Final Project Report

INERT-MATRIX FUEL:
ACTINIDE “BURNING” AND DIRECT DISPOSAL

Nuclear Engineering Education Research Program
(grant # DE-FG07-99ID13767)

Rodney C. Ewing (co-PI)
Lumin Wang (co-PI)

October 30, 2002
For the Period of 07/01/1999 to 06/30/2002

Department of Nuclear Engineering and Radiological Sciences
University of Michigan
Ann Arbor, MI 48109
1. Background

Excess actinides result from the dismantlement of nuclear weapons (239Pu) and the reprocessing of commercial spent nuclear fuel (mainly 241Am, 244Cm and 237Np). In Europe, Canada and Japan studies have determined much improved efficiencies for burn-up of actinides using inert-matrix fuels. This innovative approach also considers the properties of the inert-matrix fuel as a nuclear waste form for direct disposal after one-cycle of burn-up. Direct disposal can considerably reduce cost, processing requirements, and radiation exposure to workers.

2. Objectives

The objectives of this NEER program are to study the nuclear fuel and waste form properties of the most promising inert-matrix fuels (i.e., cubic zirconia and spinel-zirconia composites). The main topics of study as listed in the original proposal are: a) the effect of fission event (in-reactor) and alpha-decay event (in-repository) damage on the physical and chemical properties that are important to nuclear fuel (e.g., bubble formation and swelling) and nuclear waste forms (e.g., leach rate and micro-fracturing) performance; b) The solubility and the mobility of the fission and other important transmutation products in the inert fuel matrix at both high (reactor fuel condition) and low (waste form condition) temperatures. We have also stated in the original proposal that this research program would be conducted with international collaborations.

3. Research Accomplishments

During the past three years, we have made a significant accomplishment on the research program. We have completed a systematic study of some major effects on the yattria stabilized zirconia (YSZ) microstructure due to fission product incorporation and associated radiation damage. In addition, we have studied the effects of fission product incorporation and radiation on the microstructure of YSZ/spinel composite material. These results are valuable in the development and evaluation of the zirconia based inert matrix fuels. Our study supported by this NEER program has resulted in 14 scientific research papers (see 3.2) and 17 presentations at national or international conferences.
(see 3.3), including the Material Research Society (MRS) annual meeting, American Nuclear Society (ANS) annual meeting, Microscopy Society of America (MSA) and Microbeam Analysis Society (MAS) joint annual meeting, International Conference on Inert matrix Fuel and International Conference on Ion Beam Modification of Materials.

**The graduate student supported by this NEER program, Sha Zhu, has won two major national awards** at the MSA/MAS joint meeting in 2001 (Long Beach, CA): MAS Distinguished Scholar Award and the MSA Second Best Poster Award for Physical Science Applications of Microscopy. We have collaborated with researchers at Argonne National Laboratory (R.C. Birtcher), Pacific Northwest National Laboratory (W.J. Weber) and European Commission Joint Research Center in Karlsruhe, Germany (Hj. Matzke). The graduate student supported under this NEER program has been trained to use the IVEM-Tandem Facility at Argonne National Laboratory to conduct *in situ* TEM studies on radiation effects in materials during ion beam bombardment.

### 3.1 Awards

The student supported under this NEER program, Sha Zhu has won two major awards at the MSA/MAS joint meeting (Long Beach, CA, August 2001):

1. Microbeam Analysis Society (MAS) Distinguished Scholar Award;
2. Microscopy Society of America (MSA) Second Best Poster Award for Physical Science Applications of Microscopy.

### 3.2 Publications


### 3.3 Presentations


4. Main Results

4.1 Effects of radiation and Cs, I and Sr incorporation in YSZ

Cesium, iodine and strontium ions have been implanted into yttria-stabilized cubic zirconia (YSZ) to determine the effects of fission product incorporation in YSZ that is considered as an inert nuclear fuel matrix. The ion implantation was conducted at room temperature to $1 \times 10^{21}$ ions/m$^2$ for each ion with ion energies ranging from 70 to 400 keV. The peak displacement damage level and the peak ion concentration in YSZ reached 205-330 dpa and 11-26 at.%, respectively. The microstructure of the implanted YSZ was studied by in situ and cross-sectional transmission electron microscopy. In the iodine and strontium implanted samples, a damaged layer with a high density of defect clusters was observed, while in the cesium implanted specimen, most damaged layer is amorphous. Nanocrystalline precipitates were observed in the strontium implanted specimen after annealing at 1000°C. The results have been discussed in terms of the ionic size, mobility and the solubility of the implanted species in YSZ.

