First-principles Insights into the Nature of Zirconium-Iodine Interactions and the Initiation of Iodine-induced Stress-Corrosion Cracking

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Abstract

We present research relating to iodine-induced stress corrosion cracking (ISCC) and draw insights relevant to the initiation process. The means by which this corrosion initiates is currently unknown. Our previous work has highlighted some of the chemical processes and properties that must be considered in ISCC, and enable us to make some possible connections in the overall corrosion mechanism. A series of calculations has been performed to better characterize the iodine interaction with zirconium, following a hybrid approach that integrates both molecular and solid-state calculations for incorporation into large scale simulations.

I. Introduction

Iodine-induced stress corrosion cracking (ISCC) is a phenomenon that can occur on the inner diameter (ID) of the nuclear fuel assembly due to reaction of the cladding with iodine created via fission processes in the fuel. During operation of a light-water nuclear reactor, a significant fraction of the fission products is iodine, which can corrode the zirconium-based cladding. This reaction, combined with the hoop stresses induced from the build-up of fission gas pressure and/or mechanical pellet-clad interaction (MPCI), ultimately compromises the integrity of the zirconium-alloy cladding material via stress-corrosion cracking failure. The zirconium is subject to a relatively harsh environment on the ID. While chemically corrosive agents are present, a large temperature gradient can also be present, depending on the state of the fuel. Under normal conditions, the ID of the cladding can reach temperatures of 300-400°C; however, in the event of hard contact (pellet-cladding physical interaction), the cladding can reach temperatures of more than 1000°C[1]. This large range of possible temperatures can contribute to accelerated kinetics in the corrosion process. Atrens et al.[2] investigated the mechanisms behind stress-corrosion cracking (SCC), with a particular focus on reducing the effects of SCC and pellet-cladding interaction (PCI) based SCC[2-3]. There is a general lack of experimental data regarding ISCC as it occurs within reactors, due to the significant complexities of the problem, including irradiation damage, highly energetic iodine radicals, and significant temperature gradient. Additionally, due to the time required for spent fuel to remain in storage pools, the failure modes are difficult to assess[4] and the mechanism is primarily unclear. Considering the barriers to working with irradiated materials (cost, safety hazards), the lack of experimental data which reproduces reactor conditions is not surprising. Significant research has been performed looking into the influence of iodine on stress corrosion cracking, including the influence of cesium and cadmium in the materials[5-7]. The origin of PCI failure, reported by Lyons, et al[8] spurred interest in determining the nature and appropriate ac-

tions required to prevent PCI mechanisms, which in turn evolved to performance guidelines adhered to in the current operation of reactors, such as the rate of power ramp[7]. Numerous studies have been performed to investigate the stress corrosion cracking process [2, 9-12] in addition to studies also involving the compounding effects of iodine[13-23].

While the overall effects of ISCC have been characterized to some extent via post-failure analysis techniques, very little is known about the nature of the initiation process[17, 20]. This sparsity of knowledge is common for many SCC phenomena, in that the initiation period is often the hardest to characterize, because, to a large extent, SCC manifests as a stochastic phenomenon. It has been proposed[5, 24-25] that several mechanisms may be responsible for PCI iodine-induced initiation, including the reaction of ZrI_4 , CsI , and free iodine on the cladding surface, leading to intergranular fracture via diffusion of these reactive species to enable iodine deposition to the pristine zirconium. Previous research shows a propensity for pit formation, due to localized corrosion of Zircaloy surfaces; advanced materials such as niobium-containing alloys have shown resistance to such pitting[17, 20]. This may very well be linked to the fact that niobium is a grain boundary segregant[26]. From previous studies on ISCC potential mechanisms[5, 25], and analysis of materials[26-27], changes to the kinetics of the mechanism may be possible for this observed change. The challenge here is not insignificant: Even the most advanced models for stress-corrosion crack growth and propagation[9] currently use arbitrary values for the initiation and re-initiation steps, because the detailed chemistry for these steps is essentially unknown. An assumption by Lewis et al. in their 2011 model for time-to-failure by iodine SCC was introduced that initiation consumed about 18 minutes of the overall 20 minutes for time-to-failure under a typical I-SCC scenario[19]. This timescale was empirically related to the time required to first compromise the passive oxide film; clearly, this will be a system dependent parameter

related to the strain-to-failure threshold for the oxide film while it is adherent to the underlying metal/alloy substrate.

Part of the difficulty in properly characterizing the initiation stages of ISCC lies in the overall complexity of the system, and the materials/environment interface, in general. While it is known that iodine is present as a fission product, transmutation of iodine can occur via the following decay sequence:

Thus the reaction products formed when iodine reacts with the zirconium-base alloy clad material will be subject to radioparagenesis, with all of the reconstructions and additional chemistry that this may entail. The role of cesium and cesium iodides are also of significant interest for study; cesium has been shown to enable lower-stress material failure in studies by Cox[28] and Dannhäuser[3], which is supported theoretically by the findings of Wimmer[29].

Looking solely at the chemical reaction of iodine with zirconium, one encounters the following equilibrium:

While the equilibrium shown is for the overall system, a more complex system exists which includes the transient states of coordination that zirconium-iodide can adopt before reaching the saturated tetra-coordinated ZrI_4 state:

The above equilibria will be controlled by temperature and iodine partial pressure[7, 23]. Although ISCC has been observed to cause both intergranular and transgranular fracture, investigations of the initiation process point to grain boundaries as being the most sensitive to early-stage pitting with grain boundary triple points, in particular[20]. Wimmer et al.[29] describe the role of different species on modifying the grain boundary properties of zirconium. It is suspected that iodine corrosion at these locations will be most pronounced, culminating in pitting[20] and, when these pits reach a critical size, ultimately facilitating SCC initiation via intergranular cracking. Transgranular cracking may occur when the more sensitive basal planes of the material are aligned with the crack direction. For this reason, appropriate texture controls have been introduced to mitigate this latter phenomenon[26, 30].

The importance of ZrI_4 formation lies in its ability to mimic the van Arkel-de Boer process[31] of metal purification, also known as the crystal bar method. The van Arkel-de Boer process involves exposure of impure zirconium metal to an excess of iodine gas, which liberates volatile ZrI_4 , which is in turn collected and used to regenerate iodine through a disproportionation reaction at high temperature (1400°C), creating a pure Zr deposit. ZrI_4 volatilizes at ~400°C[23], which can be achieved during the standard operating conditions present within a reactor; it is expected, therefore, that when localized regions achieve the tetra-coordinated state, pitting-type corrosion can occur. Previous experimental results by Park et al.[20] and Serres et al.[22], among numerous others[2, 14-17, 19, 21, 23, 30] show that in the presence of halogens, material failure can occur at lower-than-nominal stress thresholds. In the work by Wimmer[29], it is predicted that iodine is strongly grain-boundary weakening, which will directly contribute to material failure. The mechanisms pertaining to the reaction of iodide formation, however, have yet to be determined.

