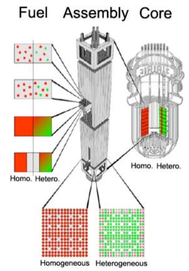
Phase Composition-Microstructure-Thermal Conductivity Relationships in $MgO-Nd_2Zr_2O_7$ Inert Matrix Composites

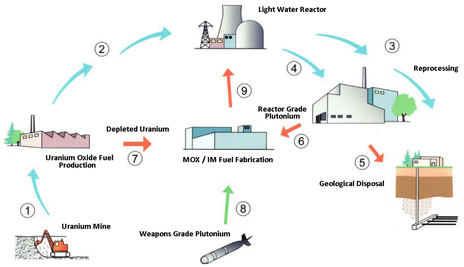
Cameron L. Tracy, Marta M. Giachino, Erik P. Luther
Los Alamos National Laboratory, Materials Science and Technology Division (MST-6)

Motivation

Approximately 2000 metric tons of plutonium from spent nuclear fuel and dismantled nuclear weapons exists in stockpiles worldwide. Furthermore, 70 to 80 metric tons of plutonium and other minor actinides (neptunium, americium and curium) are added each year. These stockpiles can be reduced through actinide transmutation and Pu burning in nuclear reactors. This process currently incorporates fissile materials into a MOX fuel which is then burned in a light water reactor (LWR).



A LWR fuel core showing two possible IM loading configurations.



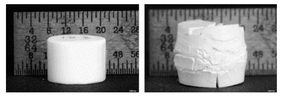
A nuclear fuel cycle using MOX and IM fuels to dispose of reactor and weapons grade Pu. For IMF use, step 7 (Depleted Uranium) would be eliminated.

Unfortunately, MOX fuels hold fissile materials in a U-238 matrix in order to dilute them to the volumetric concentrations required by reactor control considerations. During reactor operation, neutron capture by this matrix produces plutonium as a waste product. In this research, a neutron-transport inert matrix (IM) material, an $MgO-Nd_2Zr_2O_7$ composite, is being developed as a replacement for the MOX fuel matrix. When this material is combined with a fissile phase, an inert matrix fuel (IMF) is obtained. The non-fertile IM does not cause plutonium breeding through neutron capture. With a net reduction in plutonium of 80-90% by volume during standard LWR operation, IMFs have the potential to greatly increase the efficiency of nuclear material disposal.

Materials Selection

In order to be approved for use in a LWR, an IMF must fulfill four criteria:

- High thermal conductivity
- High radiation resistance
- Compatibility with reactor materials
- Favorable neutronics



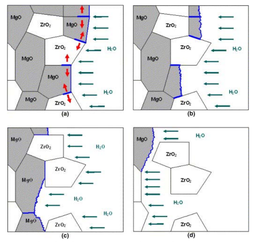
A magnesia pellet before and after submersion in boiling water for 3 hours.

ZrO_2: Low thermal conductivity.
MgO: Reacts with water, making it unsafe for use in an LWR due to the possibility of a cladding failure.

Composite approach: an $MgO-ZrO_2$ composite provides both high thermal conductivity and suitable hot water corrosion resistance. The MgO phase provides a path through which heat can flow, while the ZrO_2 phase acts as a hydration barrier.

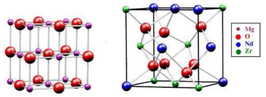
Hydration mechanism for MgO:

- Hydration begins at the MgO grain boundaries.
- The reaction between water and magnesia, forming $Mg(OH)_2$, is accompanied by a volume increase of 117%.
- This increase in volume at the grain boundaries exerts stress on neighboring grains, creating cracks at which further hydration and volume increase occurs.
- The addition of a ZrO_2 phase reduces the area of MgO exposed to hydration attack at the grain boundaries, while also reducing the stress placed on MgO grains.
- Cracking of the MgO phase does not occur.
- Without the production of new hydration-vulnerable cracks, the hydration process is dramatically slowed.



The hydration attack mechanism of an $MgO-ZrO_2$ composite.

An $MgO-Nd_2Zr_2O_7$ composite has been shown to perform similarly to the $MgO-ZrO_2$ composite with respect to hot water corrosion resistance., while offering slightly higher thermal conductivity.



Left: The rock salt crystal structure of magnesia.
Right: the pyrochlore crystal structure of neodymium zirconate.

Objectives

In previous work, various processing methods for a 70 vol% MgO / 30 vol% $Nd_2Zr_2O_7$ composite were tested in order to determine the relationships between processing, microstructure, and thermal conductivity.

