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Grand challenges in nuclear materials new insights into nuclear materials using ion irradiation, CryoEM, and *in-situ* liquid cell microscopy

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Any material used in a nuclear reactor facility must go through an extensive review and qualification, involving many tests and analyses. In late 2019, Alloy 617 was added to the American Society of Mechanical Engineers (ASME) code, representing the first high-temperature material cleared for commercial nuclear reactor use in the United States. since the 1990s. Without new materials, the promise of advanced fission and fusion reactor designs will not be realized (Allen et al., 2010). Similarly, the need to improve current designs and reactor components to extend reactor lifetimes may require deeper understanding of the behavior of nuclear materials under extreme conditions (Was et al., 2019). Advanced reactor concepts will require the materials and components to be resistant to 1) higher temperatures than experienced with current light water reactors, 2) corrosion with liquid salts and liquid metals, and 3) high radiation fields (neutron, ion, and gamma/beta radiation fields). Materials that need to be licensed for use in the nuclear fuel cycle from reactor operation to long-term geologic disposal undergo unparalleled scrutiny. How can this process be sped up without jeopardizing future operational safety? Modern computational predictive tools could help to accelerate development and qualification of advanced materials (Devanathan et al., 2010). However, this may not necessarily negate the requirement for extensive long-term testing of material properties to satisfy regulatory requirements. In this article, as well as discussing the role of ion irradiation studies for nuclear materials research, the potential opportunities for *in-situ* liquid/gas cell electron microscopy (LC-EM) and Cryo-Electron Microscopy (CryoEM) will be discussed.

Ion irradiation in the transmission electron microscope (TEM) has been an important method for testing radiation damage in materials for nuclear applications, including nuclear waste forms and nuclear reactor components. Two other microscopy-based techniques, *in-situ* liquid/gas cell electron microscopy (LC-EM) and Cryo-Electron Microscopy (CryoEM) are currently being used in several areas in materials research, including, catalysis research, battery development, and geochemistry.

Nuclear materials, whether in a nuclear reactor or disposed thousands of meters underground in a geologic repository, are subject to internal atomic displacement damage and the interaction of radiolytic species at the material's interface. Developing the tools to

experiment in this area can be a major challenge. Working with fully radioactive materials can also be expensive and hazardous. The radiolytic field can induce very complex chemical reactions in contacting gases or liquids (Kaddissy et al., 2017; Reiff and LaVerne, 2017; Parker-Quaife et al., 2020). However, it is necessary to understand these effects to develop new nuclear fuels, (Aitkaliyeva et al., 2015; Parrish and Aitkaliyeva, 2018), understand the durability fuel cladding, (Une et al., 1995; Tanaka et al., 2006; Mishra et al., 2012), and provide a scientific basis for the long-term disposal of radioactive waste forms (Ewing et al., 2000; Tribet et al., 2021), and spent nuclear fuels (SNF) (Ray et al., 1997; Jégou et al., 2010; Amme et al., 2012; Teague et al., 2014; Liu et al., 2016; Rest et al., 2019).

Tests on nuclear fuels, advanced materials, and cladding for current light water reactors (LWR) can be either performed in high flux Research Reactors (RR) or at Nuclear Power Plants (NPP). However, the materials from such tests do require dedicated shielded hot cells for Post-Irradiation Examination (PIE) that can accept either full-length fuel rods or fuel assemblies, and can perform the needed mechanical, thermal, and microstructural characterizations. Government regulations connected to the final required disposal of these materials after testing may be an additional barrier to performing this type of analysis.

Time on dedicated high flux RRs is also limited, as is the ability to work with irradiated materials in shielded hot cells. Therefore, ion beam facilities continue to be essential for studying radiation damage in new materials (Was et al., 2014; Zinkle and Snead, 2018; Wang et al., 2019). Alternative approaches, however, do exist that enable researchers to work with RR irradiated materials. Schwantes and co-workers (Schwantes et al., 2019) have developed a method for PIE of irradiated materials that may allow a wider group of researchers to study new nuclear materials. In brief, they use a Scanning Electron Microscope (SEM)-Focused Ion Beam (FIB) system to extract representative micrometer-sized samples from the bulk material and then irradiate them in a RR. Because these samples are miniscule, they are able to perform PIE safely and without the need for shielded hot cell facilities. Following this procedure, they documented the formation of fission product noble metal particles in UO_2.