The importance of the grain boundary is two-fold. First, it is known[15] that a passive oxide layer forms on the inner diameter (ID) of the zirconium cladding which is 8-10 μ m thick, which is unlikely to be penetrated by iodine due to strong electrostatic repulsion; however, the oxide may possess sufficient free-volume due to misfit dislocations that are presented along the grain boundaries, allowing iodine diffusion to the pristine zirconium below. Second, since the crystallography is disrupted at grain boundaries, any strain on the system will likely concentrate at these points, increasing the likelihood of the above diffusion scheme. For instance, the surface decohesion energy at grain boundaries and internal surfaces is typically half that of the bulk material. Additionally, beneath the oxide layer, pitting-type corrosion mechanisms are more likely at the grain boundary due to the lower coordination of zirconium, and thus, greater reactivity with iodine. Thus, the focus of the initiation problem can be shifted to the problem of obtaining a proper understanding of the interaction of iodine with either grain boundaries in the oxide, or grain boundaries in the metallic phase, and how those grain boundaries intersect with surfaces at the materials/environment interface.

While the iodine-based corrosion process alone cannot account for material failure, as seen in work by Atrens et al.[2], it has been shown that material failure at lower-than-nominal stress can occur when zirconium is exposed to halogen materials. In addition to the effects on the pristine zirconium surface, chemical and environmental effects may also play a role in oxide fracture mechanics. It is likely a combination of localized pitting corrosion - which leads to crack-tip formation[20] - as well as weakening of the material along grain boundaries, shown in work by Wimmer et al[29]. The initiation of pit and crack-tip formation, however, is not well understood, and characterization of critical iodine concentration, in addition to exposure time could provide significant insight into the prescriptive guidelines for ramp and operation procedures in nuclear power plants to avoid ISCC-based fuel rod failures. Uncovering the detailed mechanisms, however, by which iodine interacts with defects is non-trivial.

Beginning with a first-principles perspective, therefore, we have sought to map out the interaction of iodine with various surface states of the metal and the oxide phase. In the sections below we make an account of our findings made along these lines. We then provide some discussion of how these effects tie into a more general mechanism for ISCC and pave the way for future studies in which the interactions of iodine with defects and strain fields are introduced. This next generation of first-principles and atomistic studies will provide a more comprehensive model for ISCC and how either boundary conditions or materials controls can be better applied to mitigate this phenomenon without undue loss of operating efficiencies.

II. Materials and Methods

Zirconium has historically been used for nuclear fuel cladding because of its very low cross-section to thermal neutrons, 0.18 barn, ideal for use in light-water reactors, while maintaining good thermal conductivity and moderate corrosion resistance[32]. Alloys currently used in cladding consist of zirconium-base alloys in the hexagonally-closed packed structure (HCP Zr) containing niobium, tin, iron, chromium, and/or other metals in low fractions. To establish a baseline metric for iodine-induced stress-corrosion cracking of such alloys, we begin by exploring the reaction mechanism of iodine with unalloyed Zr surfaces, oxide films, and defects. Since alloys exhibit enrichment of the impurity elements at grain boundaries and other defect sites[27], subsequent studies will need to focus on the critical role these elements play in modifying the corrosion and SCC kinetics.

The computational models used varied between systems. All the computations performed in this work were based on electronic structure theory, which is necessary for the proper description of the bond making and breaking processes that occur during the corrosion reactions that are a critical component of iodine-induced SCC. For the molecular-based calculations, self-consistent calculations per-

formed on the molecular species in vacuo were used to determine the electronic structure. This class of calculations was used to describe the corrosion products in the vapor phase (i.e. the ZrI_x molecules) and the reactant state of I_2 . In previous work[33] it was shown that computational modeling can produce artifacts due to spin state, such as in the case of a pair of isolated ZrI_3 molecules. Further, it has also been shown that variations between exchange-correlation functionals can also produce artifacts[34] when computing the cohesive energies of molecular crystal species dependent on the spin states of the isolated molecules. Band structure calculations were used for solid phases and the vapor/materials interface. Periodic crystals of ZrI_2 , ZrI_3 , ZrI_4 , ZrO_2 , and HCP Zr were constructed for these studies. For the ZrI_x species, bulk models were also constructed using the structures compiled in the Inorganic Crystal Structure Database[35-38]. For the ZrO_2 and HCP Zr, both the bulk and slab models were constructed. In the case of ZrO_2 , a 2x2 model was constructed in the x and y directions, to simulate an oxygen-terminated exposed (100) facet for use in the surface diffusion calculations. For the HCP Zr slab models, a 3x3 (0001) faceted model was constructed in a similar fashion, to ensure that the surface diffusion calculations were not heavily affected by neighbor-effects due to the periodicity. Where applicable, the vacuum regions were constructed to be 10 times the unit cell length in the z-direction, to also minimize the effects of neighboring cells.

Several functional corrections were utilized to produce the best results. As shown in numerous previous studies[34, 39-45], incorporating a van der Waals correction may be necessary to properly predict structures. This is especially the case when dispersion forces provide the primary interactions between particles in the system. It has been shown[41] that density functional theory (DFT) can fail to accurately predict correct geometries and binding energies where disperse non-bonding electron interactions occur, most frequently observed in conjugated organic materials. However, such as in the case of the zirconium iodide crystals, much of the intermolecular bonding to form crystalline structures oc-

curs through iodine-iodine interactions, with ZrI_4 exhibiting the largest “I---I” character. In our previous work[34], it was shown that without some form of van der Waals correction, the predicted crystal structures poorly match the experimental results, while the more robust treatment of van der Waals forces predict the best structures. As evidenced in previous work[39-40, 42-46], the presence of dispersion correction terms are necessary in many systems, as they frequently include non-bonding interactions, such as that which occurs between iodine-iodine, and oxygen-iodine. Significant advances have been made beyond the empirical-based Grimme[41] dispersion correction, namely the vdW-DF methods developed by numerous groups. The correction functional used in this work was that of Dion, et al.[40], modified by Klimes, et al.[43], which includes a long-range correlation term into the system, which is a more robust solution compared to that of Grimme. The main importance, however, is not to choose any particular method of van der Waals correction, but rather to verify that the effects are adequately taken into account by comparing with the best available experimental data for structural or thermodynamic properties.

