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Review

Iodine stress corrosion cracking of Zircaloy reactor cladding: iodine chemistry (a review)

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Abstract

This review covers chemical aspects of the iodine stress corrosion cracking (ISCC) pellet-cladding interaction (PCI) failures which have occurred in some reactors with UO_2 fuel in unlined Zircaloy tubes. The cracking mechanism is discussed in relation to chemical factors. Cesium and iodine are released as fission products and form CsI but its dissociation iodine pressure $p(\mathrm{I})$ is many orders of magnitude greater than chemical thermodynamic calculations predict, due to radiolysis. This enhanced $p(\mathrm{I})$ can form ZrI_4 in regions where Zr is exposed (not protected by surface scale) and a van Arkel vapour transport reaction then causes rapid Zr transport from localised cladding areas, i.e. pitting, which later becomes a crack site. Requirements are a critical strain rate (which cracks protective scale), iodine pressure and time, i.e. a power ramp. Factors include that a stress caused by a power ramp may relax before the required gap chemistry is achieved and that a ramp also releases short-lived I and Cs fission products which add to the iodine pressure available. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

1.1. General

Iodine stress corrosion cracking (ISCC) is usually accepted as the cause of pellet-cladding interaction (PCI) failures of unlined Zircaloy cladding containing UO_2 reactor fuel pellets, rather than metal vapour embrittlement or hydride cracking [1]. Iodine and non-iodine types of stress corrosion cracking are reviewed by Cox [2,3] and Adamson et al. [4]. There are over 400 reactors (of all types) worldwide and there is still some interest in the mechanisms of ISCC. This review is a contribution to that.

1.2. Causes

A power ramp heats the UO_2 rapidly, which strains the (water-cooled) cladding tube and this leads to SCC, as there is almost no ductility. Failure may occur if the ramp rate is over 3% per hour. See Fig. 1 [5–7]. New UO_2 pellets placed into used irradiated tubes caused no defects on ramping but a second ramp later did produce failures, indicating a necessary build up of chemical fission products, but high burnup is clearly not a factor [1]. PCI failures usually occur in fuel rods with over 10 GW d/t burnup (necessary for UO_2-Zircaloy gap closure due to fission product swelling) which were given a rapid power ramp [8]. The essential criterion for PCI failure is a minimum change in power [9] and it is generally accepted that fission products must be present and be above a threshold concentration locally, to cause PCI cracking effects [10]. Irradiation increases ISCC susceptibility.

Knaab et al. [11] give the following requirements for ISCC: (i) a critical stress, or strain; (ii) a critical iodine concentration; (iii) a minimum time. Data is given for power ramping and cycling.

If unstressed Zircaloy (oxidised and unoxidised) is held for a time t in iodine and a stress is applied for less than 10 s, then cracks occur only if the following condition applies: 30–60 min $> t >$ 3–15 min. Thus:

(a) the incubation time is not metallurgical but is the time for chemical conditions to be established;

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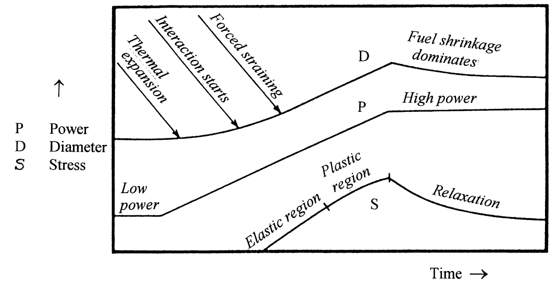

Fig. 1. The effect of a power ramp (*P*) on the diameter (*D*) and stress (*S*) in the cladding tube [6].

(b) the chemistry (for cracking) develops, at longer times, into a second condition where cracks cannot initiate. This indicates that iodine takes a non-aggressive form (e.g. harmlessly gettered as iodides on low-stress cladding areas) and further fresh fission product iodine is then needed for additional ISCC in a later power ramp;

(c) any oxide film cracks quickly when the stress is applied.

Stress corrosion cracks in Zircaloy cladding after power ramps are found in line with the ends of cracks in the UO_2 fuel pellets [1]. The Zircaloy cladding cracks show little or no gross plastic deformation and are often at pellet–pellet interfaces [12].

