Project No. 13-4818

Multiphase Nanocrystalline Ceramic Concept for Nuclear Fuel

Fuel Cycle Research and Development

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In collaboration with:
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University of Tennessee, Knoxville

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NEUP Nuclear Energy University Programs
U.S. Department of Energy

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Final Report May 9, 2017

1. COVER PAGE DATA ELEMENTS

a. Federal Agency and Organization Element to Which Report is Submitted – **Department of Energy, Nuclear Energy University Program**

b. Federal Grant or Other Identifying Number Assigned by Agency - **DE-NE0000711**

c. Project Title – **Multiphase Nanocrystalline Ceramic Concept for Nuclear Fuel**

d. PD/PI Name, Title and Contact Information (e-mail address and phone number) – **Martha Mecartney, Professor of Chemical Engineering and Materials Science, University of California, Irvine 92697-2575, martham@uci.edu, 949-824-2919**

e. Name of Submitting Official, Title, and Contact Information (e-mail address and phone number), if other than PD/PI - N/A

f. Submission Date - **May 9, 2017**

g. DUNS Number - **04-670-5849**

h. Recipient Organization (Name and Address) – **The Regents of the University of California (for the University of California, Irvine)**

i. Project/Grant Period (Start Date, End Date) **- 01/06/2014 through 01/05/2017**

j. Reporting Period End Date – **January 7, 2017**

k. Report Term or Frequency (annual, semi-annual, quarterly, other) – **Final**

l. Signature of Submitting Official (electronic signatures (i.e., Adobe Acrobat) are acceptable)

2. ACCOMPLISHMENTS

a. Goals

The goal of this research is to help develop new fuels for higher efficiency, longer lifetimes (higher burn-up) and increased accident tolerance in future nuclear reactors. Multiphase nanocrystalline ceramics will be used in the design of simulated advanced inert matrix nuclear fuel to provide for enhanced plasticity, better radiation tolerance, and improved thermal conductivity.

b. What Was Accomplished under These Goals

1. Three phase composite materials of alumina, spinel, and 8 mol% cubic yttria stabilized zirconia (surrogate for uranium oxide) were prepared with grain sizes from 100 nm (by SPS) to 500 nm (by two-step sintering) to 1.2 microns (conventional sintering). Electric field assisted sintering (FLASH sintering) could be used to sinter three phase ceramics in 30 seconds, but achieving high density resulted in large grains due to Joule heating.

2. Irradiation studies using 4 MeV Si and 1 GeV Au were conducted on single phase YSZ, spinel and alumina with 150 nm nanocrystalline grain size and single crystals, and compared to 150 nm and 500 nm grain size three-phase composites of YSZ, spinel and alumina. The results suggest that interfaces between dissimilar phases serve as more effective sinks for point defects generated during irradiation, compared to single phase grain boundaries, as evidenced by a lower dislocation loop density.

3. Room temperature mechanical tests for hardness found that the grain size from 100 to 1000 nm for single phase and three phase oxide composites followed the Hall-Petch relationship with significantly higher hardness at small grain sizes. The fracture toughness of YSZ is doubled when 33 vol% alumina and 33 vol% spinel phases were added. A small increase in toughness was also observed for the three phase composites when the grain size decreased from 1.2 microns to 500 nm. Thermal shock tests are in progress but not completed as of the writing of this final report.

4. High temperature deformation studies in compression of three phase ceramics with varying grain sizes showed the expected inverse dependence of strain rate on grain size with superplastic behavior at temperatures above 1400ºC under 50 MPa stress.

5. Computational studies of thermal conductivity studies showed a 300% increase in thermal conductivity of YSZ at room temperature and a 200% increase in thermal conductivity of YSZ at 800ºC upon addition of 33 vol.% alumina and spinel phases. However, experimental measurements of thermal conductivity using laser flash analysis showed that the thermal conductivity decreases with decreasing grain size. The thermal resistance (Kapitza resistance) of the interfaces in three phase composites was calculated to be an order of magnitude higher than for single phase grain boundaries in YSZ. Calculations using MOOSE and imported microstructures in OOF2 show that for a nanocrystalline grain size (100 nm), the thermal conductivity is reduced at room temperature by

a third and by half at 800ºC due to the Kaptiza resistance of interfaces, when compared to large grain (10 micron) materials. Thus, the use of nanocrystalline materials will negate any improvements in thermal conductivity expected by the addition of high thermal conducting alumina and spinel oxides.

c. Opportunities for Training and Professional Development

Jesse Angle, UC Irvine Ph.D. student, contributed to the OOF2 modeling work in collaboration with LANL Spring 2014. Jesse graduate in June 2014 and is now employed at Exponent.