Periodic crystal structures of the zirconium iodides were taken from the Inorganic Crystal Structure Database (ICSD)[35-38]. For the molecular models, GAMESS[47] was used to determine electronic structures using the B3LYP functional with the SBJKC basis set[48-51]. The periodic model calculations were performed using the Vienna Ab Initio Software Package (VASP)[52], with the Perdew-Burke-Ernzerhof (PBE) potentials[38, 48-49]. Where relevant, the Klimes-modified version of the Dion et al. vdW-DF van der Waals corrected functional was used[40, 43]. The VASP parameters used for the molecular models (for cohesive energy) and supercells were completed with a single k-point mesh, while intermediate range crystals were performed using a k-point mesh generated automatically in VASP with a length-scale parameter of 35, which provides modest accuracy for metallic systems. The plane-wave basis set energy cut-off used for all VASP calculations was 400eV.

One tool that can be useful in extending the length scale of atomistic simulations is ReaxFF[53], a “reactive force field”, which is built on a training set of simpler interactions and calculations. Using ReaxFF, one can quickly perform MD simulations on thousands of atoms without the large computational cost generally associated with simulating systems that may involve bond-breaking and bond-making reactions. The training set developed can use a combination of ab initio and experimental results to build analytical equations that solve for the interactions between atoms within the system. The overall goal of this work is to build a suitably robust training set that can accurately describe ISCC while allowing extension of atomistic simulations to include up to 10^5 - 10^6 atoms and time lengths up to tens of nanoseconds. We discuss briefly at the end of this report the preliminary findings on ISCC obtained using this methodology, as implemented in LAMMPS[54-55].

III. Results and Discussion

Our analysis of the ISCC problem has proceeded through a series of stages, each corresponding to a distinct mode of interaction between iodine and the zirconium surface. The reasons for this are two-fold: (1) To obtain a thorough understanding of the various modes of interaction of iodine with Zr surfaces, the bulk metal, defects and oxides and their relative importance for the problem of ISCC, and (2) To develop a database of reactive systems that can be used to benchmark a Reactive Force Field approach (ReaxFF) for the proper modeling of defect states using molecular dynamics simulation, that can be used to investigate the relation between stress and corrosivity[53].

The phenomenology we have addressed thus far may be classified as follows: Molecular effects, solid-state zirconium iodides, surface reactivity at the oxide and metallic surfaces (included in *Supplementary Materials*), diffusion and solid-state reaction. In the following, we break down the findings from each

of these sub-systems, and draw some general conclusions. In addition, we provide a path forward to extend the simulation of materials/environment effects relevant to iodine-SCC by reconciling the first-principles data obtained up to this point into a series of molecular dynamics simulations that explore ZrI_x formation in strained grain boundary systems of Zr and ZrO_2 .

III.A. Molecular effects

Zirconium iodides volatilize in the range of temperatures a fuel element is routinely exposed to during both regular operation and power transients[23]. In order to capture the chemical effects associated with volatilization and the early stages of redeposition, we have modeled some of the structural, thermodynamic and reactivity properties of these iodides. We have modeled ZrI_2 , ZrI_3 , ZrI_4 , Zr_2I_6 , and generated potential energy curves for symmetric bond stretching and bending for use in the ReaxFF training set (fig. 1a,b). The relevance of these molecular calculations may not be immediately apparent in relation to ISCC. However, if one were to consider the nucleation of iodine on the surface of zirconium, there are significant barriers to overcome such as local distortion of the lattice to accommodate iodine coordination. Such distortions will be governed by the “ease” via which iodine can incorporate itself into the lattice and form local regions of iodides, and will take part in governing the kinetics of ISCC. It can be noted that ZrI_2 has a very small energy barrier to angle distortion, likely enabling very rapid agglomeration of iodine to higher coordination. However, the higher coordination iodides are significantly more resistant to distortions, due to steric effects. This suggests that the rate limiting step for formation of ZrI_4 in ISCC is aggregation of iodine in the step $\text{ZrI}_3 + \frac{1}{2} \text{I}_2 \rightarrow \text{ZrI}_4$. Additionally, it can be noted that zirconium oxide is relatively “rigid” in comparison to ZrI_2 . Given that the kinetics of each are in direct competition, this may enable a more rapid formation of iodides, while limiting the healing of a compromised oxide film or passivation of a

pristine zirconium surface. Knowing these potential energy curves can aid in modeling aggregation and decomposition reactions involved in the corrosion process.

Furthermore, as shown in Table I, we have determined the energetics of increasing iodine coordination in zirconium-iodide molecules. From this table, it should be noted that the aggregation process is spontaneous, monotonically favoring ZrI_4 , as each reaction is exothermic. The largest energy gain per iodine bond occurs when increasing iodine coordination from 2 to 3, that is, $2\text{ZrI}_2 + \text{I}_2 \rightarrow 2\text{ZrI}_3$. It has been observed[56] that in bulk zirconium iodides coordinated in a manner ZrI_{4-x} , (where $x > 0$) a mixture of iodide phases is often present, such that upon heating, the volatile phases will also be mixed. While this process is endothermic[33], since ZrI_4 is the most volatile of the zirconium iodides, it is reasonable to expect some disproportionation of the material, as observed[56-57].

In order to examine the transition between ZrI_x molecules to form ZrI_x solid phases, we have studied the reaction mechanism to combine either ZrI_2 and ZrI_4 , or two ZrI_3 molecules, to form Zr_2I_6 [33]. This reaction was found to be exothermic, indicating a driving force for clustering. Furthermore, the potential energy surface we have determined contains no barrier for the clustering process: thus, the reaction will operate at equilibrium. This point is significant to ISCC: formation of compact iodide films on an exposed metal surface will hinder further iodide-based corrosion due to its action as a mass-transport barrier (albeit one that is likely porous and cracked – see below). On the other hand, if the temperature is such that the iodide film will vaporize into zirconium iodide molecules, then no such barrier will be present and the reaction rate will be greatly enhanced. Formation of a compact, stoichiometric ZrI_3 film (considered as the continuation of the energetically favorable dis- and comproportionation clustering into Zr_2I_6) requires significant energy input to cause such vaporization, serving essentially as a barrier to the transport-model corrosion mechanism. As is evident from the phase diagram provided by Cubicciotti et al. (Figure 2)[61], the range of temperatures and iodine partial pressures relevant to ISCC spans the thermodynamic region

pertinent to ZrI_x precipitation and decomposition. The present modeling work adds to this picture by providing a quantitative estimate for the zeroth-order ZrI_x vaporization process: the computed barrier (E^*) of 0.18 eV for the comproportionation process corresponds to rate constants of 10^{10} - 10^{11} molecules/s (Figure 3)[33]. This value follows from the usual Arrhenius expression, in which we take the prefactor k_0 to be 10^{12} Hz:

$$k = k_0 e^{\frac{-E^*}{RT}} \quad (4)$$

This rate could imply an iodide film loss rate of up to 90 m/s, depending on the competing redeposition rate (which is a function of the ZrI_x and I/I_2 concentration in the fission gas- we omit inclusion of this rate at present, until a numerical model is developed for the entire ISCC process). This extremely rapid film loss indicates that pitting is a likely mechanism for the formation of crack nuclei on the metal surfaces, once they are exposed due to fracture of the oxide film (see Supplementary Materials for oxide studies).