1.3. Iodine

High local iodine concentrations are reported on the cladding at pellet crack locations [13]. A surplus of iodine over cesium reaches the cladding in a ramp [14,15], but CsI crystals are found in the fuel-cladding gap. Thermodynamic calculations show $p(\mathrm{I}) = 10^{-19}$ bar at 600 K in the equilibrium between CsI, UO_2, O_2 (at typical value inside rod) and Cs_2UO_4 [16]. CsI and Cs_2UO_4 have been found in fuel rods. This $p(\mathrm{I})$ is enough to form a monolayer of iodine. Iodine is produced by chemical dissociation of CsI but also mainly by radiolysis [17]. Calculations of the dissociation iodine pressure over CsI under irradiation give values 10^7 times greater than with no irradiation [17]. Dissimilar (faster) transport of I than of Cs shows that all the iodine is not gettered by the amount of fission Cs formed [14]. The highest iodine concentration in the rod is in the fuel-cladding gap. Tasooji et al. [18] reports free iodine detected in irradiated UO_2 fuels.

Iodine probably removes the Zr atoms close to dislocation pileups due to their reduced bonding to the matrix [19]. This is supported by the observation that cracks in cold-worked material tend to change direction and propagate parallel to the sheet surface [19]. This accords with a conclusion that the Zircaloy tube manufacturing process is a significant factor in ISCC [20].

2. Cracking

This review is primarily on iodine chemistry and only those mechanical aspects which relate to this are included.

Cracks in failed fuel rods are tight and with little or no plastic deformation [12,21]. Texture has a major effect on ISCC [22] (discussed further in Section 3). The fracture surfaces have cleavage-like planes with some fluting; the planes are featureless and flat and probably due to chemically assisted cleavage along planes near to the basal plane [22,23]; (fluting is plastic failure of grains which are not properly oriented for cleavage). Hydrides are often found ahead of the crack but are thought to form after failure, due to water entry [24]. Yaggee et al. [25] give good crack photographs.

Transgranular crack velocity follows a well-defined velocity vs. stress intensity curve [3]. Haddad and Cox [26] consider the most likely mechanism for the fast transgranular pseudo-cleavage cracking (about 9 μm/s) is iodine atoms (at very low partial pressure around 10^{-19} bar, the value in equilibrium with a monolayer [16], being appropriate for down a narrow crack) diffusing down the crack to the tip and weakening Zr–Zr bonds there by reducing surface energy, allowing cracking at well below the rupture stress for Zircaloy. Both iodine and ZrI_4 cause ISCC: (i) an iodine monolayer is set up by a very low iodine pressure of only 10^{-19} bar and this appears to be a plausible transgranular cracking mechanism [16]; a monolayer of iodine adsorbed at a crack tip will lower surface energy and cause further cracking. (ii) ZrI_4 vapour removes Zr from pits by a van Arkel vapour transport mechanism, discussed later.

Alternatively or additionally, restricted slip processes occur at the crack tip due to adsorption of I, leading to local microvoid growth and microvoid coalescence in a narrow band at the crack tip [27]. Fractographic features which resemble shallow microvoids support this theory. A local microvoid coalescence mechanism for transgranular cracking can explain the relatively low velocities of transgranular cracks when compared with those expected for a true cleavage process. Stress intensity control takes over when crack length exceeds roughly 100 μm [26]. Most of the ISCC crack length of irradiated Zircaloy is transgranular; any intergranular cracking (at the start) is confined to the first few grains [28]. The activation energies for intergranular and transgranular cracking are about the same, suggesting a similar cause.

Cracks initiate at intermetallic and inclusion particles [7,29], at intergranular sites [5,6,30–33], at flaws and pits [7,30,33–36], at hydrides [37] and at transgranular sites [6,33,38]. Cracks in reactor fuel rods are always where oxide is absent or cracked [39]. Oxidised Zircaloy is reported as nearly immune to ISCC if the oxide is intact [40], but a strain of less than 0.5% can crack the oxide. Miller and Ocken [41] suggest local strain not stress is an important factor in ISCC. Severe ISCC occurred below 0.18/h strain rate [42].

