Uranium Nitride Corrosion

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Abstract

Abstract stuff

1. Introduction

Uranium nitride (UN) is considered a prospective fuel for both light water reactors (LWRs) and Generation IV reactors [1, 2]. The higher fissile density of UN as compared to uranium dioxide benefits fast reactors with their lower neutron cross section [3]. This higher actinide density additionally benefits LWRs because UN pellets can remain in the reactor longer, leading to longer time between shut downs, and reducing money lost [4]. For all reactor types, the high thermal conductivity and high melting temperature make UN an optimal material to resist accidents [4].

While nuclear power initially developed uranium dioxide for the fuel pellet, the call for accident tolerant fuels (ATF) after Fukushima has drawn attention back to nitrides [5]. However, ATF materials must maintain current operational standards as well as improve safety [6]. Despite the beneficial properties of UN, it is unstable the presence of steam or even air [5, 7, 4]. In the event of cladding failure in a LWR, the pellet will come into contact with steam. As UN degrades, fission products will be released from the fuel matrix, free to interact with the containment structure. Furthermore, nitrogen can react with the steam to form explosive ammonium nitrate [7].

In the case of Generation IV reactors, most designs use alternative coolants. However, the instability of UN in air hinders fabrication into a fuel pellet [4]. Short of solving UN corrosion at high temperatures and pressures for LWRs, corrosion in air must be mitigated for use as a Generation IV fuel.

To assess the current state of UN corrosion research, this review examines six studies from within the past decade. The first two studies work to better understand UN oxidation in the presence of air [5] and steam [7]. Next, Lu et al. [8] and Lopes et al. [4] each investigated a method to mitigate UN corrosion: nitriding and introduction of an intermetallic phase, respectively. The last two studies use computational modeling to probe the atomistic initiation of UN corrosion, studying oxygen [10] and water [9] at UN surfaces.

2. Review

To better understand uranium nitride corrosion, Jolkkonen et al. [7] subjected UN pellets to superheated steam. The authors tried varied densities of UN pellets, ranging from 77.6% to 97.7% of theoretical density. The lowest density pellet resulted in the greatest amount of degradation, yielding rapid H_2 production followed by a significant release of N_2 uncharacteristic of the other, denser pellets. The denser pellets could last up to 90 minutes while subjected to 300 °C steam, but degraded as the temperature was increased to 400 °C. The pellets showed different mechanical fracture, with the lowest density pellets turning to powder and the higher density pellets cracking into fragments. This fragmentation would further accelerate corrosion as additional surface is exposed.

The corrosion mechanism was first proposed as

$$UN + 2H_2O \rightarrow UO_2 + NH_3 + \frac{1}{2}H_2 \quad , \tag{1}$$
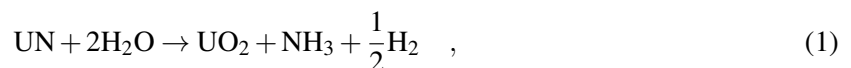
suggesting UO_2 and NH_3 form in equal proportions and both yield double that of H_2. However, Jolkkonen et al. found U_2N_3 formation, which disrupts the stoichiometry of (1) by reducing NH_3 formation and increasing H_2 formation. Additionally, even after hydrolysis finished, residual N_2 was found in the resultant powder.

Johnson et al. [5] studied UN powders and compared the time until oxidation to uranium silicide and uranium dioxide powders. The powders were ramped to 800°C while the mass was measured with thermogravimetry. At 4.4% open porosity, UN oxidized at 320 °C, determined by 5% mass increase. On the other hand, 0.0% open porosity UN performed better than even UO_2, with oxidation onsets of 440 °C and 405 °C, respectively. The UN-10%U_2Si_3 powder performed nearly the same as the low porosity UN, with a slightly higher oxidation onset temperature of 450°C but also slightly higher mass increase due to oxide formation. The authors conclude that while using U_3Si_2 in conjunction with UN may improve fabrication of UN, it does not necessarily reduce corrosion.