III.B. Solid-state zirconium iodides

The zirconium iodides may precipitate as molecular crystals, or they may form directly due to solid-state reaction, such as in the formation of zirconium iodide pits as observed by Park et al[20]. Many of the materials properties of these solid-state iodides have not been measured or theoretically determined, hence, we provide these values in this work. The iodide phases provide an end-state for the corrosion reaction that can be discussed with reference to the energies of intermediate or transition states. It should also be kept in mind that iodine will also react with the cesium which, being the other dominant fission product, is also present, forming stable cesium iodide gas at these temperatures[7, 28]. Localized regions of the clad material may exhibit bulk-like iodide structures, or zirconium iodide thin films, which can lead to transgranular corrosion via pitting, as shown in the work of Park et al.[20]. Investigation of the way that

the solid state zirconium iodides form, as well as determination of some of their physical properties can be useful when simulating larger systems, as small regions may exhibit bulk behavior (such as the grain boundary triple points). Additionally, the bulk modulus information gleaned from these calculations will prove useful in determining the mechanism behind the lower-than-nominal stress failures which occur in zirconium alloys when exposed to iodine, should local corrosion events motivate the brittle fracture of the iodide phases.

In keeping with this concept, we have performed a rudimentary computation of the Griffith's hoop stress thresholds for the failure via fracture of Zr, ZrO₂, and ZrI_x. We estimate the surface energy, γ , as half of the sublimation energy for the ZrI_x phases, and use the moduli, E , previously computed from first-principles[34]. In Table II we tabulate the first-principles versus experimental values for the sublimation and cohesive energies of the iodide phases for single crystals. Note, there is some departure from the values reported previously, due to improvements in our treatment of the van der Waals molecular solid phases[34]. The Griffith's stress, σ_G , is then computed for an initial crack opening radius of $a = 0.5 \mu\text{m}$ using the brittle cracking equation:

$$\sigma_G = \sqrt{\frac{2E\gamma}{\pi a}} \quad (5)$$

The initial crack length of $0.5 \mu\text{m}$ was chosen to ensure deep cracking sufficient to yield the maximum crack growth rate possible within the material. We estimate the surface energy of the iodide phases as half of the sublimation energy (since only half of the nearest neighbors are ruptured during surface cleavage, as opposed to complete sublimation). We then convert these failure stress thresholds into a strain to failure for each of these materials, using Young's equation:

$$\varepsilon_f = \frac{\sigma_G}{E} \quad (6)$$

This strain to failure is converted into the critical cladding hoop stress that can be sustained by the cladding before each of these materials (treated as thin films on the surface) will fail, via application of the Young's modulus for the underlying Zr metal.

$$\sigma_f = E_{Zr} \varepsilon_f \quad (7)$$

Despite the extreme simplifications of this approach, this treatment is instructive. Using a Griffith's initial crack opening of 0.5 μm , which we adopted as being the size of a nominal surface defect in the material, we find that the critical hoop stress to be sustained before fracture decreases for the materials in the following order: $\text{ZrO}_2 > \text{ZrI}_2 > \text{ZrI}_3 > \text{ZrI}_4$ (Table III and Figure 4). Furthermore, using these estimates, the critical threshold for cracking of the oxide film is around 300 MPa, which is similar to the threshold used in the Falcon fuel performance code[58]. (Falcon[58] is an industry software tool used to predict the reliability of fuel on a probabilistic basis. Falcon incorporates multiple models, ranging from the microscale (atomistic) to macroscale (finite element) sizes, over a range of steady-state and transient conditions expected to occur during the lifetime of fuel pins.) At this stress threshold, any ZrI_x that forms will also crack, thus, even in the absence of vaporization (which will occur at a rate as high as 90 m/s, see the previous section), the films will continue to expose fresh Zr surface via cracking (which usually progresses at $\sim 1/3$ of the speed of sound in the material, which we compute using our first-principles estimates to be around 915-990 m/s depending on the stoichiometry – Table III). As demonstrated further below from our molecular dynamics simulations, these films react rapidly with I and I_2 in the vapor phase, thus leading to a rapid reactive crack front, which can propagate at continued applications of hoop stresses of as little as 100 MPa, depending on the iodide phase that is formed (fig. 4). Note that this fracture speed exceeds the approximate speed of volatilization estimated from the molecular study, above. The relatively good agreement between the observed behavior of cladding I-SCC and this cursory application of Griffith's approach suggests that the ratio γ/a is sound, even though a plasticity factor should be used in place

of the surface energy, γ , when a material fails by ductile rather than brittle modes. An improved atomistic treatment of the cracking process awaits higher quality potentials for the simulation of Zr metal.

III.C. Surface Reactivity (I_2 on exposed metal)

Given that chemical attack on the oxide seems unlikely, based on results in the *Supplementary Materials*, and the oxide fracture has been demonstrated to be the predominant means by which iodine gains access to the metal surface (in line with current ISCC guidelines), we now focus exclusively on the interactions between iodine and zirconium metal, as we now find that the rate of reaction between iodine and the zirconium surface becomes potentially one of the limiting factors that controls the rate of initiation and propagation of ISCC. Sidky shows that both iodine (I, atomic) and iodine (I_2 , molecular) are present in the fission gas, as products of the dissociation of CsI[7, 28], and that the extent of these substances is enhanced by radiolysis[23]. Iodine molecules dissociatively adsorb on Zr(0001) planes, as shown by Wimmer et al[29]. Such facets become exposed when the oxide is mechanically fractured, as proposed, for instance in the Lewis model[19], and demonstrated to be feasible by our analysis in Table III and figure 4. In figure 5, we plot the potential energy surface for molecular iodine (I_2) over the basal (0001) Zr surface. The dissociation of I_2 as it approaches the (0001) plane of Zr is shown to be free (i.e. barrierless), thus confirming the one-dimensional analysis made by Wimmer[29]. The analysis we have made utilized a van der Waals corrected density functional theory approach[41], which differs from the GGA-only approach used in Wimmer's study, even though essentially the same result was determined. Given the essentially free dissociation process of iodine, we now move on to analyze the interactions of atomic iodine with the zirconium surface, particularly, diffusion into the material, across the surface, and, finally, the solid-state reaction mechanism that leads to formation of ZrI_x material.

