Interaction between metal fission products and TRISO coating materials: A study of chemical bonding and interdiffusion

Clemens Heske

University of Nevada, Las Vegas, heske@unlv.nevada.edu

Follow this and additional works at: http://digitalscholarship.unlv.edu/hrc_trp_fuels

Part of the Metallurgy Commons, Nuclear Engineering Commons, Oil, Gas, and Energy Commons, and the Physical Chemistry Commons

Repository Citation


This Grant is brought to you for free and open access by the Transmutation Research Program Projects at Digital Scholarship@UNLV. It has been accepted for inclusion in Fuels Campaign (TRP) by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.
Interaction between metal fission products and TRISO coating materials:
A study of chemical bonding and interdiffusion

Principal Investigator (PI): Clemens Heske
Department of Chemistry, UNLV
4505 Maryland Parkway, Las Vegas, NV 89154
Phone: (702) 895-2694   Email: heske@physik.uni-wuerzburg.de

Collaborators (UNLV): TBD-A (Graduate Student) – to start June 1, 2004
TBD-B (Graduate Student) – to start Sept. 1, 2004
TBD-C (Graduate Student) – to start Sept. 1, 2004
(Sufficient office space for the students has been affirmed by the UNLV Chemistry Department within the start-up package of the PI)

Collaborators (DOE): David Williams
Oak Ridge National Laboratory
PO Box 2008 MS6170
Oak Ridge, TN 37831-6170
Phone: (865) 574-5769   Email: williamsdf2@ornl.gov

AFCI Research Area: Fuels: TRISO Fuel Development

Abstract:
The goal of this project is to elucidate the chemical bonding and interface formation of metal fission products with the coating materials used in state-of-the-art TRISO fuel particles. Particular emphasis is placed on an analysis of intermediate chemical phases at the interface, the intermixing/diffusion behavior, and the electronic interface structure as a function of material choice (metal and coating materials), temperature, and external stress.
Furthermore, we intend to assess the chemical state of some of the metal fission products. The findings are expected to give valuable information about failure mechanisms of TRISO particles and fission product transport. Secondly, through simulating experiments, the project is intended to give indications for optimized irradiation testing and post-irradiation examinations within the AFCI effort at ORNL. Third, it is a goal of the project to derive strategies to tailor the interface properties for an optimization of TRISO particles in terms of, e.g., chemical and long-term stability.

In detail, we propose to study the interface formation of Pd, Ag, and Cs with SiC and pyrolytic carbon. Using the TRISO coating materials (and single crystal references) as substrates, interfaces will be prepared under controlled conditions in an ultra-high vacuum environment and will be studied with a variety of different spectroscopic and (when applicable) structural methods. In addition, realistic microstructures will be studied. The combination of surface sensitive techniques (e.g., photoelectron spectroscopy) with bulk sensitive methods (e.g., X-ray emission spectroscopy) will probe the chemical properties as well as the diffusion behavior in several complementary ways. In addition, spatially resolving methods will be employed to characterize cross sectional profiles. A variety of surface modification methods will be applied ex-situ (e.g., for stressed coating layers) or in-situ (e.g., by ion bombardment) prior to or after the interface formation to study the dependence of the interface properties on the surface/interface morphology and quality of the coating material.
Work Proposed for Academic Year 2004-2005, Goals, and Expected Results:

In the summer of 2004, the formation of the Ag/SiC interface formation will be studied for selected SiC substrates (student A, PI). The impact of surface modification treatments (both in-situ and ex-situ) on the interface properties will be investigated, and the use of various annealing procedures will give insight into the temperature stability of the Ag/SiC-interface (this work will be performed at the University of Würzburg, Germany). In October 2004 (after completion of the lab renovation at UNLV), the instrument will be relocated to UNLV, and an estimated 6 months after relocation will be dedicated to the reassembly, installation (i.e., peripheral connections) and the possibly required removal of damages incurred in transit (all students and PI). During the summer and fall of 2005, the Ag/SiC results will be finalized (student A) and first experiments on the Pd/SiC interface (student B) as well as the Cs/SiC interface (student C) will be conducted.

