

Task 17

Interaction between Metal Fission Products and TRISO Coating Materials

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BACKGROUND

This project focuses on the chemical bonding and interface formation of metal fission products with the coating materials used in tri-isotropic (TRISO) fuel particles for gas-cooled reactors. By combining surface- and bulk-sensitive spectroscopic and microscopic methods, intermediate chemical phases at the interface, intermixing/diffusion behavior, and the electronic interface structure for different coating materials and metals are examined.

In detail, the project studies the interface formation of Pd, Cs, and Ag with SiC and pyrolytic carbon. Using SiC single crystals and highly-ordered pyrolytic carbon (HOPG) as substrates, interfaces are prepared under controlled conditions in an ultra-high vacuum environment and are studied with a combination of experimental methods, including Photoelectron Spectroscopy, Auger Electron Spectroscopy, X-Ray Emission Spectroscopy, and X-Ray Absorption Spectroscopy. Furthermore, microscopic techniques (in particular Atomic Force Microscopy) are being employed.

RESEARCH OBJECTIVES AND METHODS

By combining results for the electronic and chemical structure of the fission product/TRISO layer interfaces, the research results give information about failure mechanisms of TRISO particles and fission product transport.

Furthermore, they can be used to derive strategies to tailor the interface properties for an optimization of TRISO particles in terms of, e.g., chemical and long-term stability.

The experiments use two different experimental set-ups. First, a multi-chamber ultra-high vacuum system at UNLV houses the majority of surface-sensitive methods. Second, the soft X-ray fluorescence (SXF) endstation at Beamline 8.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory is used to perform X-ray absorption and emission spectroscopy. The apparatus at UNLV consists of two different surface spectroscopy chambers, a preparation chamber, and an ultra-high vacuum (UHV) scanning probe microscope. Samples can be introduced into the machine through a glove box with integrated load-lock and then transferred to each of the chambers via a distribution chamber. The analysis chambers are each

equipped with a state-of-the-art electron analyzer, an X-ray source, an ultraviolet (UV) source, and an inverse photoemission setup consisting of a low-energy high-flux electron gun and a UV detector. The preparation chamber is used for cleaning samples with an ion source and for the deposition of metal films with an electron-beam evaporator (Pd, Ag) or a dispenser element evaporator (Cs).

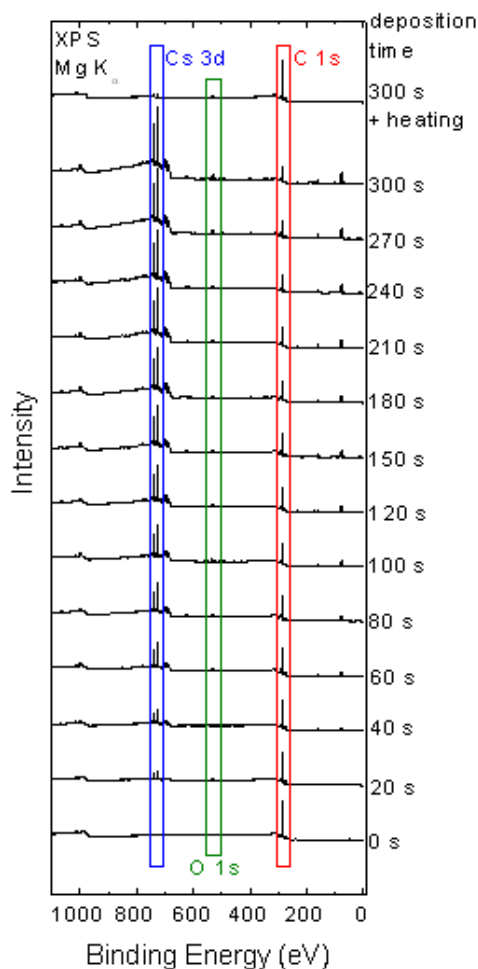
RESEARCH ACCOMPLISHMENTS

In the past year, emphasis was placed on a detailed analysis and description of the Cs/SiC and Cs/HOPG interface formation processes. Here, some of the results for Cs/HOPG will be briefly described.

A series with Cs films of different thickness on HOPG were prepared. UV photoemission (UPS), x-ray photoemission (XPS), and in-vacuum atomic force microscopy (AFM) experiments were performed for each Cs film thickness. HOPG substrates were prepared by cleaving under nitrogen in the glove box directly connected to the surface analysis system at UNLV and then directly introduced into the UHV apparatus without any air exposure.

In the figure to the left, the XPS survey spectra for different Cs evaporation times (and hence different Cs film thicknesses) are shown. The cleaving of the sample under nitrogen clearly results in a very clean and nearly adsorbate-free surface, as can be seen from the weak O 1s line in the bottom-most spectrum. After Cs evaporation, all expected Cs lines can be found in the spectra. The intensity of the lines, which can be related to the film thickness, increases for increasing deposition time, as expected. In parallel, the lines of the HOPG substrate (i.e., the C 1s photoemission line and the C KVV Auger line) decrease in intensity due to the attenuation by the covering Cs layer.