III.D. Diffusivity of iodine on exposed metal surfaces and/or crack faces

After adsorbing onto the surface as atomic iodine, the corrosion reaction can initiate either laterally, by diffusion and reaction with adatoms, kinks or steps, or vertically, by diffusing into the zirconium-base alloy (at pristine sites, or defects, such as grain boundaries). As shown in fig. 6, penetration of the basal plane through an interstitial migration mechanism has a very high energy barrier. Unlike hydrogen, which can travel readily through the interstices, iodine is a large atom that cannot easily penetrate the lattice, and instead causes large, localized lattice distortions, which are responsible for the large observed energy barriers. We, therefore, discount a vertical diffusion based mechanism for iodide film formation as a primary means of ISCC.

It has been suggested that fast iodine diffusion on the metallic and/or oxide surfaces is deleterious in that it allows mass transport down a fracture surface to be rapid, thus providing a short time for ISCC reinitiation[18]. This may be especially pertinent when crack tips are too narrow or tortuous to allow access for vapor phase species. At the same time, the diffusion constants for I on Zr surfaces have not been determined. Furthermore, comparison of oxygen and iodine diffusivity can provide some estimate of the relative propensity for crack healing versus continued iodination of the metal. The potential energy surface for nascent iodine (fig. 7a,b) moving across the basal (0001) plane of HCP zirconium shows a thermodynamic energy barrier of 0.2 eV to diffuse between neighboring three-fold coordination sites. We can relate that activation barrier to the diffusivity using an Arrhenius form based on the random walk model. In so doing we obtain the diffusivity as a function of temperature as shown in Figure 8. The diffusion constants are relatively high- much higher than solid-state diffusion (for instance, hydrogen in iron has a diffusivity of 10^{-9} cm²/s at 100°C[59] compared to 10^{-2} cm²/s for iodine on Zr(0001)). It is therefore feasible to consider that iodine diffusion is rapid enough to facilitate crack propagation, although integration into a numerical (continuum based) fracture model would be needed to completely validate this point.

III.E. Solid-state reaction

In addition to the valuable insights gained already from the first-principles database, our primary goal was to utilize the first-principles reference information to develop a reactive force field potential that could be used to simulate the ZrI_x film formation on the surface. As our rudimentary fracture mechanics analysis indicates (Table III, Figure 4), the iodide film can fracture far below the threshold stress required to fracture the oxide or the zirconium metal. Since iodine (atomic or molecular) is most likely to react with defect sites at the metal surface to form iodides via solid-state reaction, it is important to develop a theoretical methodology that is capable of handling a multiplicity of coordination and oxidation states. Since ReaxFF was specifically developed for this purpose, we have used the density functional theory-based dataset to develop an appropriate Zr-I potential.

In preliminary simulations we have confirmed the fidelity of the potential via simulations of the reactivity of I and I₂ with Zr particles to form iodides at reasonable threshold temperatures, and the modeling of the volatilization of ZrI_x solids into the vapor constituents (i.e. sublimation). Following these confirmations, we then performed a preliminary simulation that modeled the reaction of an iodine vapor space with an exposed metallic Zr surface. This model has also been extended to include grain boundaries and notched pre-crack type geometries, as well as grain-boundaries pre-doped with iodine atoms. We will use these simulations to study the interplay between iodine content, surface presentation, grain boundary orientation, stress and temperature. In this way, we can investigate the essential mechanism, which thus far appears to rely on the formation of iodide films, that then rapidly crack, and a continuation of this process over and over again as the SCC propagates through the material. By applying these simulations to obtain a firm grasp of the interplay between the above parameters, we should be able to provide much greater clarity regarding the mechanics of ISCC initiation, growth and propagation.

IV. Conclusions

Intergranular cracking has been the suspected mechanism for ISCC, however the initiation stage is poorly characterized[16, 60]. As indicated in this report, oxide failure is strongly correlated with the critical threshold stress required for ISCC failure, and hence, appears to be critical for allowing the chemical contact required for iodine to form ZrI_x films on the fresh metal surface. This fracture is more likely to take place at defects, such as intergranular attack, due to the weakening in local cohesive strength at these sites. Furthermore, we find that once these films form, the same hoop stress required to fracture the oxide critically exceeds the hoop stress required to fracture the developing iodide films, where again, these are likely to have reduced resistance at grain boundary sites. Thus, it is likely that ISCC occurs through a continually developing, chemically reactive crack front, with a particular emphasis on defects, particularly the grain boundary triple points at which ZrI_x pits are observed, for instance, by Park[20].

An alternative explanation for intergranular cracking exists in the literature: the work of Wimmer et al.[29] points towards the importance of iodine penetration to grain boundary weakening. However, we show that iodine penetration into the material and subsequent segregation at grain boundaries appears highly unlikely, as the barriers to iodine entering into interstitial sites at the metal are prohibitive. A mechanism where iodine adopts substitutional sites (i.e. vacancy-iodine complexes) may still be pertinent, and provide for this, but appears less likely than a mechanism that involves the formation of zirconium iodide, because of the kinds of arguments we have made above.

We have also investigated the possibility of volatilization through the study of molecular aggregates via van Arkel type mechanisms[31]. The volatilization rate can be quite fast, depending on the rate of the reverse deposition rate, however, it is expected to be significantly slower than a cracking

mechanism, which would proceed at rates bounded by the speed of sound in the material (Table III), though actual SCC fracture rates are considerably less. Notably, at the micro-scale, the brittle fracture of zirconium iodides will occur rapidly where present, and the fracture velocity of such iodides is limited to the transport and kinetics of iodide formation. The position of the pressure-temperature coordinates of the environment, however, may favor one form of iodide versus another (Figure 2) that could alter both the importance of volatilization, as well as the particular resistance of the emerging iodide film, thus modifying crack growth kinetics.

Given the lower thermodynamic barrier to diffusion of iodine along several surfaces, it is likely that iodine will move freely through the system, and bind to lower-coordination sites such as surface and ledge atoms within the lattice, enabling higher degrees of iodine complexation, and either forming pits through volatilization, or localized region of solid state zirconium iodides. In both cases, given the hoop stress, it is likely that such regions are increasingly more reactive in a manner which allows further corrosion.