Austin Travis, UC Irvine PhD student, continued the modeling research and incorporated Kaptiza resistance into the modeling. Austin spent two different 3 month internships at LANL working on computational modeling of thermal transport in uranium silicide/nitride composites and phase separation in reduced phases of uranium oxide. He learned MOOSE and was able to incorporate MOOSE into modeling of thermal transport of composites. Austin is expected to graduate in Spring 2018 and hopes to land a post-doctoral research position at a national laboratory. Austin was supported, when not at LANL, on an NRC Fellowship for two years.

Kenta Ohtaki, UC Irvine PhD student, conducted irradiation studies and TEM evaluation of irradiated materials. He was able to use facilities at the University of Tennessee, Knoxville (UTK) for 4 MeV Si irradiation, and facilities at the Swift Heavy Ion Institute (GSI) in Darmstadt, Germany for 1 GeV Au irradiation. Kenta is expected to graduate Spring 2018 and will seek post-doctoral opportunities that can use his TEM expertise.

David Kok, UC Irvine PhD student, conducted initial studies on the feasibility of using electric field assisted sintering without pressure or dies (FLASH sintering) to achieve fine grain sizes in multiphase materials. David will graduate in Spring 2019 and currently has an NDSEG Fellowship. His career goal is to work in a DOD or NASA laboratory.

Keyur Karandikar, UC San Diego PhD student conducted studies on grain growth in multiphase composites using SPS. He will graduate in Spring 2017 and plans to seek employment in industry. His advisor was Prof. Olivia Graeve.

Kara Phillips, UC Irvine PhD student, worked one year on this project and spent summer 2014 at LANL working with Dr. Nelson. She returned to UCI from LANL in Fall 2014 and changed PhD projects and advisors. She worked on the initial preparation of materials for thermal measurements.

Two M.S. students worked on this project for their M.S. theses. **Neshat Jalali Heravi** investigated routes to the formation of LaPO4 for use in multiphase composites for her M.S. in Chemical Engineering. She is now working at Statek Corporation in Orange as a Process Engineer. **Hemanth Shankar Vijaya Kumar**, M.S. in Materials Science and Engineering conducted mechanical property measurement and is completing thermal shock studies. He expects to graduate in Summer 2017 and work in industry.

One additional UCI graduate student, **Eric Casavant**, spent winter quarter 2014 on a research rotation working with OOF2 to simulate random microstructures.

Undergraduate researchers who worked on this project include the following: (1) Summer 2014 undergraduate research student **Raku Watari** from MIT on developing a model for the influence of grain boundaries on thermal conductivity using OOF2, (2) UCI undergraduate researcher **Rea Reyes** worked on preparation of ceramic powders for the fabrication of multiphase ceramics, (3) undergraduate **Stoney Middleton** worked on high temperature deformation of multiphase composites, (4) undergraduate **Dania Alfeerawi** worked on polishing and etching materials for SEM, (5) undergraduate **Michael Dixon** worked on preparation of three phase ceramics, (6), and undergraduate **Zari Ahvazi** worked on mechanical property measurements of hardness.

d. Results Disseminated to Communities of Interest

See Products for papers published and conference presentations given.

3. PRODUCTS

a. Publications, conference papers, and presentations

The following papers have been published. Additional papers are in preparation.