Recently, a surface-mobility SCC mechanism has been used to predict crack velocities; it is suggested that ZrI_4 (mp 499°C) can induce SCC in Zr and Zr alloys by the surface mobility mechanism and the mechanism predicts crack velocities as high as those found in practice [43,44]. Galvele considers that surface contaminants can greatly increase surface self diffusion and that metal vacancy capture by a crack tip can contribute to SCC [43].

Une [45] reviews threshold values of stress, stress intensity factor, strain, strain rate and iodine concentration. A fracture mechanics treatment of ISCC is given by many workers but falls outside this iodine chemistry review.

Yaggee et al. [39] report a unique feature on the inner surface of a cladding from a reactor following ultrasonic cleaning: axial hairline cracks in patches of oxide not removed by ultrasonic cleaning nor by chemical attack, are surrounded on both sides by dark areas 0.75 μm wide. X-ray micro-analysis of the dark areas showed iodine with Zr, whereas X-ray micro-analysis of another section of the oxide showed only Zr. This feature is of interest as it could be a hard-to-find precursor of an SCC crack. The axial alignment of the hairline cracks may be an effect of the applied hoop stress, and the presence of iodine after vigorous ultrasonic cleaning indicates a strong bond between the iodine and the oxide layer.

3. Laboratory experiments

In ISCC laboratory experiments, no effect of air was found, for un-pre-oxidised Zircaloy tubes [46]. Fracture surfaces appeared similar to those of cracked reactor power-ramped tubes.

Many laboratory studies are reported [20,47–55]. There is a narrow borderline between cracking and pitting [20,49,56]; some oxygen is needed [51,57]. Adding oxygen extends iodine availability by forming an oxide film which prevents 'gettering' of iodine by adjacent low-stressed Zircaloy areas. Steel wool promotes ISCC by forming an iron iodide of lower volatility than ZrI_4, which stores the iodine near a high-stress (crackable) area and stops it escaping and being gettered harmlessly by an adjacent low-stress Zircaloy area [3,51,58,59].

Laboratory tests found an iodine pressure of 10^{-6} bar was needed to cause brittle rupture [59]. A $p(\mathrm{CsI})$ value of 10^{-6} bar can be achieved if the fuel surface exceeds 460°C, which can clearly be exceeded in a power ramp; the corresponding chemical thermodynamic $p(\mathrm{I})$ is very much lower, as CsI is the stablest iodide known (but see further discussion of this point later, where it is pointed out that the radiolytic $p(\mathrm{I})$ far exceeds the thermodynamic equilibrium value).

Different unirradiated tubes vary in susceptibility to ISCC but irradiated tubes (above a critical dose) are all equally sensitive to ISCC. Failure mechanisms have been discussed [60,61]. The results (for non-irradiated material) showed that texture has a strong effect on ISCC of Zircaloy-4 and that the mechanical properties have no effect; also the better performance of recrystallized material (compared with stress-relieved material) can be explained solely by the texture effect; texture is more important than chemical composition of Zircaloy-4 (for variations within the ASTM specification).

Laboratory tests at constant strain rate, on Zr 1% Nb showed better ISCC resistance than Zircaloy-2 and Zircaloy-4 [62]. The propagation of ISCC cracks in Zr 1% Nb cladding tubes has been studied at 350°C and a threshold stress intensity factor (K_{1c}) of 4.8 MPa $m^{1/2}$ was found [63].

Zircaloy-4 and Zr foils have been studied in molten Cs_2Te plus Cs and Te at various oxygen pressures [64,65]. Formation kinetics of solid iodides on Zr was studied by [66].

4. Iodine chemistry and irradiation effects

4.1. Iodine concentration

Iodine isotopes are about 15% of the total U-235 fission isotopes [19]. In a 3 kg fuel rod, about 0.5 g of I-129 forms after a burnup of 30 MWd per kg UO_2 [19]. Iodine reacts with cesium (15% of the fission products) forming stable CsI. Fig. 2 shows cesium, iodine and bromine production [67].