Funding Profile:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total (k$)</td>
<td>181</td>
<td>197</td>
<td>205</td>
</tr>
</tbody>
</table>

Background and Rationales:

Over the past decades, the study of interfaces in view of their chemical and electronic structure has been at the center of attention for many material science studies of layered systems. In most cases, the observed interface properties differed strongly from those, which were expected based on the bulk and surface properties of the two junction partners alone. Most notably, interdiffusion and secondary (chemical) phase formation at interfaces are a common find, and can hardly be predicted due to the oversimplicity of most existing models.

In the field of coated nuclear fuel particles, interface reactions between selected metals and SiC have been the subject of many studies over the last three decades (see, e.g., Refs. 1 and 2 and references therein), because it was realized early on that corrosion of the SiC layer in coated TRISO fuel particles, e.g., by the metal fission product Pd, will limit the fuel life time at higher temperatures. Furthermore, it was found that silver and cesium diffuse through intact SiC [3,4]. Since then, great efforts have been undertaken to understand and quantify the internal fission product release [5], the diffusion coefficient [6], and, in particular, the impact of elevated temperatures [6-8]. In the case of Pd, the Pd-Si-C phase diagram was investigated, and the interdiffusion at the Pd/SiC-interface was interpreted based on solid-state equilibria arguments [9]. To avoid corrosion, additional SiC-containing trap layers inside the SiC layer of the TRISO-coating were successfully tested [10]. Alternatively, research has focused on replacing SiC by a more corrosion-resistant material, in particular ZrC [7, 11], which shows good retention capabilities for Cs [12] and no interaction with Pd [13]. Nevertheless, the development of fuel particles containing ZrC layers is still in an early stage, and hence the present proposal aims at an analysis of the SiC and the carbon layers only, while ZrC may be addressed in a future proposal. Compared to the large number on publications about fission product / SiC interfaces in TRISO particles, much less publications have been published on the interaction and interface formation between fission products and the carbon layers, even though, as reported in [14], both precipitation and intercalation of a variety of metal fission products can occur.

Despite the large number of publications in the field, significant research efforts have still to be undertaken in order to understand the interaction of fission products with the TRISO coating materials. For this reason, such studies have been given "HIGHEST" priority in the latest Research Topic List (Nov. 7, 2003) of the UNLV Transmutation Research Program.

Using the experimental evidence discussed above as a starting point, we propose to utilize surface- and interface-sensitive spectroscopic methods to elucidate the chemical nature of the interfaces between metal fission products (Pd, Ag, Cs) and TRISO coating layers. These studies will add a new point of view to the existing discussion,
because they give a direct insight into the electronic structure and hence into the nature of the chemical bonding. In contrast, the existing studies use a multitude of bulk-sensitive methods, such as electron probe microscopy, Gamma-ray spectrometry, X-ray microradiography, optical microscopy, X-ray diffraction, energy-dispersive X-ray analysis, ceramography, and fractional release measurements, all of which are (at best) only indirectly sensitive to the chemical state and hence to the local chemical environment of a selected atomic species (e.g., the metal fission product). In contrast, the here-proposed combination of photoelectron spectroscopy and soft X-ray emission spectroscopy (the latter at a third-generation synchrotron light source) has in the recent past been shown to present an excellent opportunity to study the chemical environment of selected atomic species, both at surfaces and (buried) interfaces [a-e].

Furthermore, the use of these techniques on realistic microstructures will enrich the TRISO community by establishing the connection to a multitude of studies in surface science which involve material combinations relevant for the present case. In surface science, many studies can be found which deal with the combination of a metal adsorbate (Ag, Pd, Cs) and SiC or graphite as a substrate. Studies on graphite are motivated by the possibility to form metal nanoparticles or clusters on the graphite surface [15-17], due to its inherent chemical inertness. Also, a variety of applications are associated with metal intercalation systems [18,19]. The oxidation of the graphite surface can be promoted by a co-adsorption of Cs atoms, such that controlled thin layers of a protective oxide can be formed [20,21]. Metal adsorbates on the SiC substrate class are frequently used for applications in hydrogen sensor technology [22], high temperature electronics (putting stringent demands on ohmic contacts and/or Schottky-barrier formation [22-26]), and catalysis [27-29]. Despite the large number of publications for these applications, however, information on the chemical bonding and the long-range interdiffusion (in particular after high-temperature annealing) is still very limited in this community (with some notable exceptions, see Refs. 30-35). This is in part due to the lack of suitable spectroscopic techniques to study the electronic and chemical structure of buried interfaces (a shortcoming which can now be overcome by using soft X-ray emission spectroscopy [b], as mentioned above). Furthermore, the chemical (long-term) stability, which is of central importance in the case of TRISO particles, is presently not considered to be of large relevance in the above-mentioned research fields.