Ion irradiation creates damage over short time frames, enabling *in-situ* analysis of the effects and careful control of experiments (Lewis et al., 1979; Wang et al., 1999; Ewing et al., 2000; Jiang et al., 2017; Sassi et al., 2019; Lang et al., 2022). Both *ex-situ* and *in-situ* facilities are available for performing these types of experiments (Wirth, 2007; Li et al., 2015; Taylor et al., 2017b); although, there is a pressing need for these to be improved and equipped with more modern instrumentation. TEM and Scanning TEM (STEM) are ideal tools to image and describe the nature of defect formation and dislocation loop growth, bubble evolution, grain nucleation and growth, as well as phase transformations and segregation. Consequently, *in-situ* ion irradiation has been used extensively to evaluate potential materials for nuclear applications. For example, *in situ* TEM studies have shown that dislocation loops that form during ion irradiation of high purity Fe are more mobile than those formed in Fe-8%Cr alloys. *In-situ* TEM imaging of oxide-dispersion strengthened (ODS) ferritic alloys has been used to characterize damage during high levels of ion irradiation (200dpa) at high temperatures (500°C) (Kirk et al., 2009). The grain morphologies, dislocation networks, and voids that were qualitatively imaged in the TEM, were comparable to similar neutron irradiation experiments that were run at the now shutdown Fast Flux Test Facility (FFTF) on ODS alloys (Gelles, 1996). Indeed, the unique capabilities of TEM can be used to determine the exact nature of any radiation induced defects that affect the macroscopic properties of materials. For instance, weak-beam TEM, where the thin-foil is tilted away from the Bragg position, and image contrast is low, radiation induced defects may create a strain field that bend the reflecting planes back to the Bragg condition, resulting in images with localized high contrast at the defect. Hence, very minor defects can be characterized. TEM thin-foil specimens are not necessarily artifact-free and specimens which are now routinely prepared with SEM-FIB, can possess surface defects and amorphous zones, making the visibility of some characteristic radiation effects features, such as He bubbles, difficult to reveal. Cryo-FIB methods may improve the preservation of features but traditional electropolishing remains a useful method for preparing irradiated steels.

In the last two decades, TEM/STEM has undergone a revolution in resolution that began with the implementation of the aberration corrector, which improved the spatial resolution to below 50 p.m. When combined with direct-detection electron-counting (DDEC) cameras and mono-chromated electron gun sources, aberration-corrected (AC) STEM/TEM with atomic resolution Electron Energy-Loss Spectroscopy (EELS) and X-ray Energy Dispersive Spectroscopy (EDS) has enabled probing amorphization and chemical state changes at unprecedented resolution, sensitivity, and precision. These capabilities are now being used in nuclear materials research (Clark et al., 2020; Popel et al., 2020; Müller et al., 2021). Here we highlight a few examples: AC-STEM-EELS has been used to characterize the ion irradiated $LaMnO_3/SrTiO_3$ interface and the oxidation of UO_2 at atomic resolution to describe subtle changes in structure over nanometer-sized regions (Spurgeon et al., 2019; Matthews et al., 2021). The process of amorphization in nuclear materials considered for the immobilization of plutonium, such as zirconolite ($CaZrTi_2O_7$) and zircon ($ZrSiO_4$), has been monitored through *in-situ* ion irradiation in the electron microscope (Weber et al., 1994; Wang et al., 2000). A better understanding of these processes will lead to improved performance assessment models of geologic repositories. Experiments with ion beams can induced high dpa within a few minutes to hours and the pathway to amorphization or phase

modification can be clearly defined using TEM (Ewing et al., 2000; Hattar et al., 2014; Lu et al., 2014; Li et al., 2017; Sassi et al., 2019), secondary ion mass spectrometry (SIMS) (Jiang et al., 2018), atom probe tomography (APT) (Marquis et al., 2011), or x-ray absorption spectroscopy (XAS) (Cureton et al., 2019). However, as the rate of damage may exceed any self-annealing processes, ion irradiated materials may go amorphous at much lower dpa than natural radioactive mineral counterparts. Although these experimental artifacts need to be considered, ion irradiation can be effective to compare potential radioactive waste forms for immobilization and evaluate materials for their potential response in a nuclear reactor.