- Mortar and pestle
- Magnetic bar stirring
- Spex blending
- Ball milling

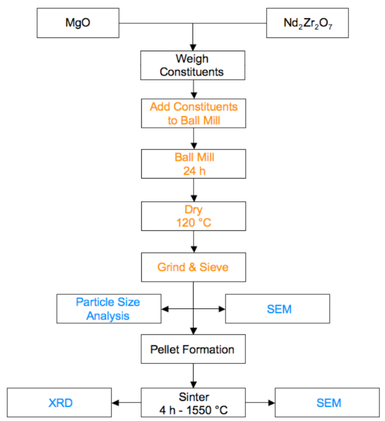
It was concluded that Ball milling produced the most consistency with respect to microstructural and thermal properties.

In this work, we are testing $MgO-Nd_2Zr_2O_7$ composites of various compositions to determine the relationship between phase composition, microstructure, and thermal conductivity. We are using the processing methods previously developed.

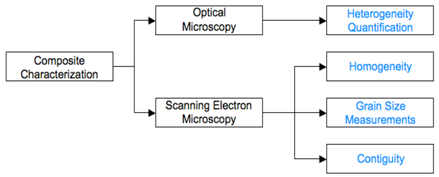
- 70 vol% MgO / 30 vol% $Nd_2Zr_2O_7$
- 60 vol% MgO / 40 vol% $Nd_2Zr_2O_7$
- 50 vol% MgO / 50 vol% $Nd_2Zr_2O_7$
- 40 vol% MgO / 60 vol% $Nd_2Zr_2O_7$

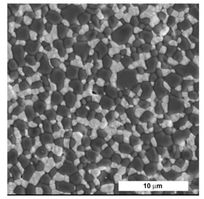
Methods

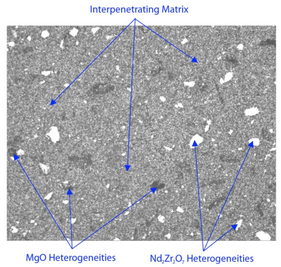
Materials processing:



Microscopy and Image Analysis:



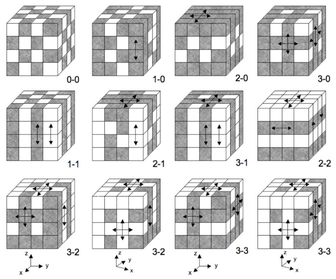




Top Left: The imaging methods used in microstructural characterization, along with data collected.
Left: The macrostructure of the composite at 50x magnification. Shown are heterogeneities that form due to poor mixing between the two phases.
Top: The composite's microstructure at 2000x magnification. Taken in the interpenetrating matrix
Bottom: The ten possible connectivities for a two-phase composite. The 3-0 connectivity, shown in the top right, is expected to yield the highest thermal conductivity.

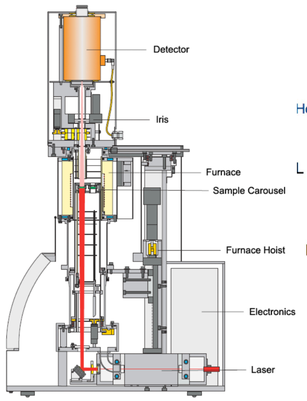
Connectivity:

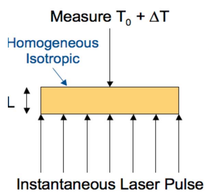
- This data will be used to study the composite's connectivity.
- It is hypothesized that the ideal connectivity for maximum thermal conductivity is 3-0. This allows heat to flow through the MgO phase while minimizing heat flow impedance by the $Nd_2Zr_2O_7$ phase.

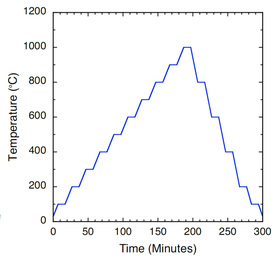


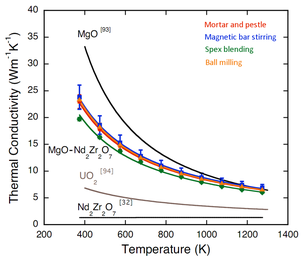
Thermal Property Analysis:
The samples will be mounted in a Netzsch laser flash analyzer (LFA).