Critical iodine concentrations for causing SCC are tabulated by Une [42,68]. Tasooji et al. [18] give iodine concentrations in PWR and BWR rods at typical and high burnups [69,70]. Iodine is assumed to be released

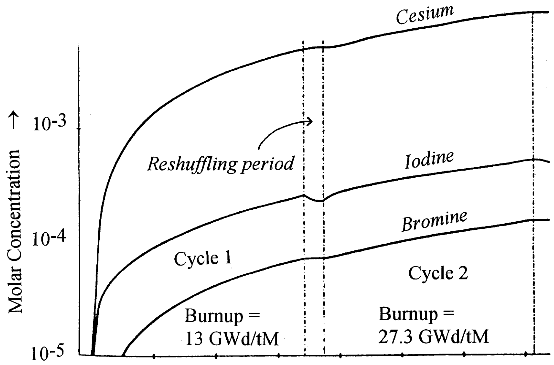

Fig. 2. Total production of Cs, Br and I in a 17 × 17 fuel rod [67].

from the fuel to the gap at the same rate as fission gas is released [53]. Iodine concentrations have been calculated assuming [34] that it all stays within a 1 mm wide zone at each pellet–pellet interface. Tasooji et al. [18] give 10^{-4} g/cm^2 of iodine in a 1 mm wide zone at the pellet-cladding gap in partly burned up rods. This converts to a volume of 1 mg/cm^3, the same figure as given by Une [42,68] for the ISCC threshold for irradiated Zircaloy-2 in laboratory tests. Both of these data are roughly equal to a surprising 0.4 bar of iodine vapour. A much lower threshold of 10 μg/cm^3 has been reported at 500°C and 50 mg/cm^3 at 900°C [71]. Studies of pressurised tubes with iodine and chlorine present show that only 5 μg/cm^2 Zircaloy surface affects failure time [72]. Studies using iodine in organic solvents are reported [47,73,74].

If gaseous iodine is postulated it should be expressed as g/cm^3 or similar units, but if solid iodine is involved, in g/m^2 of surface (units are used variously by different workers) [16].

It is likely that ISCC occurs in irradiated Zircaloy in reactors at much less than the critical value obtained from laboratory test data on unirradiated Zircaloy. Williford [75,76] considers a competition between chemical reaction and creep rate to be the important factor.

All the iodine released is to be available for SCC. Tasoojo et al. [18] consider that the SCCIG model can explain completely transgranular failures which are preceded by an induction period (previously only explained by assuming a slow intergranular initiation followed by a rapid transgranular propagation). At high applied stress (above $\sigma_{O,C+F}$), time-dependent SCC will still be simulated since the local iodine concentration in each element must take some time to reach a failure limit before that element fails; for $\sigma > \sigma_{O,C+F}$ the transgranular SCC line (Fig. 2 in Ref. [18]) will be reached before the intergranular line.

4.2. I–Zr thermochemical calculations

The chemical thermodynamic calculation (neglecting radiolysis) for finding the pressures of gaseous iodides in equilibrium with Zr at a given iodine pressure is reported by Cubicciotti et al. [16], and the results are shown in Figs. 3 and 4 [16]. Fig. 3 applies where enough iodine is present to form some ZrI (with excess Zr metal present), and to result in 0.01 bar of gaseous species if all species vaporise completely. ZrI_4 has the highest vapour pressure (dominant species). Below 850 K, $ZrI_{1.1}$ is solid and its presence controls the iodine pressure through

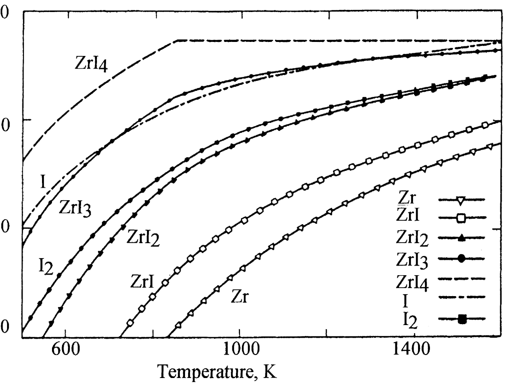

Fig. 3. Thermochemical calculation of gaseous iodide species in equilibrium with Zr. Quantity of iodine present is enough to produce a total pressure of 0.01 bar. Below 850 K, solid ZrI forms so the pressures are fixed by the Zr/ZrI solid equilibrium; above 850 K pressures are fixed by equilibrium with Zr [16].