1. Jesse P. Angle, Andrew T. Nelson, Danju Men, Martha Mecartney, "Thermal Measurements and Computational Simulations of Three-Phase (CeO2 - MgAl2O4 - CeMgAl11O19) and Four-Phase (3Y-TZP - Al2O3 - MgAl2O4 - LaPO4) Composites as Surrogate Inert Matrix Nuclear Fuel" *Journal of Nuclear Materials*, **454** [1-3] 69–76 (2014).
2. Andrew T. Neson, Dylan R. Rittman, Joshua T. White, John T. Dunwoody, Masato Kato, and Kenneth J. McClellan, "An Evaluation of the Thermophysical Properties of Stoichiometric CeO_2 in Comparison to UO_2 and PuO_2," *Journal of the American Ceramic Society*, first published on-line 7 AUG 2014, DOI: 10.1111/jace.13170
3. Travis, A.W., Nelson A.T., and Mecartney M.L., "Computational Studies of Thermal Conductivity of Multiphase Ceramics for Inert Matrix Fuel", *Transactions of the American Nuclear Society*, Vol. 115, 110-111 (2016).
4. Travis, A.W., Andersson D.A., and Nelson A.T., "Continuum Scale Modeling of the Thermal Conductivity of Hyperstoichiometric UO_2," *Transactions of the American Nuclear Society NSFM 2016*, Vol. 114, 1185-1186 (2016).
5. Kenta Ohtaki, Maulik Patel, Martha L. Mecartney, "Radiation Damage Behavior in Multiphase Ceramics," Microscopy and Microanalysis, vol. 22, Issue S3 pp. 1464-1465 (2016)
6. Kenta Ohtaki, Maulik Patel and Martha Mecartney, "Radiation Damage in Multiphase Ceramics" Transactions of the American Nuclear Society, Vol. 115, Las Vegas, NV, November 6–10, 2016

Conference Presentations are listed below.

1. K. Karandikar and O.A. Graeve, "Analysis of Grain Size and Particle Size in Ceramic Powders," 3rd International Symposium on Nanoscience and Nanomaterials (Ensenada, México. Date: March 10-14, 2014).

2. Ceramics Gordon Research Conference, July 20-25, 2014 – “Challenges in the Synthesis of Nanocrystalline, Multiphase Ceramics for Inert Matrix Nuclear Fuel,” Kara Phillips, Austin Travis, Keyur Karandikar, Olivia Graeve, and Martha Mecartney

3. **Travis A.W.**, Angle J.P., Morgan P.E.D., and Mecartney M.L., “XRD Analysis of Novel Magnetoplumbite Structures”, Denver X-Ray Conference (DXC), Big Sky, Montana, July 2014.

4. Denver X-Ray Conference, 28 July - 1 August, 2014, “XRD Analysis of Doped Monoclinic LaPO4 (Monazite),” Kenta Ohtaki, Neshat J. Heravi, Peter E. D. Morgan, and Martha L. Mecartney

5. **Travis A.W.**, Phillips K.J., Nelson A.T., and Mecartney M.L., “Computational Simulations of Thermal Conductivity of Multiphase Ceramics for an Inert Matrix Nuclear Fuel”, Materials Science and Technology 2015, Columbus Ohio, October 2015.

6. K.K. Karandikar and O.A. Graeve, "Correlation Between Particle Size and Grain Size Distributions in Single/Multiphase Ceramics," Materials Science and Technology 2015 Conference & Exposition (Columbus, OH. Date: October 4-8, 2015).

7. M. Mecartney, “Using Multiple Phases to Achieve Fine Grain Sizes with Spark Plasma Sintering (SPS) and Two-Step Reactive Sintering,” MS&T 2015, Columbus, OH, October 2015.

8. M. Mecartney, “Thermal Properties of Nanocrystalline Multiphase Oxide Ceramics,” MS&T 2015, Columbus, OH, October 2015.

9. Maulik K. Patel, Kevin J. Mathew, Kenta Ohtaki, Martha Mecartney, Kurt Sickafus ,”Thermal effects in 3-phase composites containing $MgAl_2O_4$ + YSZ + Al_2O_3: an in-situ high temperature XRD study,” Spring 2016 MRS Meeting.

10. **Travis A.W.,** Andersson D.A., and Nelson A.T., “Continuum Scale Modeling of the Thermal Conductivity of Hyperstoichiometric UO_2”, American Nuclear Society (ANS) National Meeting, New Orleans Louisiana, June 2016.

11. Kenta Ohtaki, Maulik Patel, and Martha Mecartney, “Radiation Damage Behavior in Multiphase Ceramics,” Microscopy and Microanalysis Conference, Nuclear and Irradiated Materials, Columbus Ohio July 28 2016

12. Martha Mecartney, “Design of Ceramics Using Multiple Phases for Optimized Properties,” Gordon Research Seminar, Mt. Holyoke, MA, July 2016.

