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Review of recent experimental results on the behavior of actinide-bearing oxides and related materials in extreme environments

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ABSTRACT

Oxide materials find use throughout the nuclear fuel cycle, from actinide-bearing ores and commercial reactor fuels to wasteforms for radionuclide disposal. In geological, reactor, and waste repository conditions, these materials are often exposed to ionizing radiation, high temperatures, and mechanical stresses. Recently, a large body of work has investigated the response of actinide oxides and analogue compounds to extreme environments, including the individual and combined effects of radiation, temperature, and pressure. Study of the phase behavior of these materials under such conditions can lead to improved understanding of their stability throughout the nuclear fuel cycle, as well as strategies for the mitigation of associated performance degradation. This article reviews some recent experimental work on this topic, highlighting advanced techniques developed for the exposure of materials to extreme environments, and for the *in situ* characterization of their structural and chemical responses. The study of two classes of nuclear materials is reviewed: binary oxides typical of nuclear fuels, and complex oxides typical of geological materials and wasteforms. Particular emphasis is placed on the individual and combined effects of modifications to the atomic and electronic structures of materials by exposure to extreme environments.

1. Introduction

Oxides are found throughout the nuclear fuel cycle, most often as actinide-bearing materials. Uranium is extracted from ores consisting primarily of the mineral uraninite (UO_{2+x}), along with coffinite ($USiO_4$) and brannerite (UTi_2O_6) (Finch and Murakami, 1999). Solid mill tailings, usually disposed of near uranium ore mines, are composed of various actinide-bearing silicate, sulfate, and oxyhydroxide minerals (Abdelouas, 2006). Most commercial nuclear reactors use UO_2 as a fissile fuel, sometimes accompanied by PuO_2 in mixed oxide (MOX) fuels. Many proposed methods for actinide waste management, including geological disposal and transmutation to shorter-lived isotopes in inert matrix fuels (IMFs), require the development of stable materials to dilute and immobilize radionuclides (Degueldre and Paratte, 1999; Degueldre, 2007; Ewing, 2011). Complex oxides, based on minerals that are known to incorporate actinides over geological timescales, have garnered substantial interest for this purpose (Ewing, 2011, 2007; Ewing et al., 2004; Lumpkin, 2001). Finally, the interaction of nuclear fuel with groundwater or coolant, as can occur in a reactor accident or cladding failure scenario, can yield various oxyhydroxide, carbonate, silicate, and phosphate phases (Burns et al., 2012).

Common to all such actinide-bearing oxide nuclear materials is their exposure to extreme environments including energetic radiation, high temperatures, and high pressures or stresses. Ionizing radiation, wherein particles of high specific energy (above approximately 1 MeV/u) interact with matter primarily via electronic excitation, is particularly relevant for actinide-bearing nuclear materials (Matzke, 1992). It is encountered in the form of alpha particles produced by radionuclide decay (helium nuclei with typical energies around 5 MeV) and fission fragments produced by

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the induced or spontaneous fission of actinides (heavy element nuclei with energies of 80–120 MeV). Atomic displacement can result from either the modification of interatomic forces following excitation of electrons from bonding to antibonding orbitals, or local heating due to phonon emission during the non-radiative decay of excited electrons (Duffy et al., 2012). These displacements can generate diverse defects and phase modifications in the irradiated material (Zhang et al., 2011a,b). In the case of fission fragments, ionizing radiation produces cylindrical "ion tracks" of damage with diameters around 10 nm and lengths of up to tens of micrometers. The nanoscale, highly transient thermal spike that accompanies particle-solid interactions at high specific energies produces very high local temperatures and pressures (Ronchi and Wiss, 2002), along with atomic displacement and modified interatomic forces (Duffy et al., 2012), making the interior of an ion track an extreme environment. Exposure of nuclear materials to highly ionizing radiation can cause degradation of properties important to their performance, such as thermal conductivity (West et al., 1968).

Nuclear fission and decay also induce bulk heating of radionuclide-bearing materials, requiring them to operate under high temperatures that can alter phase stability and modify the kinetics of atomistic processes. High pressures are encountered in reactors in the form of stresses caused by, for example, fuel swelling or cladding failure. Such loading is generally localized. Stresses at crack tips, for example, can be much higher than those applied to bulk fuel pellets. High pressure is also encountered in geological conditions which, while not directly related to nuclear fuel performance, are relevant to the mineralogy of actinide-bearing ores from which fuel materials are extracted. Within Earth's mantle, where pressures on the order of 10 GPa are encountered, there exist significant quantities of natural uranium and thorium (Helffrich and Wood, 2001; Turcotte et al., 2001). The phases in which this material is incorporated are not known, so study of the behavior of actinide oxides at high temperature and high pressure is needed to constrain their geological behavior. As with temperature, changes in pressure can significantly modify the phase stability of a material.