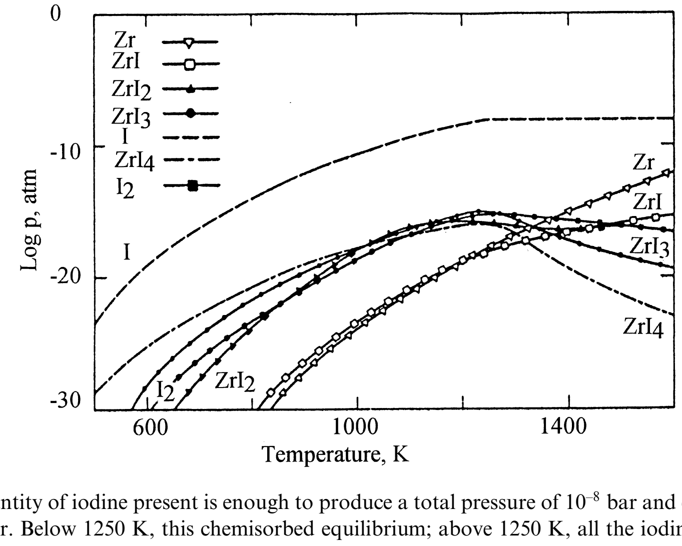

Fig. 4. As Fig. 3, except quantity of iodine present is enough to produce a total pressure of 10^{-8} bar and enough Zr is present to adsorb all the iodine in a monolayer. Below 1250 K, this chemisorbed equilibrium; above 1250 K, all the iodine is in the vapour (monolayer dissociates) and pressures are fixed by equilibrium with the metal [16].

the equilibrium equation $2Zr + I_2 = 2ZrI$ in which the equilibrium constant $K_p = 1/p(I_2)$ (since the activities of Zr and ZrI are both unity so long as any of these phases are present at all, however much or little). $p(I_2)$ and $p(I)$ vary below 850 K because K_p for the above equation varies with T. However, a much greater contribution to the actual iodine pressure present comes from radiolysis effects (see Section 4.3).

Fig. 4 [16] shows where $p(I)$ is sufficient to reach 10^{-8} bar only, when vaporized. This is insufficient to form ZrI etc and the gas consists of monatomic iodine vapour. Below 1250 K, $p(I)$ is fixed by equilibrium with the chemisorbed monolayer. At 600 K, most iodine is in this layer and $p(I) = 10^{-19}$ bar.

Cubicciotti et al. [16] give the chemical thermodynamics of the Zr–I system. Ranges of solid solubility correspond to $ZrI_{1.1}$ to $ZrI_{1.3}$ (i.e. a non-stoichiometric monoiodide), $ZrI_{1.9}$ to $ZrI_{2.1}$ (diiodide), $ZrI_{2.8}$ to $ZrI_{3.4}$ (triiodide), and the volatile tetraiodide (ZrI_4). Solids with intermediate composition are mixtures of two phases. Figs. 5 and 6 [3,16] facilitate finding the chemical equilibrium phases present and the gas pressures expected for any temperature, iodine pressure and zirconium activity. Cubicciotti et al. [16] confirm that iodine is adsorbed (chemisorbed) onto a Zr surface. The heat of adsorption of this chemisorbed iodine is 146 kJ/g atom iodine adsorbed and is independent of coverage at up to 1 monolayer thick. This value is approximately equal to the heat of formation per g atom iodine for all the four solid iodides [16]. The entropy of chemisorbed iodine is also required, to calculate thermodynamic activities of phases present. The authors [16] give S^0 (for chemisorbed iodine at 298 K) as $(175 - 63x)$ J/K mol where x is the fractional surface coverage, applicable to values near $x = 1$ (a monolayer).