13. **Travis A.W.**, Karandikar, K., Nelson A.T., Graeve O., and Mecartney M.L., “Thermal Conductivity of Multiphase Ceramics for an Inert Matrix Fuel”, Materials Science and Technology 2016, Salt Lake City Utah, October 2016.

14. K. Karandikar, A. Travis, K. Ohtaki, M. Mecartney, and O.A. Graeve, "Correlation Between Particle Size and Grain Size Distributions in Single/Multiphase Ceramics," Materials Science and Technology 2016 Conference & Exposition (Salt Lake City, UT. Date: October 23-27, 2016).

15. Kevin J. Mathew, Kenta Ohtaki, Martha Mecartney, Maulik K. Patel, "Thermal expansion of a 3-phase ceramic composite: an *in-situ* high temperature x-ray diffraction study," MS&T Nov. 2016.

16. Kenta Ohtaki, "Radiation Damage in Multiphase Ceramics," Research by U.S. DOE NEUP-Sponsored Students, Las Vegas November 9 2016

17. **Travis A.W.**, Nelson A.T., and Mecartney M.L., "Computational Studies of Thermal Conductivity of Multiphase Ceramics for Inert Matrix Fuel" American Nuclear Society National Meeting, Las Vegas Nevada, November 2016.

18. K.K. Karandikar, A.W. Travis, K. Ohtaki, M.M. Mecartney, and O.A. Graeve, "Correlation Between Particle Size and Grain Size Distribution in Single/Multiphase Ceramic Oxide Surrogate Materials," 2017 TMS Annual Meeting & Exhibition (San Diego, CA. Date: February 26 - March 2, 2017).

b. Websites
   A website for the team was not developed.
c. Technologies or Techniques
   The integration of MOOSE with OOF2 is a promising technique that will be reported in an upcoming paper by Austin Travis.
d. Inventions, Patents, Licenses
   None at this time.
e. Other Products
   None at this time.

4. PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

a. Individuals Working on the Project

1. Name: Martha Mecartney
2. Project Role: PI
3. Nearest person month worked: 1
4. Contribution to Project: Supervised research
5. Funding Support: DOE NEUP only
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Jesse Angle
2. Project Role: PhD Graduate student researcher
3. Nearest person month worked: 2

4. Contribution to Project: worked on computational modeling
5. Funding Support: UC Irvine Fellowship
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Kara Philips
2. Project Role: PhD Graduate student researcher
3. Nearest person month worked: 4.5
4. Contribution to Project: worked on synthesis of multiphase ceramics by conventional sintering
5. Funding Support: DOE NEUP, DoEd GAANN Fellowship, and LANL summer internship
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Eric Casavant
2. Project Role: PhD Graduate student researcher
3. Nearest person month worked: 1.5
4. Contribution to Project: worked on computational modeling
5. Funding Support: UC Irvine Fellowship
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Austin Travis
2. Project Role: PhD Graduate Student Researcher
3. Nearest person month worked: 18
4. Contribution to Project: Computational Modeling of Thermal Properties
5. Funding Support: DOE NEUP, UC Irvine Fellowship, NRC Fellowship, and 2 LANL internships
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Kenta Ohtaki
2. Project Role: PhD Graduate Student Researcher
3. Nearest person month worked: 18
4. Contribution to Project: Radiation Damage Experiments and TEM Studies
5. Funding Support: DOE NEUP, UC Irvine Fellowship,
6. Collaborated with individual in foreign country: Yes, GSI in Darmstadt, Germany, Dr. Christina Trautmann for irradiation with 1 GeV Au
7. Country(ies) of foreign collaborator: Germany
8. Traveled to foreign country: Yes, but no travel funds from this grant
9. If traveled to foreign country(ies), duration of stay: 3 months

1. Name: David Kok
2. Project Role: PhD Graduate Student Researcher
3. Nearest person month worked: 18
4. Contribution to Project: Electric Field Assisted Sintering to prepare fine grain size materials
5. Funding Support: DOE NEUP, GAANN Fellowship, NDSEG Fellowship
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: Yes, to Portugal to present at a conference, no travel funds were used from this grant
9. If traveled to foreign country(ies), duration of stay: 1 week

