Minimisation code

- Predict phase equilibria in ZrC-TRISO
- Components of system: ZrC, graphite, UO₂, and fission products

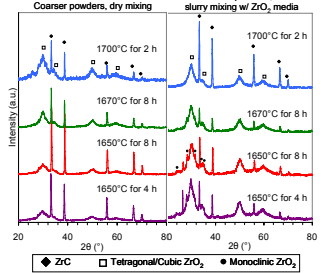
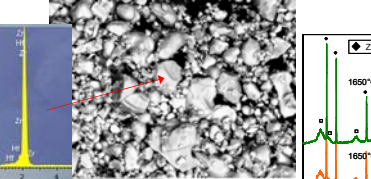


Results: Carbothermal Reduction Synthesis

Backsatter electron image and EDS of ZrO₂-C mixture fired for 2 h at 1700°C. Inhomogeneous composition, unreacted ZrO₂ and C.

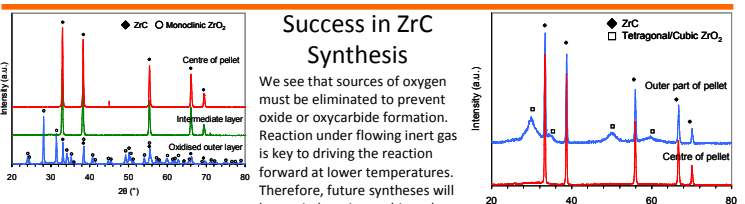


Backsatter electron image and EDS of commercial ZrC (ABCR). Homogeneous in composition.



XRD of ZrO₂-C pellets fired in enclosed graphite crucible in chamber furnace (no atmosphere control). Various firing parameters (time and temperature) and reactant characteristics (powder size and mixing) lead to varying extent of conversion of oxide to carbide.

Buildup of CO produced from the reaction appears to hinder carbide formation when reacting in an enclosed crucible, according to Le Chatelier's Principle.



XRD of 3 distinct components of ZrO₂-C pellet fired under flowing Ar in alumina tube furnace at 1600°C for 4 h. Pellet oxidised on outside, pure ZrC on inside.

Success in ZrC Synthesis

We see that sources of oxygen must be eliminated to prevent oxide or oxycarbide formation. Reaction under flowing inert gas is key to driving the reaction forward at lower temperatures. Therefore, future syntheses will be carried out in graphite tube furnace in inert atmosphere.

XRD of 2 distinct components of ZrO₂-C pellet fired in enclosed graphite crucible in chamber furnace (no atmosphere control) at 1670°C for 8 h. Carbide formed at centre of pellet.

References

1. U.S. Dept. of Energy, <http://nuclear.energy.gov/genIV/neGenIV3.html>
2. US DOE Nuclear Energy Research Advisory Committee & Generation IV International Forum, *A Technology Roadmap for Generation IV Nuclear Energy Systems*, 2002, <http://www.gen-4.org/PDFs/GenIVRoadmap.pdf>
3. General Atomics & US DOE, "Development Plan for Advanced High Temperature Coated-Particle Fuels", 2003, http://nuclear.inl.gov/deliverables/docs/pc-000513_0_rel.pdf
4. IAEA-TECDOC-978, "Fuel performance and fission product behavior in gas cooled reactors," IAEA, November 1997, <http://www.iaea.org/inis/aw/htr/fulltext/29009817.pdf>
5. M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne. "First-principles simulation: ideas, illustrations and the CASTEP code", *J. Phys. Cond. Matt.* **14** (2002) 2717-2743
6. A. Fernandez Guillermet, "Analysis of thermochemical properties and phase stability in the zirconium-carbon system." *Journal of Alloys and Compounds* **217** (1995) 69-89
7. Generation IV International Forum, "Very High Temperature Reactor." <http://www.gen-4.org/Technology/systems/vhtr.html>

Acknowledgments

This work was carried out as part of the TSEC programme KNOO and as such we are grateful to the EPSRC for funding under grant EP/C549465/1. This work is also supported by the ORS Awards Scheme.