The amount of iodine chemisorbed depends on the amount of Zr surface available, but the amount of iodine which will go to form zirconium iodide depends on the total amount of Zr available [16].

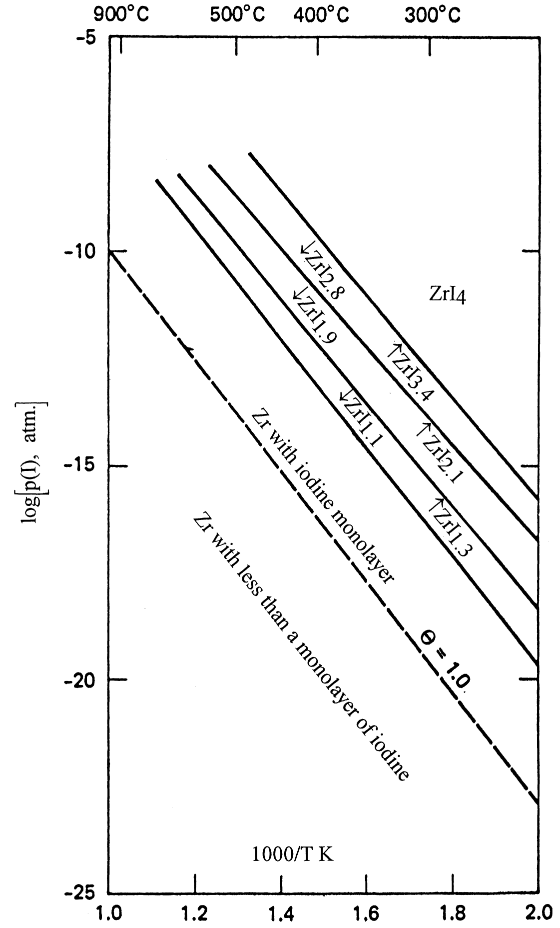

Fig. 5. Partial pressures of monatomic iodine with various solid zirconium iodide phases. For the chemisorbed state, θ is the fractional monolayer surface coverage [16].

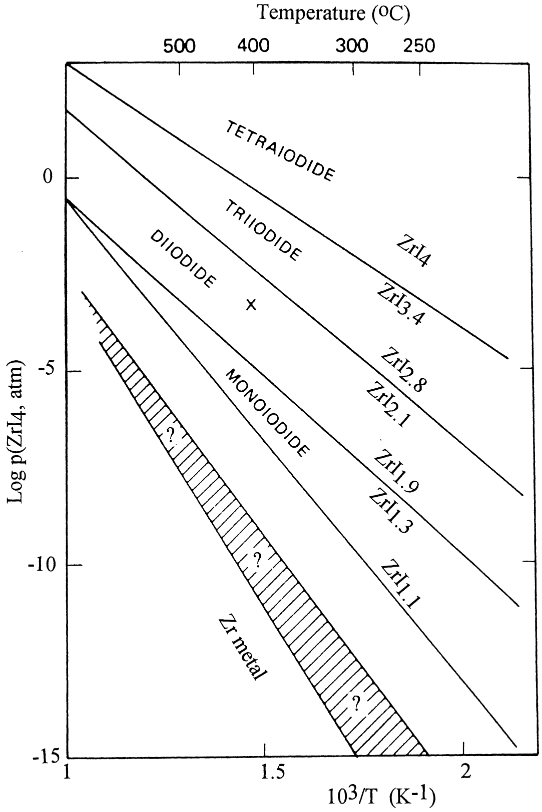

Fig. 6. ZrI_4 pressures in thermodynamic equilibrium with solid iodide phases. Lines are stability boundaries of solid phases. Area with question marks is probable location of chemisorbed iodine on Zr. The cross (×) is the lowest iodine concentration where ISCC was observed by Peehs et al. [34].

Cubicciotti et al. [16] calculate equilibrium values of $p(\mathrm{I})$ for: $x = 0.1$ (fractional Zr surface coverage) for a monolayer and for the lower and progressively higher Zr iodides. These chemical thermodynamic $p(\mathrm{I})$ values are obtained from K_p values as shown by [16].