By using ion irradiated materials, it is also possible to study the synergistic effects of radiation damage and high temperature reactions. (Taylor et al., 2017a) have developed methods to study the complex microstructural effects due to simultaneous gas accumulation and displacement cascade damage, which occurs in NPP components, such as Zircaloy cladding. The instrumentation includes the ability to heat and irradiate the specimen with multiple ion beam systems resulting in damage from both heavy ions and implantation of hydrogen ions. The formation of hydrides can then be observed with electron energy-loss spectroscopy.

A current grand challenge in materials science, is the role of the interface. This is true also of nuclear materials science. The interface may be defined as the region between two different solid phases but also the region between the solid and any contacting solution or gas. *In-situ* methods such as liquid cell (LC), gas flow cells, and CryoEM that are effective tools for investigating the solid-solution interface, could also be used to study materials under high temperature conditions relevant to NPPs (de Jonge and Ross, 2011; De Yoreo and Sommerdijk, 2016). When steam at high temperatures reacts with Zircaloy cladding and B_4C absorber materials, an exothermic reaction results with the generation of H_2 gas. Under severe accident scenarios, high temperature water may also react with UO_2 nuclear fuels, resulting in rapid oxidation to UO_{2+x}, and release of fission products possibly into the environment. These interfacial reactions occurred following the magnitude 9.0 Tohoku-oki earthquake and tsunami in March 2011, and subsequent disaster at the Fukushima-Daiichi NPPs, in Japan, (Burns et al., 2012; Kurata et al., 2018). How reactor materials and components react at high temperature can be addressed with *in-situ* EM and CryoEM and could provide critical information on the operational safety of these materials. When combined ion irradiation, *in-situ* methods could provide further insight into potential deleterious reactions.

Both solid-solid, solid-gas, and solid-liquid reactions are important interfacial processes that may occur in materials for nuclear applications. Studying these systems with *in-situ* heating, *in-situ* LC and gas-flow methods can provide important insights into materials behavior. Khanolkar et al. (2021) used *in situ* TEM heating to follow the evolution of a series of uranium-zirconium phases, including U20Zr, with increasing temperature. The initial lamellar microstructure consisting of rod-like α-U precipitates embedded in a hexagonal δ-U-Zr matrix underwent spinodal decomposition at 600°C to a body centered cubic form. High temperature gas phase TEM holders are being used to study the reaction of high-entropy alloys with hydrogen (Song et al., 2021). High-entropy alloys are being considered in advanced reactor designs owing to their potential radiation resistance. Song et al. (2021) used an *in-situ* gas-flow TEM holder to view the formation of a porous structure in a high-entropy alloy as hydrogen penetrated the material. Conroy et al. (2017) used LC TEM to study the t dissolution of boehmite in water, as influenced by the electron beam, a phase found in alkaline nuclear waste sludge from the high temperature reaction of Al in solution. The dissolution of these phases is crucial for effective waste processing (Peterson et al., 2018).

The dose that can be induced by the electron beam can be exceptionally high, easily exceeding that experienced in a reactor environment (Abellan et al., 2014; Moser et al., 2018). Schneider and co-workers have reported doses in the range of 10^7 Gy/s within an area with a radius of 1 μm in an *in-situ* liquid cell (Schneider et al., 2014). In contrast, reactor coolant doses range from 10^{-17} to 10^{-13} Gy/h•cm^2 which calls into question the use of *in-situ* liquid cell observations on any system, including those that would normally be exposed to radiolytic fields. Consequently, observations made with *in-situ* LC electron microscopy should be confirmed with CryoEM and other techniques. Furthermore, materials such as hydrated phases that often form on the surfaces of nuclear materials exposed to high temperature steam (Kubatko et al., 2003; Bolling et al., 2019), may also be sensitive to the electron beam. Knock-on damage in materials depends on the beam energy and the displacement energy of atoms in the structure but radiolytic effects can result in rapid decomposition of materials containing structural or interlayer/interstitial water if the beam energy is sufficient to induce radiolytic decomposition of water (Egerton, 2012). Many of the issues associated with radiolytic beam damage can be reduced (but not eliminated) by studying systems at cryogenic temperatures, in combination with higher performance DDEC cameras that enable low dose techniques.