These extreme conditions limit the performance and operational lifetime of actinide oxide components throughout the nuclear fuel cycle. Understanding the responses of actinide-bearing materials to extreme environments is necessary to improve the efficiency and safety of nuclear energy generation. For example, achieving increased burn-ups in nuclear fuels is economically favorable, but requires mitigation of the fuel performance degradation induced by in-reactor radiation and high temperatures (Grimes et al., 2008). The development of suitable wasteforms for actinides requires the development of materials that are structurally and chemically stable under crustal conditions for the long periods of time during which these wastes remain dangerously radioactive (Ewing, 2011, 2007). Tolerance of extreme environments is also important with respect to the development of Gen IV reactors, which are planned to operate under conditions more extreme than those of current Gen III facilities (Grimes et al., 2008). For these reasons, significant effort has been dedicated, in recent years, to study of the behavior of actinide oxide materials in extreme environments. Recently, emphasis has been placed on the use of combined extreme conditions of irradiation, temperature, and pressure. This allows for more accurate simulation of the conditions encountered in the operating environments of nuclear materials. For example, irradiation of a material under high temperature or pressure can modify the character of the damage induced, compared with irradiation at ambient conditions, and the radiation tolerance of a nuclear component is therefore dependent on these parameters. Additionally, experimental study of material behavior at far-from-equilibrium conditions, beyond those that might be encountered in the nuclear fuel cycle, provides insight into the fundamental mechanisms controlling the phase responses of actinide materials to irradiation, heating, and the application of mechanical stresses. Better understanding of these behaviors at the atomistic scale is crucial to modeling and simulation efforts.

Experimental study of the behavior of nuclear materials in extreme environments is necessarily restricted by the safety precautions required for such work. To minimize the risk of radionuclide release and the associated regulatory burden, studies of actinide materials are often limited to small sample volumes, making many techniques that require the use of large bulk samples unsuitable for this purpose. Additionally, containment of the samples is usually necessary, which can render samples inaccessible to certain experimental probes. However, advanced experimental techniques, many based on the use of synchrotron radiation (Shi et al., 2014), have been developed to allow for observation of the structural effects of irradiation, temperature, and pressure on actinide materials. Additionally, some insight into the potential behavior of actinide-bearing materials can be gained from the study of lanthanide-bearing materials, given their similarities in crystal chemistry and thermophysical properties. This manuscript reviews recent developments in the experimental study of the response of actinide-bearing oxide nuclear materials, and some non-actinide analogue materials, to extreme environments. Emphasis is placed on the responses of these compounds to ionizing radiation, high temperature, and high pressure. While property degradation is of primary interest from a nuclear engineering outlook, this review focuses instead on the underlying structural and crystal chemical responses of nuclear materials to these conditions, which yield mechanistic insight into the processes controlling the tolerance of nuclear materials for extreme conditions.

This review focuses on experiments that seek to access extremes of temperature (on the order of 1000 K), pressure (on the order of 10 GPa), and energy deposition by radiation (particle energies in the MeV-GeV range and resulting target energy densities on the order of 10 eV/atom). These are not necessarily representative of the conditions most frequently encountered in the nuclear fuel cycle, and instead represent the conditions most challenging to simulate in laboratory experiments. For example, pressures in the GPa range are not typically encountered by nuclear fuels, and the applications of studies under these conditions pertain mainly to the behavior of materials in Earth's mantle. However, such basic science can be of great importance for materials design throughout the nuclear fuel cycle. For example, high pressure equations of state for actinide materials have been used to quantify the damage induced in UO_2 by fission fragment irradiation (Ronchi and Wiss, 2002). This demonstrates the connection between studies of nuclear material behavior in a pressure regime far beyond that which might be encountered under reactor conditions, and the in-reactor behavior of a nuclear fuel.

The radiation energy range addressed in this review largely limits its scope to radiation-induced electronic excitation, excluding study of the elastic collisions between nuclei that dominate energy transfer in the case of neutron and alpha decay recoil damage. Readers are referred to earlier reviews which comprehensively discuss radiation damage in this and other energy regimes (Hobbs et al., 1994; Robinson, 1994; Weber and Ewing, 1998). Additionally, it is important to consider separately the steady state behavior of materials in extreme environments and the responses of materials to transient application of temperature and pressure. Due to the limited data available regarding the behavior of actinide-bearing materials in these transient conditions, results obtained using relatively slow heating, cooling, and pressurization rates are emphasized here. For the purposes of this review,

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