In situ TEM during the 70 keV $\text{Cs}^+$ implantation revealed a high density of defect clusters on the nanometer scale after ~$2 \times 10^{20}$ Cs/m$^2$. The defect clusters with characteristics of interstitial type dislocation loops are interpreted to be the result of planar precipitates of Zr and/or O interstitials displaced from their original lattice site by the collisional events. The formation of dislocation loops indicates a high defect mobility in YSZ at the room temperature, and this is consistent with previous results of radiation studies that did not result in amorphization even at a dose of 680 dpa. However, amorphous domains in the thin regions of the specimen were observed after $1 \times 10^{21}$ Cs/m$^2$ with ex situ high resolution TEM (HRTEM) and nanobeam electron diffraction in areas with a Cs concentration of 11 at.%, as measured by energy dispersive x-ray spectroscopy (EDS). Because the 70 keV implanted Cs ions were only present in a thin layer of ~30 nm at the surface and the ion distribution is depth dependent, only the average Cs concentration through the entire thickness can be obtained from the plan-view TEM sample. Cross-sectional TEM of the 400 keV Cs-implanted specimen (Fig. 1) confirmed the formation of an amorphous layer that is approximately centered at the depth of peak Cs-concentration, rather than the peak-damage depth. The nature of the amorphous layer was confirmed by both high resolution TEM and convergent beam electron diffraction (Fig. 2). The top and lower boundaries of the amorphous band correspond to a Cs-concentration of ~8 at.%. Strain contrast in the TEM image at the top of the amorphous layer indicates the formation of a high density of defect clusters and local lattice distortion.
The results of the 200 keV I+ implantation on the microstructure of YSZ are shown by the bright- and dark-field TEM images in figure 4. A band (~50 nm wide) of defect clusters was apparent towards the end of the calculated ion and damage range, but no amorphization was observed throughout the thickness even at depths with ~26 at. % I or ~200 dpa. Although a more detailed study of the damaged band revealed some morié fringes which may be indications of the formation of precipitate phases, the selected area electron diffraction pattern from the damage band showed that the area is still a single crystal (insert of Fig. 4a). The defect clusters may include dislocation loops (two dimensional point defect clusters), as well as small three dimensional precipitates of interstitials. Because of the high concentration of implanted iodine in the region, most of these defect clusters probably contain iodine.

Fig. 1 Bright-field cross-sectional TEM micrograph showing the depth dependent microstructure of YSZ after 400 keV Cs implantation to 1x10^21 ions/m^2 at room temperature.

In situ TEM during the 200 keV Sr+ implantation also revealed a high density of defect clusters on the nanometer scale after ~2x10^20 ions/m^2, but no evidence of amorphization or secondary phase precipitation after 1x10^21 ions/m^2. The results were confirmed by
cross-sectional TEM after 400 keV Sr\(^+\) implantation to 1×10\(^{21}\) ions/m\(^2\) as shown in a dark-field image (g=220) of figure 3. The defect clusters appear to be dislocation loops with diameters ranging from 3-20 nm. The depth of the damage distribution is 50 nm deeper than the calculated damage range and occurs closer to the implanted ion concentration maximum, rather than the displacement damage maximum, which may be due to the high interstitial concentration at the peak ion concentration. Annealing of the Sr-implanted sample at 1000°C for two hours did not remove the dislocation loops from the damaged microstructure, as shown in a g=220 dark field TEM micrograph (Fig. 4a). However, when the strain field of dislocation loops were tilted out of contrast, small precipitates and cavities were observed in the damaged band (Fig. 4b). The precipitates have dimensions ranging from 5 to 25 nm, and the cavities are of much smaller size (~3 nm in diameter) but with a much higher density (Fig. 4b insert). The depth at which the precipitates form corresponds to the depth of the maximum concentration of implanted Sr, and the precipitates have been identified to be SrZrO\(_3\) (perovskite structure).