Research Objectives and Goals:
The objective of this project is to investigate the interface formation between Ag, Pd, and Cs and the coating materials employed in TRISO particles (in particular silicon carbide and pyrocarbon). By using a variety of spectroscopic techniques, as described below in the section "Research Approach", we intend to elucidate the chemical and electronic interface structure, study short- and long-range interdiffusion processes, the chemical state of the metal layer and of metal fission products in realistic microstructures, the presence of secondary chemical interface species, and the overall chemical stability of TRISO particles. Since both the interface formation as well as the spectroscopic analysis will be performed under strictly controlled conditions in ultra-high vacuum, it is possible to test schemes for a deliberate interface "tailoring", e.g., by plasma-modification of substrate surfaces prior to the interface formation. Also, interfaces involving stressed coating layers will be analyzed. Thus, in addition to obtaining a detailed picture of the chemical and electronic interface properties, it is the goal to derive schemes for an optimized interface formation for long-term stable TRISO particles, and to give helpful indications for optimized irradiation testing and post-irradiation-examination at ORNL.

Technical Impact:
The proposed work is expected to shed light on the chemical stability of TRISO particles with respect to diffusion of metal fission products (Ag, Pd, Cs) through the coating material layers and interfaces. In particular the chemical state of the fission products will be assessed, and further information on fuel failure mechanisms will be collected. Based on a detailed analysis of the interface properties, we intend to propose surface and interface modification treatments
for an enhanced stability of TRISO particles, and simulation experiments are expected to give indications for optimized irradiation testing and post-irradiation examinations within the AFCI effort at ORNL.

**Research Approach:**
Preparation, manipulation, and spectroscopic analysis of metal/coating-material interfaces will be performed in a controlled ultra-high vacuum (UHV) environment to reveal the chemical and structural properties of the interface, in particular in view of interdiffusion and secondary phase formation at the interface (including the chemical state of the metal fission product). In the first phase of the project, experiments will be performed at UNLV in the UHV chamber system to be relocated from the University of Würzburg, Germany. Since the relocation will be conducted after completion of the lab renovation at UNLV (October 2004), the *very first* experiments will be performed at the University of Würzburg. In the second phase, the laboratory experiments will be complemented by investigations at the Advanced Light Source, Berkeley, using third-generation synchrotron radiation, as well as by other experimental methods available within the TRP program (in particular Transmission Electron Microscopy of cross sectional samples).

Thin metal films will be prepared by electron beam evaporation (Pd and Ag) or by evaporation from commercial dispenser sources (Cs; SAES Getters, Italy). The coating materials (SiC, pyrolytic carbon) will be taken from the TRISO coating process as well as from commercial suppliers of single crystal reference materials (SiC single crystals, highly-oriented pyrolytic graphite - HOPG) and will serve as substrates for the metal deposition. Whenever possible, CVD coating layers with realistic microstructures will be used, and ex-situ stress treatments of the coating layers will be included as an important variation parameter. In the UHV system, the surfaces of the coating material substrates can be modified in-situ in several different ways, in particular by ion beam etching with noble gas ions (Ar, Ne, He) and by plasma etching in an electron-cyclotron-resonance (ECR) etching chamber, which is part of the UHV chamber system. In the latter case, a large variety of gases can be used for the ECR etching, including all noble as well as several hydrocarbon gases, such that the impact of other carbon-containing interface layers can be studied. The ECR etching process will be monitored in-situ by optical ellipsometry, while the electron beam evaporation of Ag and Pd is monitored by source flux monitors as well as a quartz microbalance. In addition to the surface cleaning, the samples under study will be annealed in UHV, both before and after the interface formation (up to approx. 900 °C – higher temperatures will require ex-situ annealing, e.g., by using a SiC-Ag-SiC sandwich structure). The study of the chemical properties and the stoichiometry will give direct insight into the diffusion behavior and the interface properties as a function of annealing temperature and time.