The 2017 Nobel Prize in Chemistry was awarded to Dubochet, Frank, and Henderson for contributions that have enabled the imaging of biological macromolecules down to the atomic level (Callaway, 2015). CryoEM involves the rapid freezing (or vitrification) of solutions in liquid ethane and the imaging of thousands of identical particles, which can then be used to develop a structure of the specific macromolecular crystal. A significant technical advancement that has enabled CryoEM to become a viable competitor to x-ray methods, has been the development of the DDEC camera. The DDEC camera has vastly improved signal capture relative to traditional digital cameras, enabling the observation of beam sensitive materials.

New challenges include increasing the speed of the vitrification process to capture chemical processes at earlier stages of reaction and making sample preparation more reliable, routine, and reproducible.

As well as capturing crystal nucleation phenomena, CryoEM may preserve hydrated phases that often form in reactor steam environments or enable observation of beam sensitive materials, such as uranyl oxyhydrates, zeolites, and metal-oxygen framework (MOF) structures. There is continued interest in the sorption or incorporation of radionuclides into secondary phases such as clays, iron oxides (Ilton et al., 2012), zeolites (Maddrell et al., 2015), and MOF structures. MOFs have been engineered to incorporate various radionuclides including americium and plutonium (Ridenour et al., 2019; Surbella et al., 2021). Current vitrification tools typically operate at ambient conditions and use liquid ethane to freeze the specimen to liquid nitrogen temperatures. To study faster chemical processes or reactions, the speed of freezing process may need to be improved. Modern CryoEM techniques can utilize all the normal TEM modes, including scanning TEM (STEM), diffraction, and analytical spectroscopy.

CryoEM provides snapshots in time during a reaction process such as the precipitation of plutonium oxalates, a separation step used in the production of plutonium metal (Meadows et al., 2020). CryoEM can be used to study the effect of the interface on surface reactions. Future advancements that enable atomic resolution of beam sensitive materials, and single atom detection, will be accomplished with a combination of CryoEM and imaging with the more sensitive direct electron detectors, enabling the imaging of sorption process of radioactive waste species in MOF or zeolite structures, for instance. The paragenesis of uranium oxide corrosion is fundamental to understanding the long-term behavior of disposed spent nuclear fuel (Finch and Ewing, 1992; Ewing, 2015), including transport of uranium and plutonium colloids (Novikov et al., 2006; Bots et al., 2014; Zhao et al., 2016). Our understanding of the complexity of mineral precipitation has vastly improved through the application of CryoEM and *in-situ* liquid cell EM, firmly establishing the importance of non-classical crystal growth mechanisms such as particle attachment and the realization that crystallization can occur over multiple complex pathways. However, it is unclear whether such processes also occur during the corrosion of nuclear waste glass and uranyl oxyhydrate precipitation. Recent work by Whittaker and co-workers has shown that the electrical double layer (EDL) can now be analyzed with CryoEM and Cryo-Electron Tomography (Whittaker et al., 2022). Through careful computational control of the imaging conditions and image reconstruction, the nature of the EDL was revealed. Direct analysis of the EDL in highly alkaline radioactive sludge, could lead to improved understanding of the rheology of the waste. If CryoEM can be used to measure the interaction of radiocolloids, it could provide inputs to atomistic models for predicting the interionic and inter-colloidal forces under specific conditions. As colloids sorb to a surface or diffuse along a pathway, CryoEM could describe the dynamics of these interfaces, improving models for radionuclide transport for nuclear waste repositories.

These new tools from the biological and material sciences, CryoEM and LC TEM, have made significant contributions to our understanding nucleation and growth phenomena, dissolution, and oxidation processes. These processes are important to many nuclear materials and understanding them improves our ability to predict materials properties. Using these new tools with irradiated and radioactive materials could provide new insights into materials properties and enable us to speed up the development of new materials for advanced nuclear reactors as well as improving methods for radioactive waste clean-up and disposal.

The goal of the Nuclear Materials Section of *Frontiers in Nuclear Engineering* will be to bring together researchers from the global community and associated interdisciplinary materials science fields to foster new collaborative research and accelerate the developments of materials for nuclear applications.

Author contributions

The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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