Previous irradiation studies have demonstrated that cubic zirconia is one of the most radiation-resistant of ceramics. Naguib and Kelly have classified zirconia as an oxide that is among the most resistant to irradiation-induced amorphization based on its high bonding ionicity. Swelling in cubic zirconia, without excess gas implantation during neutron irradiations, is minimal although prismatic dislocation loops can be easily generated. Stabilized cubic zirconia can also be destabilized to the monoclinic structure under ionizing irradiation. Recently, irradiations to doses as high as 680 displacement per atoms (dpa), at temperatures as low as 20 K, with an implanted xenon concentration as high as 37 at. % have failed to amorphize cubic zirconia. The observation of dislocation loops at cryogenic temperatures and the readily formed xenon bubbles confirm the high mobility of point defects and implanted xenon atoms in zirconia. This high mobility promotes the defect recombination and precipitation, and this prevents the build-up of defects or impurity concentrations required for solid-state amorphization. The recently reported radiation-induced polygonization of cubic zirconia at 120 K is consistent with the structure's strong tendency to crystallize as polygonization is a result of the competition between radiation-induced amorphization and radiation-enhanced...
Fig. 4 Bright-field (a) and dark field (b) cross-sectional TEM images of a YSZ single crystal after a 200 keV I implantation to 1×10^{21} ion/m^2. The selected area electron diffraction pattern in (a) shows that the damaged layer remained a single crystal.

An important parameter in determining the effect of the implanted species on the threshold amorphization dose is the relative atomic size. The atomic size ratio in crystalline materials has been used to estimate phase stability. As an example, the atomic size ratio (R_A/R_B) determines the occurrence of hydrogen-induced amorphization in the AB_2-type cubic Laves phase system, for which compounds with a ratio >1.37 are amorphized by hydrogenation.

Cubic zirconia has the fluorite structure in which zirconium is 8-coordinated by oxygen and oxygen is 4-coordinated by zirconium. To maintain the fluorite structure, the radius ratio of cation to anion should typically be in the range of 0.732 to 1. In pure zirconia, the ratio is 0.79 (radius of Zr^{4+} = 0.098 nm in 8-fold coordination). Zr^{4+} may be substituted by larger cations. However, the maximum cation radius is 0.124 nm which is approximately that of O^{2-}. Cs^{+} is a large cation with an effective ionic or crystal radius

crystallization that is usually observed just above the critical amorphization temperature. Our observation of radiation-induced dislocation loops in the ion-implanted YSZ is consistent with previous observations.

Although cubic zirconia is known to have high solubility for actinides, there are only limited data on the solubility and mobility of Cs, I and Sr in cubic zirconia. Pouchon et al. recently estimated by thermodynamic calculations that the solubility of Cs_2ZrO_3 (at 1000 K) and Cs (at 2000 K) in ZrO_2 may only be 1.5 at. %, although the highly defective zirconia structure may incorporate higher concentrations of impurities because the impurities may be trapped at the boundaries of crystal defects. The relatively low solubility of Cs in cubic zirconia suggests that Cs tends to precipitate in the secondary phases. The precipitation of a secondary phase is prevented by the extremely low Cs-mobility in cubic zirconia at temperatures below 873 K. Apparently, the amorphization of YSZ implanted with excess Cs is related to the low solubility and mobility of Cs in YSZ.

An important parameter in determining the effect of the implanted species on the threshold amorphization dose is the relative atomic size. The atomic size ratio in crystalline materials has been used to estimate phase stability. As an example, the atomic size ratio (R_A/R_B) determines the occurrence of hydrogen-induced amorphization in the AB_2-type cubic Laves phase system, for which compounds with a ratio >1.37 are amorphized by hydrogenation.
ranging from 0.174 or 0.188 (8-coordinated) to 0.188 or 0.202 nm (12-coordinated). In comparison, the effective ionic radii of Sr and I (as cations) have ranges up to 0.140 and 0.109 nm, respectively, and the effective ionic and crystal radii of xenon ranges from 0.04-0.062 nm. Thus, Cs\(^+\) is incompatible in the cubic zirconia structure. The incorporation of Cs\(^+\) or cations with ionic radii larger than 0.124 nm disrupts the local topology in cubic zirconia which leads to amorphization of the structure at high ion fluences. The monovalent charge of Cs\(^+\) is also incompatible with the fluorite structure. Cs\(^+\) may try to react with O\(_2\) to form Cs\(_2\)O which has the inverse fluorite structure (i.e., with Cs ions occupying the 4-coordinated anion positions and O occupying the 8-coordinated cation positions in YSZ). For such a reaction, large amount of local atomic rearrangement has to be made.