When using single crystal substrates as model systems for the coating materials, low energy electron diffraction (LEED) will be used to study the geometric structure of the surfaces and interfaces. LEED gives detailed information about the local *structural* environment of the metal atoms at the interface. However, LEED is not applicable to the interface formation on realistic CVD coating layers due to the lack of macroscopic order, and hence the use of single crystal references will give valuable structural information, complementary to the chemical information gained from the metal/coating-layer interfaces. Furthermore, studies on single crystals also allow to relate the results obtained here to surface science studies of Ag, Pd, or Cs on SiC or HOPG already published in the literature (see discussion above).

As spectroscopic methods, we will primarily use surface-sensitive photoelectron spectroscopy, both with X-rays (XPS) as well as with UV photons (UPS), and soft X-ray emission spectroscopy (XES). XPS gives direct information about the chemical state of a particular atomic species, and UPS gives insight into the electronic valence structure and hence into the electronic states directly involved in the chemical bond. The combination of XPS and UPS has, in the past, proven extremely powerful for the study of a large number of interfaces (see, e.g., [c,d]). Within the UHV-apparatus at UNLV, these techniques will be complemented by Auger electron spectroscopy (AES).
with a lateral resolution of down to 200 nm. In the second phase of the project, we will perform XES studies at the
Advanced Light Source (Lawrence Berkeley National Lab) to elucidate the chemical interface properties in a more
bulk-oriented approach (e.g., to study buried interfaces). In XES, the use of soft X-ray spectrometers with high
spectral resolution gives insight in the chemical structure of the valence bonds in a complementary way to
photoelectron spectroscopy \[e\]. Furthermore, we plan to study cross-sectional samples of the in-situ prepared
interfaces by spatially resolving methods, in particular transmission electron microscopy (at UNLV), soft X-ray
spectromicroscopy, and fluorescence microprobe analysis (both at the Advanced Light Source).

**Expected Technical Results:**

- Detailed information about the interface formation between selected metals (Ag, Pd, and Cs) and TRISO
coating materials (in particular in view of intermixing and diffusion, chemical bonding, electronic structure,
and chemical state of the fission products)
- Knowledge about the impact of surface modification schemes on the interface properties, in particular
regarding stressed coating layers
- Detailed indications for optimized irradiation testing and post-irradiation examinations within the AFCI
effort at ORNL
- Detailed preparation recipes for an optimized formation of long-term stable interfaces

**Capabilities at the University and ORNL**

Most of the experiments will be conducted in a four-chamber UHV apparatus (as described in the "Research
Approach" section) to be relocated from the University of Würzburg, Germany, to UNLV in October 2004. First
experiments will be performed during the summer of 2004 at the University of Würzburg. In the second project
phase, experiments will also be conducted at existing endstations at the Advanced Light Source, Lawrence Berkeley
National Lab, in close collaboration with the respective Beamline scientists.

Within the AFCI effort, ORNL is performing coating studies of TRISO particles, and if directed and supported by
DOE, can supply well-characterized non-radioactive TRISO particles for study. ORNL maintains an extensive High
Temperature Materials Laboratory for the characterization and study of novel materials, as well as a state-of-the-art
Post-Irradiation-Examination Facility for TRISO particles.

The PI has extensive experience in the spectroscopic analysis of surfaces and interfaces, the in-situ preparation of
heterointerfaces, the construction, commissioning, and use of UHV-equipment, as well as the mentoring of diploma
and PhD students.

**Equipment Requested for TRP User Labs:**

During the second and third year of the project, cross sectional samples shall be investigated by Transmission
Electron Microscopy at UNLV (as well as by spectroscopic methods at the ALS in Berkeley).