Lopes et al. [4] took the work of Johnson et al. a step further by fabricating full pellets of UN and UN-10%U_3Si_2. In order to reach the high densities sufficient to reduce oxidation, UN must be sintered at over 2000 °C. However, this results in accelerated grain growth, creating fast diffusion pathways for both oxygen to enter and fission products to escape. To reduce this necessary temperature, an intermetallic phase of U_3Si_2 can be added during sintering.

Lopes et al. placed the pellets in an autoclave, heated to 300 °C, and added 9 MPa steam. Like Jolkkonen et al. and Johnson et al., the authors found reduced reactivity with reduced porosity. They found degradation increased in time, and suggested the mechanism depended on the OH and NH_3 formed during the reaction. The oxygen formed a non-protective layer and larger grains were easily fragmented due to mechanical instability.

While the first three cases have considered bulk forms of UN, the next study by Lu et al. used UN films [8]. To reduce the reactivity of U, which will react when coated with Al or Ti for spent fuel storage, the authors created nitrided U films by sputtering. Films of UN_x were prepared at stoichiometries of x = 0.23, 0.68, and 1.66. Their results suggested the formation of an oxynitride, OU_xN_y, phase in the $UN_{1.66}$ film. This film formed the thinnest oxide layer, suggesting the greatest resistance to corrosion. The authors reasoned that the poor oxidation resistance of the $UN_{0.68}$ film may be due to the ease with which oxygen can fill a nitrogen vacancy in UN.

Density functional theory has been used in several studies to probe the atomistic UN corrosion mechanism, notably by the groups Bocharov et al. [10] and Bo et al. [9]. Bocharov studied oxygen atoms and nitrogen vacancies at the UN (100) and (110) surfaces along with a tilt grain boundary. The Gibbs free energy of defects, such as a nitrogen vacancy discussed above, can be calculated using

$$\Delta G_F^N(T) = \frac{1}{2}\left(E_{def}^{UN} - E^{UN} + 2\mu_N^0(T)\right) \quad , \qquad (2)$$

where E_{def}^{UN} is the energy of the surface with the nitrogen vacancy , E^{UN} is the energy of the defect free surface, and μ_N^0 is the standard nitrogen chemical potential. Bocharov et al. find that an N vacancy can forms preferentially at the (110) surface followed by the grain boundary and then the (100) surface, but the oxygen prefers to enter at the grain boundary. Regardless, oxygen incorporation yields negative energy in each case. The study ends with a proposed oxidation mechanism of [10]:

1. chemisorption of O_2
2. dissociation of adsorbed O_2
3. adsorption of O atop U atoms
4. high mobility of O along the surface
5. incorporation of O at N vacancies.

Bo et al. [9] extended examination of the UN surface to a full study in the presence of water. Using the (100) surface, Bo et al. studied water coverages ranging from one to four molecules (0.25 to 1 monolayer coverage). They report the adsorption energies for molecular, partially dissociated, and fully dissociated water, with partially and fully dissociated water being equally favorable. After adsorption,

the authors deconstructed the energy levels using local density of states. These plots showed that the valence electrons lie on the U atoms, while the N electronic densities go to zero around 2 eV below the Fermi level.

3. Discussion

Combination of nitriding, adding dopants, intermetallics Nitriding reduces interactiong at room temperature, however at higher temperature higher stoichiometric UN decays to UN. Add intermetallics for ease of fabrication, nitride for room temp handling

Bo et al. [9] used DFT towards determining the initiation of UN corrosion, but while they report optimally water species and adsorption sites, this does little to reveal a reaction mechanism like (1). Computational studies at odds with experiment: experiment changes starting conditions, comp changes type of study

Table 1. Experimental Parameters

	Starting Material	Temperature	Pressure
Jolkkonen et al. [7]	UN pellets (77 - 97%TD)	400 - 425 °C	0.05 MPa
Johnson et al. [5]	UN powder ($\approx$20 mg)	800 °C	not reported
Lu et al. [8]	UN films	AFG	UHV
Lopes et al. [4]	UN pellets (95 - 99 % TD)	300 °C	9 MPa

4. Summary

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