The ionic radii of I\(^-\) is large (0.22 nm), however, it is unlikely that implanted I\(^-\) will be present in the zirconia as an anion. As cations, iodine radii are much smaller than that of Cs. According to the measurement of I\(^-\) implanted YSZ by Rutherford Backscattering (RBS), iodine diffusion in YSZ is limited below 1373 K, indicating a high iodine retention capacity and a rather low iodine mobility in YSZ at lower temperatures. Although the formation of Sr-containing precipitates in the Sr-implanted specimen after annealing suggested a relatively low Sr-solubility and mobility at the room temperature in the YSZ matrix, excess Sr (because of the relatively small ionic size) did not cause amorphization of YSZ.

Because the operating temperature of an inert matrix-fuel in nuclear reactors will be quite high (ranging from >1600 K at the core to 873 K at the rim), Cs-migration, release and precipitation are expected. It is unlikely that the Cs-concentration will be greater than 8 at. % in the fuel. Thus, zirconia used as an inert matrix fuel will not become amorphous due to in-reactor irradiation. Actually, our later study has indicated that Cs would migrate in YSZ to form bubbles in YSZ at elevated temperatures. Nevertheless, our results show that if excess Cs is generated and retained in the YSZ structure at lower temperatures, radiation-induced amorphization can occur. Amorphization can cause a significant volume swelling and increase in the leach rate of a nuclear waste form.

4.2 Formation of pyrochlore nanodomains in Ti implanted YSZ

The microstructural evolution of a single crystal of yttria-stabilized zirconia (YSZ) implanted with Ti has been studied by cross-sectional transmission electron microscopy (TEM). The implantation of 180 keV Ti ions to a dose of 1×10\(^{17}\) ions/cm\(^2\) was completed at room temperature. After annealing at 1100 °C in an Ar atmosphere for 2 hours, a phase transition from the fluorite structure of ZrO\(_2\) to an isometric pyrochlore structure-type, A\(_2\)B\(_2\)O\(_7\), occurred due to cation ordering. High-resolution TEM (HRTEM) revealed nanodomains of pyrochlore, Y\(_2\)(Ti\(_x\)Zr\(_{1-x}\))\(_2\)O\(_7\), with \(a \approx 10.24\pm0.05 \text{ Å}\). The nanodomains of the pyrochlore phase, embedded within the YSZ fluorite substrate, occurred in a depth range from 45 to 105 nm below the surface, which corresponds to Ti-concentrations from ~10 to ~15 at. % (Fig. 5). The nanoscale pyrochlore precipitates and the YSZ matrix have a completely coherent orientation.
Fig. 5 (a) Bright-field cross-sectional TEM micrograph showing the depth dependent microstructure of YSZ after 180 keV Ti-implantation to $1 \times 10^{17}$ ions/cm$^2$ at room temperature; (b) selected area electron diffraction (SAD) pattern of [110] zone from the surface area in showing YSZ structure; (c) SAD pattern of [110] from the implantation peak revealing superlattice spots corresponding to the cation ordering in the pyrochlore structure.

4.3 Effects of Xe implantation in spinel-zirconia/ceria composites

The spinel-YSZ composite is considered as a good candidate for inert fuel matrix based on the following considerations: (1) YSZ is isostructural (fluorite structure) with UO$_2$, PuO$_2$, AmO$_2$ and ThO$_2$, it has a high solubility for actinides and is considered to be an excellent actinide host phase. For example, PuO$_2$ and ZrO$_2$ form solid-solutions over the entire binary composition range above 1473 K. (2) The relatively low thermal conductivity of YSZ is not desirable for its use as an inert fuel matrix. On the other hand, spinel has a higher thermal conductivity, but is not a good host for the actinides.