**Project Timeline:**

**Timeline Narrative:**

The proposed research is planned to cover three years, starting in June 2004. After an initial experimental summer
research period (PI and graduate student A, summer of 2004) at the University of Würzburg, devoted to the study of
in-situ prepared Ag/SiC interfaces, the 4-chamber UHV instrument required for this project will be relocated to
UNLV (Oct. 2004). After relocation, approximately 6 months are scheduled for reassembly, installation (periphery),
commissioning, and removal of potential transit damage (until May 2005). In this period, all three graduate students
(as well as the PI) will be actively involved to keep the experimental downtime of the instrument at a minimum.
Once the equipment is back in operation, the Ag/SiC work will be continued and first work on Pd/SiC and Cs/SiC...
interfaces will be started. The data taking for the latter two projects is expected to finish by June 2006, after which the focus will be shifted towards interfaces involving pyrolytic carbon as well as graphite ("X/Carbon").

Due to the permanent accessibility of the instrument, the milestone plan given below serves as a first estimate. The short-term allotment of experimental time for the different sub-projects and the three graduate students strongly depends on the experimental progress in the sub-projects. Experimental runs at the Advanced Light Source in Berkeley are not listed in the milestone plan, because they are scheduled in a separate process involving the respective beamline scientists. Also, TEM experiments in the second and third project are not yet listed, because they will be scheduled after discussion with the responsible scientists at UNLV.

Expected Technical Results:
- Detailed information about the interface formation between selected metals (Ag, Pd, and Cs) and TRISO coating materials (in particular in view of intermixing and diffusion, chemical bonding, electronic structure, and chemical state of the fission products)
- Knowledge about the impact of surface modification schemes on the interface properties, in particular regarding stressed coating layers
- Detailed indications for optimized irradiation testing and post-irradiation examinations within the AFCI effort at ORNL
- Detailed preparation recipes for an optimized formation of long-term stable interfaces

Milestones:
- Completion of summer research on Ag/SiC at the University of Würzburg: Sept. 2004
- Completion of relocation of 4-chamber UHV system: Nov. 2004
- Completion of reassembly, installation, and transit damage removal: May 2005
- Completion of Ag/SiC experimental campaign: Nov. 2005
- Completion of Pd/SiC and Cs/SiC experimental campaign: Jun. 2006
- Completion of experimental campaigns on pyrocarbon and graphite: Jan. 2007
- Completion of data analysis: May 2007

Deliverables:
- **Collaboration with DOE project:** Monthly communications (by phone or in person) with National Project collaborator to update on progress, discuss problems, and allow for refocusing if necessary to address shifts in direction by the National Project.
• **Progress Reports (P):** Reports indicating progress will be provided every month, quarter, and year (to support DOE AFCI reports).
• **Bi-Annual Reports (B):** Written reports detailing experiments performed, data collected, and results to date to support Semi-Annual Review presentations and reports.
• **Final Report (F):** Written report detailing experiments performed, data collected, results, and conclusions, to be submitted at the end of the project.

References:

Selected related publications of the PI:
February 10, 2004

Tony Hechanova  
UNLV - Harry Reid Center  
4505 Maryland Parkway  
Box 454009  
Las Vegas, Nevada 89154-4009

Subject: Support Letter for Heske TRP Proposal

Dear Tony,

I have reviewed the TRP proposal by Clemens Heske, "Interaction between metal fission products and TRISO coating materials: A study of chemical bonding and interdiffusion". I believe this work supports the Advanced Fuel Cycle Initiative (AFCI) goals for TRISO fuel because fission product transport and coating layer failure mechanisms are key issues. This work can help the AFCI in two ways:

a) by developing a better understanding of fission product transport and chemical interactions in coating layers, and

b) by simulating what is expected in AFCI irradiation testing, in order to optimize irradiation testing and post-irradiation examination.

Please feel free to contact me if I can be of any further assistance.

Sincerely,

David F. Williams, Ph.D.  
ORNL Coated Particles PI - Advanced Fuel Cycle Initiative  
Nuclear Science and Technology Division