Focus was also placed on understanding the HOPG surface morphology changes when annealing the Cs/HOPG interface at 600 °C. A series of stepwise Cs depositions was performed on a cleaved HOPG surface at room temperature under ultra-high vacuum conditions and monitored with photoelectron spectroscopy. After 300 seconds of Cs deposition, the surface was imaged by UHV-AFM. The AFM image clearly shows Cs atoms forming clusters



XPS survey spectra of an HOPG substrate, as well as after stepwise deposition of Cs and subsequent heating under inert conditions.

on the HOPG surface, which is corroborated by a detailed intensity analysis of X-ray photoelectron spectroscopy (XPS) data. Next, the sample was removed from UHV, annealed in a furnace in air (600 °C) for 60 minutes, and reintroduced into UHV. The center image (below figure) shows the AFM image after annealing. As again corroborated by the XPS data, most of the Cs atoms/clusters are removed from the surface. Furthermore, a significant formation of craters and voids were found that can act as diffusion pathways for various metallic species (e.g., for fission products diffusing through pyrolytic carbon layers in TRISO fuel). To verify whether the crater formation is induced by the presence of Cs clusters on the surface, a second HOPG sample was prepared that was cleaved, characterized, and annealed in the exact same fashion as the first sample (but not exposed to Cs). The right image (see figure below) shows a corresponding AFM image of the HOPG surface after annealing. Similar cracks are observed as in the Cs/HOPG samples, but no evidence of crater formation could be found (in any of the AFM images). This supports the conclusions (a) that Cs grows in a cluster-like fashion on HOPG (at room temperature), and (b) that the presence of Cs clusters on the surface of pyrolytic graphite can lead to the formation of crater- and crack-like diffusion pathways during annealing at 600 °C, while the annealing of pyrolytic graphite only leads to the formation of cracks, but not craters.

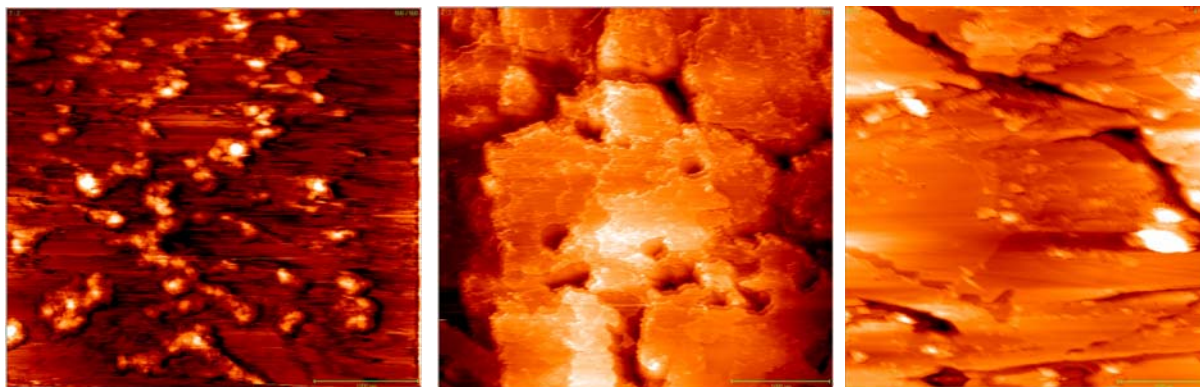
FUTURE WORK

The experiments on Cs/SiC and Cs/HOPG will be completed, in particular by varying the substrate temperature during deposition (up to approximately 1200 °C). These experiments will allow the study of both the temperature dependence as well as the influence of air (in particular oxygen) on the high-temperature behavior and the crater- and crack-formation results of the present study. In

ACADEMIC YEAR HIGHLIGHTS

- ◆ Participation of graduate and undergraduate students in experimental campaigns at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA (September 2007, January 2008, May 2008).
- ◆ Sharath Sudarshanam passed his M.S. prospectus presentation meeting in March 2008.
- ◆ C. Heske, “Using XES and RIXS to investigate the chemical and electronic structure of materials for energy conversion,” RIXS 08 Workshop, Uppsala, Sweden, June 13-14, 2008.
- ◆ C. Heske, “Soft X-rays and the electronic structure of buried things – interfaces, liquids, and below dirty surfaces”, Materials Science Institute, University of Oregon, Eugene, February 26, 2008.
- ◆ C. Heske, “Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft X-ray spectroscopy,” Chemical Engineering Department, University of California at Santa Barbara, October 25, 2007.
- ◆ C. Heske, “Surface and Interface Science on Devices for Energy Conversion,” X-ray and Neutron Scattering Contractor’s Meeting, Division of Materials Sciences and Engineering (DMS&E), DOE Office of Basic Energy Sciences (BES), Warrenton, VA, October 18, 2007.
- ◆ C. Heske, “Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft X-ray spectroscopy,” Cornell University, Materials Science and Engineering Department Seminar, October 11, 2007.

addition, the experiments will simulate the “natural” high temperature environment present in the nuclear reactor. Furthermore, it is planned to initiate first interface studies involving ZrC layers.



Left: AFM picture of a highly ordered pyrolytic graphite (HOPG) substrate after deposition of Cs for 300 seconds. Center: AFM picture Cs/HOPG substrate after annealing at 600 °C for 60 minutes in a furnace. Right: AFM picture of HOPG without cesium deposition, annealed at 600 °C for 60 minutes in a furnace. All image scales are 4 x 4 μm².

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