Taken all in all, one can infer a scheme that may be pertinent to the true processes occurring during ISCC. Such a scheme has been constructed (fig. 9), which shows several different possible pathways for material compromise, which we are currently working to simulate portions of via larger scale molecular dynamics simulations. Starting in the upper left corner of fig. 9, step 1, there is zirconium coated with a protective oxide (see Supplementary Materials for a detailed description of the oxide studies.) The calculated energy of iodine displacement of oxygen in the oxide structure shows that a direct chemical attack of iodine on the oxide (fig. 9, steps 2a-2b) is unlikely due to a strong endothermal opposition which responds to the localized changes in charge state and steric effects). This suggests that oxide compromise does not occur via a direct replacement mechanism; however, in the event of oxygen displacement through other means, such as neutron bombardment, iodine may take

advantage of these defects to prevent healing of the oxide and instead lead to a strained oxide-iodide system, bypassing new oxide formation (fig. 9, step 3). While direct iodine penetration of the Zr(0001) plane is unlikely (fig. 9, step 5b), the exposed surface is vulnerable to chemical attack, and may form a mixture of ZrI_x phases along the surface (fig. 9, step 5a). As the hoop stress increases (as occurs during the life of the fuel pin), the iodide-enriched grain boundary is prone to fracture, allowing pitting, and ultimately, becomes an initiation site for stress corrosion (fig. 9, step 6).

A likely mechanism relates to a pre-cracking of the oxide, which tentative estimates, based on brittle fracture given an initial defect size of $0.5\mu\text{m}$, indicate can occur at clad hoop stress of ~ 300 MPa, consistent with current fuel performance codes. This could be further lowered via accumulation of radiation damage[23]. This event then allows exposure of the zirconium alloy to iodine attack. Any I_2 is immediately dissociated upon chemical contact to form adsorbed atomic iodine. Formation of an iodide phase is then exothermic, and takes place through a mechanism we have yet to fully determine, but are beginning to simulate using ReaxFF molecular dynamics simulation. We have shown that, thermodynamically, iodine is unlikely to penetrate the surface. Instead, iodine can rapidly diffuse to adatoms, kinks or steps, where iodide formation can be initiated. We have, furthermore, shown that iodide films cannot support high hoop stress loadings, but will fail above 100 MPa (using the above estimates), depending on the iodide film that is formed (Figure 4). If failure of the oxide via cracking is considered, the mechanism considered is then pitting at local regions where the oxide has failed, rather than the bulk material.

Presently, molecular dynamics (MD) simulations are being performed in order to extend our atomistic investigation into the true nature of ISCC initiation. Key properties that can be gleaned from such simulations include stress/strain relations as a function of iodine concentration in grain boundaries, iodine diffusion rates, pit growth rates, and other kinetic data related to iodine chemistry on the zirconium-

um. Examinations of the plastic response of the materials to deformation could also be investigated using the ReaxFF potential. Once these simulations have been completed, it is likely that a useful time-to-failure damage model can be constructed to complement and provide additional support/insights into the structure and fundamental parameters used as inputs for the existing empirical models. Furthermore, knowledge of the materials properties that control the response of zircalloys to ISCC will provide a basis for future materials-engineering solutions that can mitigate this potential failure mechanism. Such simulations are beyond the scope of this manuscript, but warrant investigation to determine the effects of iodine on mechanical strength.

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VI. References

- [1.] Azevedo, C.R.F., Selection of fuel cladding material for nuclear fission reactors. *Engineering Failure Analysis*. 18 (8) (2011) 1943-1962.
- [2.] Atrens, A., Dannhäuser, G., and G. Bärö, Stress-corrosion-cracking of Zircaloy-4 cladding tubes. *J. Nuc. Mater.* 126 (1984) 91-102.
- [3.] Dannhäuser, G., Atrens, A., and G. Bärö, Stress-Corrosion Cracking of Zircaloy-4 Cladding Tubes, Part 2. *J. Nuc. Mater.* 126 (1984) 103-110.
- [4.] Deshon, J., Kucuk, A. EPRI Fuel Reliability Executive Committee Meeting. in EPRI Fuel Reliability Program. 2008. Dallas, TX.
- [5.] Konashi, K., Kamimura, K., and Y. Yokouchi, Estimation of Irradiation Induced Iodine Pressure in an LWR Fuel Rod. *J. Nuc. Mater.* 125 (1984) 244-247.
- [6.] Götzmann, O., Thermochemical Evaluation of PCI Failures in LWR Fuel Pins. *J. Nuc. Mater.* 107 (1982) 185-195.
- [7.] Cox, B., Pellet-Clad Interaction (PCI) Failures of Zirconium Alloy Fuel Cladding - A Review. *J. Nuc. Mater.* 172 (1990) 249-292.
- [8.] Lyons, M.F., Coplin, D.H., and G.G. Jones, High Performance UO₂ Fuel Program, in Quarterly Progress Reports. 1963/1964, General Electric Co.
- [9.] Musienko, A. and G. Cailletaud, Simulation of inter- and transgranular crack propagation in polycrystalline aggregates due to stress corrosion cracking. *Acta Mater.* 57 (2009) 3840-3855.
- [10.] Newman, R.C., Stress-Corrosion Cracking Mechanisms, in *Corrosion Mechanisms in Theory and Practice*, P. Marcus, Editor. Marcel-Dekker, New York. 2002.
- [11.] Nikulin, S.A. and A.B. Rozhnov, Corrosion cracking of zirconium cladding tubes (A review). I. Methods of study and mechanisms of fracture. *Metal. Sci. Heat Treat.* 47 (2005) 71-79.
- [12.] Staehle, R.W., A critical analysis of tight cracks. *Corrosion Reviews*. 28 (2010) 1-103.
- [13.] Duffo, G.S. and S.B. Farina, Diffusional control in the intergranular corrosion of some hcp metals in iodine alcoholic solutions. *Corr. Sci.* 47 (2005) 1459-1470.
- [14.] Farina, S.B., Duffo, G.S., and J.R. Galvele, Localized corrosion of zirconium and zircaloy-4 in iodine alcoholic solutions. *LAAR*. 32 (2002) 295-298.
- [15.] Farina, S.B., Duffo, G.S., and J.R. Galvele, Stress Corrosion Cracking of Zircaloy-4 in Halide Solutions. Effect of Temperature. *Mat. Res.* 5 (2002) 107-112.
- [16.] Goryachev, S.B., Gritsuk, A.R., Prasolov, P.F., Snegirev, M.G., Shestak, V.E., Novikov, V.V., and Yu.K. Bibilashvili, Iodine induced SCC of Zr alloys at constant strain rate. *J. Nuc. Mater.* 199 (1992) 50-60.
- [17.] Jacques, P., F. Lefebvre, and C. Lemaignan, Deformation-corrosion interactions for Zr alloys during I-SCC crack initiation. Part I: Chemical contributions. *J. Nuc. Mater.* 264 (1999) 239-248.
- [18.] Legris, A. and C. Domain, Ab initio atomic-scale modeling of iodine effects on hcp zirconium. *Phil. Mag.* 85 (2005) 589-595.
- [19.] Lewis, B.J., Thompson, W.T., Kleczek, M.R., Shaheen, K., Juhas, M., and F.C. Iglesias, Modelling of iodine-induced stress corrosion cracking in CANDU fuel. *J. Nuc. Mater.* 408 (2011) 209-223.
- [20.] Park, S.Y., Kim, J. H., Choi, B. K., and Y.H. Jeong, Crack initiation and propagation behavior of zirconium cladding under an environment of iodine-induced stress corrosion. *Metals and Mat. Intl.* 13 (2) (2007) 155-163.
- [21.] Schuster, I. and C. Lemaignan, Influence of texture on iodine-induced stress corrosion cracking of Zircaloy-4 cladding tubes. *J. Nuc. Mater.* 189 (1992) 157-166.
- [22.] Serres, A., L. Fournier, Fregonese, M., Auzoux, Q., and D. Leboulch, The effect of iodine content and specimen orientation on stress corrosion crack growth rate in Zircaloy-4. *Corr. Sci.* 52 (2010) 2001-2009.
- [23.] Sidky, P.S., Iodine stress corrosion cracking of Zircaloy reactor cladding: iodine chemistry (a review). *Journal of Nuclear Materials*. 256 (1998) 1-17.
- [24.] Busol, F.I., Kinetics of the reduction of ZrI₄ vapors by metallic zirconium. *Russ. J. Phys. Chem.* 33 (1959) 799-807.
- [25.] Olander, D.R., A Thermodynamic Assessment of In-Reactor Iodine SCC of Zircaloy. *J. Nuc. Mater.* 110 (1982) 343-345.