1. Name: Keyur Karandikar (UC San Diego)
2. Project Role: PhD Graduate Student Researcher
3. Nearest person month worked: 18
4. Contribution to Project: Preparation of nanocrystalline materials, grain growth studies
5. Funding Support: DOE NEUP
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Hemanth Shankar Vijaya Kumar
2. Project Role: MS Graduate Student Researcher
3. Nearest person month worked: 6
4. Contribution to Project: Measurement of mechanical properties
5. Funding Support: self supporting MS student
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

1. Name: Neshat Jalali Heravi
2. Project Role: MS Graduate Student Researcher
3. Nearest person month worked: 4.5
4. Contribution to Project: evaluated methods to produce monazite to use in multiphase ceramics
5. Funding Support: None except for project expenses (MS students are not supported)
6. Collaborated with individual in foreign country: No
7. Country(ies) of foreign collaborator:
8. Traveled to foreign country: No
9. If traveled to foreign country(ies), duration of stay:

b. Other Organizations Involved as Partners

1. Name: Olivia Graeve, UC San Diego
2. Project Role: co-PI
3. Nearest person month worked: 3
4. Contribution to Project: Supervised research on nanocrystalline ceramic synthesis
5. Funding Support: DOE NEUP, $160,000

1. **Name:** Andrew T. Nelson, LANL
2. **Project Role: LANL co-**PI
3. **Nearest person month worked:** 3
4. **Contribution to Project:** Supervised research on thermal transport
5. **Funding Support:** DOE NEUP, $160,000

1. **Name:** Maulik Patel, UT Knoxville
2. **Project Role: co-**PI
3. **Nearest person month worked:** 3
4. **Contribution to Project:** assisted with radiation damage studies
5. **Funding Support:** DOE NEUP, $146,500

c. Have other collaborators or contacts been involved?
Informal collaboration, Dr. Christina Trautmann of GSI Darmstadt.

5. IMPACT

What is the impact of the project?
The project found that nanocrystalline multiphase materials can be made by spark plasma synthesis with improved radiation damage tolerance but with lowered thermal conductivity.

a. What is the impact on the development of the principal discipline(s) of the project?
This approach using multiphase oxides can be used to improve mechanical properties but not thermal stability of nuclear fuels.

b. What is the impact on other disciplines?
Nothing to report.

c. What is the impact on the development of human resources?
Three PhD students were primarily supported on this grant, and three additional PhD students worked on secondary aspects.

d. What is the impact on physical, institutional, and information resources that form infrastructure?
Nothing to report.

e. What is the impact on technology transfer?
Nothing to report.

f. What is the impact on society beyond science and technology?
Nothing to report.

g. What dollar amount of the award's budget is being spent in foreign country(ies)?
No money was spent in foreign countries.

6. CHANGES/PROBLEMS:

a. Changes in approach and reasons for change

The depleted UO2 experiments were not conducted at LANL as the initial results from the three phase composite with YSZ-Al2O3-MgAl2O4 were not deemed promising enough.

b. Actual or anticipated problems or delays and actions or plans to resolve them
Sample preparation for the nanocrystalline samples was slow due to difficulty in synthesis, but were eventually made.

c. Changes that have a significant impact on expenditures
The furnace in the Mecartney Lab for preparing bulk samples became contaminated necessitating the purchase of a new replacement high temperature furnace on this grant. The new furnace was dedicated for exclusive use for research on this NEUP project. A GAANN Fellowship received by Kara Phillips January – August 2014 in Year I freed up funds that could be used for this purpose so there was no net increase in the cost of the project.

d. Significant changes in use or care of human subjects, vertebrate animals, and/or Biohazards
None.

e. Change of primary performance site location from that originally proposed
No change.

7. SPECIAL REPORTING REQUIREMENTS:
None.

8. BUDGETARY INFORMATION: Quarterly budget information of actual expenditures was submitted by UC Irvine as required directly to DOE. All funds were expended by the end of the project. *Reporting of funds spent through the end of the project is attached as pdf document* **DE NE0000711 22411 Final Fiscal Report as of 01-05-17.**

9. PROJECT MANAGEMENT PLAN (PMP)
Iterations and Maintenance
The PI, Martha Mecartney was in charge of regular communication between group members and supervision of tasks via phone and email with LANL, UC San Diego and UTK collaborator. Three in person participant meetings were held, two at UC Irvine and one at MS&T in Pittsburgh.