In our study, two spinel based composite specimens containing either $(Zr_{0.8}Y_{0.15})O_2$ or $(Zr_{0.5}Ce_{0.5})O_2$ particles were implanted with 200-400 keV Xe ions at 873 K using the IVEM-Tandem Facility at Argonne National Laboratory. Ce is used as a simulant for Am, an element to be transmuted in the inert matrix fuel, as the two elements have similar chemical properties. In situ transmission electron microscopy (TEM) was conducted during the implantation in order to follow the evolution of the microstructure. At a fluence between $2.4 \times 10^{20}$ to $3 \times 10^{20}$ ions m$^{-2}$ (up to 50 dpa and 4.7 at %), large Xe bubbles of 50-100 nm developed at the boundaries of the small oxide particles (Figs. 6 and 7), while a high density of dislocation loops (up to 8 nm in diameter) and much smaller bubbles (up to ~4 nm in diameter) formed in the spinel matrix. No large bubbles were observed at the boundaries between the spinel grains. These results suggest that the boundaries between spinel and oxide particles are preferred sites for fission gas accumulation.
Fig. 6. TEM micrograph from a spinel-(Zr$_{0.5}$Ce$_{0.5}$)O$_2$ composite after implantation with 200 keV Xe$^+$ to 2x$10^{20}$ ions m$^{-2}$ plus 400 keV Xe$^+$ to 3.75x$10^{19}$ ions m$^{-2}$ at 873 K showing the formation of large Xe bubbles at the (Zr$_{0.5}$Ce$_{0.5}$)O$_2$ particle boundaries.

Fig. 7. TEM micrographs from a 400 keV Xe$^+$ implanted spinel-(Zr$_{0.85}$Y$_{0.15}$)O$_2$ composite after 3x$10^{20}$ ions m$^{-2}$ at 873 K showing the formation of large Xe bubbles at the (Zr$_{0.85}$Y$_{0.15}$)O$_2$ particle boundary. The bubbles on the YSZ particle in (b) are believed to be at the boundary above or below the particle.
4.4 Effects of temperature on the behavior of fission products in YSZ

The temperature effects on the behavior of long-lived fission product, such as cesium, xenon and iodine, in YSZ based inert matrix fuel and waste form have been investigated through ion implantation and thermal annealing. Implantation of 400 keV Cs+ and 200 keV I- were conducted at room temperature with ion fluences up to $1 \times 10^{21}$ ions/m². Subsequent annealing was completed at 800°C and 1000°C. Cross-sectional TEM was performed to reveal the depth-dependent microstructure. As previously reported, amorphization of YSZ occurred where Cs+ concentration exceeds 8 at. % (300 dpa) upon Cs+ implantation. After annealing at 1000°C, a high density of bubbles ($2 \times 10^{16}$ bubbles/cm³) with diameters from 6 to 60 nm formed while the amorphous band crystallized. No amorphization was observed upon I- implantation. I- bubbles formed after annealing and the bubble density reached $8 \times 10^{16}$ /cm³ at 1000°C. The diameters of bubbles ranged from 3 to 18 nm. At higher annealing temperatures, the bubble size increased causing larger volume swelling. The distribution and migration of implanted ions in a spinel-YSZ composite material have also been studied. The most recent results on this topic have been presented at the 8th International Workshop on Inert Matrix Fuel held at Tokai, Japan.

Summary and Future Work

In this NEER program, we investigated the effects of radiation and fission product incorporation for the in-reactor performance of a variety of inert matrix fuels. The results of this research have been published in 14 research papers and been presented in 17 national or international conferences. The graduate student supported under this NEER grant has been trained not only at the University of Michigan, but also at Argonne National Laboratory to use a national facility for research. As the result of the support of this NEER grant, the student received two prestige awards at national conferences.

This work has lead us to realize that special application nuclear fuels can also find dual application as durable waste forms. The inert matrix fuel is designed to contain a balanced mixture of inert material, fissile nuclides and neutron absorbers that then controls the reactivity of the fuel. Such a strategy should also allow direct disposal of the used fuel as a waste form, without reprocessing after once-through burn-up. The development of inert-matrix fuels/waste forms is not only a part of the solution for the disposition of plutonium from dismantled nuclear weapons, but such fuels can be a necessary component of reprocessing strategies for commercial nuclear fuels.

We have been participating in an international research collaboration on inert matrix fuels (IMF) that was initiated at the Paul Scherrer Institute (Switzerland) in 1994. We have attended and presented research results at each annual workshop (most recently at Tokai, Japan, in October 2002), and future work is needed to extend this work to include the development of new nuclear waste forms (NNWF).