- A laser of known energy will be fired at one side of the sample, while the temperature of the opposite side is measured as a function of time.
- From these data, the thermal diffusivity of the sample is determined.
- The thermal diffusivity is then used to calculate thermal conductivity.









Left: A cross section of the LFA used in this research.
Top Left: Sample mounted in the LFA. Sample length is denoted as it is used to calculate the thermal diffusivity of the sample.
Top Middle: Temperature of the sample as a function of time. This data is measured by the LFA during operation.
Top Right: Thermal conductivity curves generated from the measured thermal diffusivity of a sample. Data gathered from $MgO-Nd_2Zr_2O_7$ composites is compared to that of its individual phases and UO_2 whish it is deisgned to replace in LWRs.

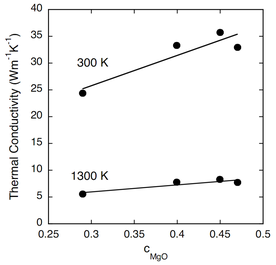
Results

Phase composition-microstructure relationship:

- In the $MgO-ZrO_2$ composite, there is a clear correlation between phase composition and connectivity, with the 60 wt% MgO / 40 wt% ZrO_2 composition appearing as a dispersion of zirconia in the magnesia phase, while the 40/60 composition appears as a dispersion of magnesia in the zirconia phase.

Microstructure-thermal conductivity relationship:

- Homogeneity and grain size were found to have no correlation with thermal conductivity.
- The contiguity of the thermally conductive MgO phase shows a clear proportionality with thermal conductivity, as does the related property connectivity.



Thermal conductivity graphed as a function of continuity of the MgO phase for two temperatures tested.

Phase composition-thermal conductivity relationship:

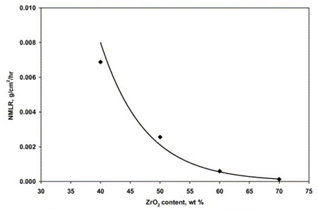
- Decreasing the vol% of the MgO phase will likely decrease its connectivity and contiguity, which has been demonstrated to decrease the material's thermal conductivity.
- It is hypothesized that the ideal IM material will have a phase composition with the highest vol% of MgO possible while still maintaining suitable hot water corrosion resistance.

Future Research

This project aims to optimize only one of the four main criteria which an IM material must meet. Further research will be necessary to collect quantitative data on the remaining properties.

Compatibility with reactor materials:

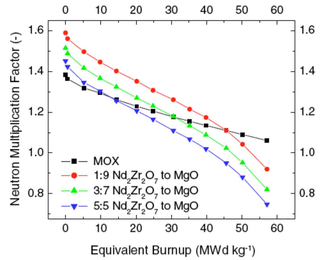
- As the vol% of the zirconia phase in a $MgO-ZrO_2$ composite decreases, so does the material's hot water corrosion resistance.
- A balance in the phase composition between thermal conductivity and corrosion resistance must be obtained.



The normalized mass loss rate (NMLR) of an $MgO-ZrO_2$ composite in 100 °C water as a function of ZrO_2 vol%.

High radiation resistance:

- Three zirconium based pyrochlores were tested: $La_2Zr_2O_7$, $Pr_2Zr_2O_7$, and $Nd_2Zr_2O_7$. The former two materials decayed to the fluorite crystal structure during irradiation. Other pyrochlores still require testing.



Reactor burnup data for three phase compositions tested.

Favorable neutronics:

- Nd has a large thermal neutron absorption cross-section; the neutron multiplication factor (NMF) of the IM is inversely proportional to the $Nd_2Zr_2O_7$ concentration.
- Simulations show that a 50/50 composition has an unfavorably low NMF, while a 90/10 composition requires the use of a neutron poison.
- Further testing is needed to quantify the relationship between phase composition and neutronics.

Selected References

- S. Yates, "Processing-thermal conductivity relationships In MgO-pyrochlore composite inert matrix materials," Dissertation, University of Florida, 2009.
- P.G. Medvedev *et al.*, "Dual phase $MgO-ZrO_2$ ceramics for use in LWR inert matrix fuel," *Journal of Nuclear Materials*, Volume 342, Issues 1-3, June 2005, p. 48-62.
- W.J. Carmack *et al.*, "Inert matrix fuel neutronic, thermal-hydraulic, and transient behavior in a light water reactor," *Journal of Nuclear Materials*, Volume 352, Issue 1-3, June 2006, p. 276-284.
- IAEA, "Viability of inert matrix fuel in reducing plutonium amounts in reactors," 2006.