- [26.] Kim, H.-G., and Y.-H. Jeong, Effect of Annealing Conditions on the Microstructure and Corrosion Characteristics of Zr-xNb Alloys. *Solid State Phenomena*. 118 (2006) 77-82.
- [27.] Marquis, E.A., Miller, M.K., Blavette, D., Ringer, S.P., Sudbrack, C.K., and Smith, G.D.W., Structural Materials: Understanding Atomic-Scale Microstructures. *MRS Bulletin*. 34 (2009) 725-730.
- [28.] Cox, B., Surette, B.A., and J.C. Wood, Environmental Degradation of Engineering Materials in Aggressive Environments, R.P. McNitt, and R.D. Sisson, Editor. 1981, pp. 293.
- [29.] Wimmer, E., Najafabadi, R., Ballard, J.D., Angeliu, T.M., Vollmer, J., Chambers, J.J., Niimi, H., Shaw, J.B., Freeman, C., Christensen, M., Wolf, W., and P. Saxe, *Ab initio* calculations for industrial materials engineering: successes and challenges. *J. Phys.: Condens. Matter*. 22 (2010) 384215.
- [30.] Francon, V., Fregonese, M., Abe, H., and Y. Watanabe, Iodine-Induced Stress Corrosion Cracking of Zircaloy-4: Identification of Critical Parameters Involved in Intergranular to Transgranular Crack Propagation. *Solid State Phenomena*. 183 (2012) 49-56.
- [31.] van Arkel, A.E., and J. H. de Boer, Darstellung von reinem Titanium-, Zirkonium-, Hafnium- und Thoriummetall. *ZAAC*. 148 (1) (1925) 345-350.
- [32.] Concise Encyclopedia Chemistry. 1994, Walter De Gruyter Inc. 1199.
- [33.] Rossi, M.L., and Taylor, C.D., Atomistic Simulations of Formation of Elementary Zr-I Systems. *O. J. Phys. Chem*. 1 (2011) 104-108.
- [34.] Rossi, M.L., and Taylor, C.D., Equations of State for Crystalline Zirconium Iodide: The Role of Dispersion. *J. Nuc. Mater*. 433 (1-3) (2013) 30-36.
- [35.] Guthrie, D.H. and J.D. Corbett, Synthesis and Structure of an Infinite-Chain Form of Zr I₂ (alpha). *J. Solid State Chem*. 37 (1981) 256-263.
- [36.] Krebs, B., G Henkel, and M, Dartmann, Kristallstruktur von Zirkoniumtetrajodid Zr I₄. Ein neuer A B₄ - Strukturtyp. *Acta Cryst. B*. 35 (1979) 274-278.
- [37.] Lachgar, A., D.S. Dudis, and J. D. Corbett, Revision of the structure of zirconium triiodide. The presence of metal dimers. *Inorg. Chem*. 29 (2242-2246) (1990).
- [38.] Martin, U., Boysen, H., and F. Frey, Neutron Powder Investigation of Tetragonal and Cubic Stabilized Zirconia, TZP, and CSZ, at Temperatures up to 1400K. *Acta Cryst. B*. 49 (1993) 403-413.
- [39.] Cooper, V.R., Van der Waals density functional: An appropriate exchange functional. *Phys. Rev. B*. 81 (2010) 161104.
- [40.] Dion, M., Rydberg, H., Schröder, E., Langreth, D.C., and B.I. Lundqvist, Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett*. 92 (2004) 246401.
- [41.] Grimme, S., Semi-empirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem*. 27 (2006) 1787.
- [42.] Hult, E., Hyldgaard, P., Rossmeisl, J., and B. I. Lundqvist, Density-functional calculation of van der Waals forces for free-electron-like surfaces. *Phys. Rev. B*. 64 (2001) 195414.
- [43.] Klimes, J., Bowler, D.R., and A. Michaelides, van der Waals density functionals applied to solids. *Phys. Rev. B*. 83 (2011) 195131.
- [44.] Lee, K., Murray, E. D., Kong, L., Lundqvist, B. I., and D. C. Langreth, Higher-accuracy van der Waals density functional. *Phys. Rev. B*. 82 (2010) 081101.
- [45.] Tkatchenko, A., and M. Scheffler, Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett*. 102 (2009) 073005.
- [46.] Li, G., Tamblyn, I., Cooper, V.R., Gao, H.-J., and J.B. Neaton, Molecular adsorption on metal surfaces with van der Waals density functionals. *Phys. Rev. B*. 85 (2012) 121409.
- [47.] Gordon, M.S., and M.W. Schmidt, Advances in electronic structure theory: GAMESS a decade later, in *Theory and Applications of Computational Chemistry, the first forty years*, C.E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria, (editors). Elsevier, Amsterdam. 2005, pp. 1347-1363.
- [48.] Hay, P.J. and W.R. Wadt, *Ab initio* effective core potentials for molecular calculations - potentials for the transition-metal atoms Sc to Hg. *J. Chem. Phys*. 82 (1985) 270-283.
- [49.] Hay, P.J. and W.R. Wadt, *Ab initio* effective core potentials for molecular calculations - potentials for K to Au including the outermost core orbitals. *J. Chem. Phys*. 82 (1985) 299-310.
- [50.] Stevens, W.J., H. Basch, and M. Krauss, Compact effective potentials and efficient shared-exponent basis sets for the first- and second-row atoms. *J. Chem. Phys*. 81 (1985) 6026-6033.
- [51.] Stevens, W.J., M. Krauss, H. Basch, P.G. Jasien, Relativistic compact effective potentials and efficient, shared-exponent basis-sets for the 3rd-row, 4th-row and 5th-row atoms. *Can. J. Chem*. 70 (1992) 612-630.
- [52.] Kresse, G., M. Marsman, and J. Furthmüller, Vienna *Ab-initio* Simulation Package (VASP): Wien, Austria.

