PHASE TRANSFORMATION AND MICROSTRUCTURAL EVOLUTION OF NANOSTRUCTURED OXIDES AND NITRIDES UNDER ION IRRADIATIONS

by

Fengyuan Lu

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Approved by the
Examining Committee:

_____
Prof. Jie Lian, Thesis Adviser

_____
Prof. Yaron Danon, Member

_____
Prof. Theodorian Borca-Tasciuc, Member

_____
Prof. Liping Huang, Member

Rensselaer Polytechnic Institute
Troy, New York

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ABSTRACT

Material design at the nanometer scale is an effective strategy for developing advanced materails with enhanced radiation tolerance for advanced nuclear energy systems as high densities of surfaces and interfaces of the nanostructured materials may behave as effective sinks for defect recovery. However, nanostructured materials may not be intrinsically radiation tolerant, and the interplay among the factors of crystal size, temperature, chemical composition, surface energy and radiation conditions may eventually determine material radiation behaviors. Therefore, it is necessary to understand the radiation effects of nanostructured materials and the underlying physics for the design of advanced nanostructured nuclear materials. The main objective of this doctoral thesis is to study the behavior of nanostructured oxides and nitrides used as fuel matrix and waste forms under extreme radiation conditions with the focus of phase transformation, microstructural evolution and damage mechanisms.

Radiation experiments were performed using energetic ion beam techniques to simulate radiation damage resulting from energetic neutrons, alpha-decay events and fission fragments, and various experimental approaches were employed to characterize materials' microstructural evolution and phase stability upon intense radiation environments including transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. Thermal annealing experiments indicated that nanostructured ZrO_2 phase stability is strongly affected by the grain size. Radiation results on nanostructured ZrO_2 indicated that thermodynamically unstable or metastable high temperature phases can be induced by energetic beam irradiation at room temperature. Various phase transformation among different polymorphs of monoclinic,

tetragonal and amorphous states can be induced, and different mechanisms are responsible for structural transformations including oxygen vacancies accumulation upon displacive damage, radiation-assistant recrystallization and thermal spike by ionization radiation.

The radiation response of nanosized pyrochlores indicated that the radiation tolerance of nanoceramics is highly dependent on the composition and size. Nanosized tantalate pyrochlores $K_xLn_yTa_2O_{7-v}$ (Ln = Gd, Y, Lu) with the average grain size around 10 - 15 nm are highly sensitive to radiation-induced amorphization. The pyrochlore A to B site ionic radius ratio r_A/r_B is crucial in determining the radiation tolerance of pyrochlores, and a minimum r_A/r_B of 1.605 exists for the occurring of radiation induced amorphization. The interplay among chemical compositions, structural deviation and grain size eventually determines the phase stability and structural transformation processes of tantalate pyrochlores under intense radiation environments.

ZrN shows extremely high phase stability under both displacive ion irradiation and ionizing swift heavy ion irradiation. However, a contraction in lattice constant up to ~ 1.42 % can be induced in nanocrystalline ZrN irradiated with displacive ion beams. In contrast, the strongly ionizing swift heavy ions cannot induce any lattice contraction. Such lattice contractions may be due to a negative strain field in the ZrN nanograins related to N vacancies built up upon displacive radiation. Ion irradiations also lead to the formation of orthorhombic ZrSi phase at the interface between ZrN and Si substrate, resulting from atom mixing and precipitation upon ion irradiations.

The fundamental knowledge provides critical data for assessing and quantifying nanostructured ceramics as fuel matrix and waste forms utilized in the extreme

environments of advanced nuclear energy systems. Further possibilities are being pursued in manipulating microstructure at the nano-scale, controlling phase stability and tailoring the physical properties of materials for various important engineering applications.