- [53.] van Duin, A.C.T., S. Dasgupta, Lorant, F., and W.A. Goddard III, ReaxFF: A reactive force field for hydrocarbons. *J. Phys. Chem. A*. 105 (2001) 9396-9409.
- [54.] <http://lammmps.sandia.gov>. [cited 2012 August 6].
- [55.] Plimpton, S., Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comp. Phys.* 117 (1995) 1-19.
- [56.] Lamoreaux, R.H., and D. Cubicciotti, Estimated Thermodynamic Properties of the Solid Zirconium Oxides. *J. Electrochem. Soc.* 128 (2) (1981) 457-460.
- [57.] van der Vis, M.G.M., Cordfunke, E.H.P., and R.J.M. Konings, Thermochemical properties of zirconium halides: a review. *Thermochimica Acta*. 302 (1997) 93-108.
- [58.] EPRI, Fuel Analysis and Licensing Code: Falcon Mod01. Theoretical and Numerical Bases. 1 (2006) 5-41.
- [59.] Cussler, E.L., Mass Transfer in Fluid Systems, in *Diffusion*. Cambridge University Press, Cambridge, UK. 1997, pp. 226-227.
- [60.] Likhanskii, V.V. and L.V. Matweev, The development of the crack growth model in zirconium claddings in iodine environment. *Nuc. Eng. Des.* 213 (2002) 133-140.
- [61.] Cubicciotti, D., Jones, R.L., Syrett, B.C., in: D.G. Franklin (Ed.), *Zirconium in the Nuclear Industry*, Fifth Conference, ASTM STP 754, American Society for Testing and Materials, 1982, p. 146.

Tables

Table I: Energetics of iodine aggregation into zirconium iodide molecules (energy given per molecular reaction)

	Reactants	Products	ΔE (eV)
$Zr + I_2 \rightleftharpoons ZrI_2$	$Zr + I_2$	ZrI_2	-4.59
$ZrI_2 + I_2 \rightleftharpoons ZrI_4$	$ZrI_2 + I_2$	ZrI_4	-6.78
$2ZrI_2 + I_2 \rightleftharpoons 2ZrI_3$	$2ZrI_2 + I_2$	$2ZrI_3$	-9.50
$2ZrI_3 + I_2 \rightleftharpoons 2ZrI_4$	$2ZrI_3 + I_2$	$2ZrI_4$	-5.24

Table II: Energies of formation and sublimation for zirconium iodides, per single-crystal.

Molecular species	ΔE_f (eV)	ΔE_f (eV, <i>lit</i> [57])	ΔE_{sub} (eV)	ΔE_{sub} (eV, <i>lit</i> [56])
ZrI ₂	2.90	2.96	4.65	4.29
ZrI ₃	4.33	4.17	3.01	2.73
ZrI ₄	4.81	5.06	0.73	1.38

Table III. Mechanical properties computed for the failure criterion of these films, based upon the sublimation energy (used to estimate the surface energy of the iodide phases) and the moduli computed in this work. The Young's modulus is estimated from the bulk modulus using a Poisson ratio of 1/3. The crack velocity is estimated at 1/3 of the speed of sound in the material, which is derived from the bulk modulus and the density. The fission gas pressure is deduced from the hoop stress using typical dimensions for clad material.

	E (GPa)	Gamma (J/m²)	Griffith Stress (MPa)	Strain to failure	Cladding Hoop stress (MPa)	Crack velocity (m/s)
ZrO₂	250	2.0	798	0.003	303	2211
ZrI₂	53	0.28	137	0.003	246	989.0
ZrI₃	41	0.13	82.0	0.002	191	945.0
ZrI₄	37	0.050	49.0	0.001	125	915.0

Figures

Figure 1a: Relative energies for bond stretching and compression of zirconium species.

Figure 1b: Relative energy curves for angle distortion of zirconium species.

Figure 2. From Cubicciotti, [61]. The critical region is from $\log[p(I)]$ between -8 and -15, and T from 300-500C. During this region, iodine is going to be present on the surface as either an adsorbed monolayer, or solid iodide phases up to ZrI_4 .

Figure 3. Zeroth order rate constant for ZrIx decomposition, based on the activation barrier computed for the unimolecular dissociation of Zr_2I_6 into 2 ZrI_3 molecules. This decomposition reaction follows a mechanism that is expected to be typical for the sublimation of the ZrIx solid phases during ISCC.

Figure 4. Hoop stress (based on the brittle failure model) required to fracture the following materials on the zircaloy clad, given a 0.5 μm pre-crack: the oxide film on the clad, and three solid iodide phases.

Figure 5: The potential energy surface for iodine dissociation as I_2 approaches the basal (0001) plane of Zr. It can be noted that as I_2 approaches the surface of Zr, it freely dissociates and binds to the surface. The z-axis is the relative energy, while the x-axis is the bond length (ranging from 2.88-2.28 Å), and y-axis is the distance from center-of-mass of I_2 to the Zr surface.

Figure 6: Schematic of iodine (large black atom) penetration through the Zr (gray atoms) basal plane. Local distortions in the lattice give rise to the large energies (all energies show relative to the surface adsorbed system, shown left).

Figure 7a: Representative diagram of iodine atom diffusion along the Zr 0001 (basal) plane. Arrows indicate movement along the x and y coordinates.

Figure 7b: Potential energy surface of an iodine atom moving across the basal (0001) plane of zirconium, represented schematically in Figure 7a.

Figure 8. Diffusivity for iodine atom migration along the Zr(0001) close-packed surface.

Figure 9: A schematic representation of possible pathways for transgranular corrosion to occur within oxide-protected zirconium alloys. In the case of intergranular cracking, the existence of a grain boundary at the oxide-fracture location may result in significantly increased rates of corrosion, as well as diffusion of iodine into the grain boundary, allowing fracture without pitting.