At 600 K, without stress, Fig. 3 shows solid $\mathrm{ZrI_{1.1}}$ and $\mathrm{ZrI_4}$ vapour at 10^{-9} bar. When the Zircaloy is strained, forming fresh metal surface (as in a crack), Fig. 4 applies since iodine is transferred as gaseous $\mathrm{ZrI_4}$ (or by surface diffusion) at about 10^{-9} bar into the crack. Iodine becomes chemisorbed and weakens the bonds in the Zircaloy substrate and crack propagation occurs by bond cleavage [16]. Peehs et al. [77] propose a similar mechanism.

$\mathrm{AlI_3}$ also causes SCC of Zircaloy, due to the equilibrium: 0.37 $\mathrm{AlI_3}(s)$ + Zr = $\mathrm{ZrI_{1.1}}(s)$ + 0.37 Al(s) for which $\Delta G^0 = -40$ kJ at 600 K [78,79]. Similarly: $0.37\mathrm{FeI_3}(s)$ + Zr = $\mathrm{ZrI_{1.1}}(s)$ + 0.37Fe for which $\Delta G^0 = -75$ kJ at 600 K. The thermodynamic $p(\mathrm{I})$ {monatomic I} over Zr/$\mathrm{ZrI_{1.1}}$ is about 10^{-15} bar at 600 K (neglecting radiolysis) [16] which is greater than $p(\mathrm{I})$ of 10^{-19} over a chemisorbed monolayer, so that iodine can transport down a crack as explained above. Peehs et al. [77] suggest a mechanism involving solid iodides. When less than 10^{-3} g/cm^2 of iodine was placed near a stressed Zircaloy surface, microcracks started in 'islands', which suggests a non-uniformly distributed condensed layer, although this could also indicate preferred nucleation sites on the Zircaloy (such as impurities). Also, small amounts of iodine placed near a flaw caused SCC, but remote from the flaw did not [77]. This indicates solid iodides are effective because if gaseous iodides were the primary active species they would transport evenly and rapidly and the cracks would not be so locally distributed on the surface. Thus the effect of iodine or iodides should be considered on an area basis. The lowest surface concentration [77] was 3×10^{-6} g iodine/cm^2 Zircaloy, smaller than the value given by Cox and Wood [30], 1.5×10^{-5} g/cm^2. If the I atoms were uniformly distributed over a specular surface, the above value of 3×10^{-6} g I/cm^2 represents about 15×10^{15} iodine atoms/cm^2 or about 30 monolayers of iodine over the whole surface (assuming 2 nm per iodine atom) [16]. But clusters of acicular crystals are observed at only slightly higher concentrations [66].

Götzmann [80] reports $p(\mathrm{ZrI_4})$ over the systems Zr/ZrI, $\mathrm{ZrI/ZrI_2}$, $\mathrm{ZrI_2/ZrI_3}$ and $\mathrm{ZrI_3/ZrI_4}$. He also gives the corresponding $p(\mathrm{I})$ values and other thermochemical data. Thermodynamics show that monatomic I is the predominant gaseous iodine species at low pressures [80].

Peehs et al. [10] studied the kinetics of $\mathrm{I_2}$/Zr reactions at 400°C in laboratory experiments and analysed the ZrI_x layers produced. They confirmed [10] that an I:Zr ratio >2 is needed to cause SCC on Zircaloy [77,81].

ZrI_n with n from 1 to 4 can exist; iodine can also exist adsorbed on Zr [34]. Cubicciotti [82] reports $\mathrm{I_2}$ and $\mathrm{ZrI_4}$ are the only gaseous components independent of the substrate stoichiometry and then the following four permissible reactions can occur:

$$\mathrm{Zr} + (n/2)\mathrm{I_2}(g) = \mathrm{ZrI}_n(s), \tag{1}$$

$$\mathrm{ZrI}_n(s) + (m-n)/2\mathrm{I_2}(g) = \mathrm{ZrI}_m(s), \quad m > n, \tag{2}$$

$$\mathrm{Zr} + (n/4-n)\mathrm{ZrI_4}(g) = (4/4-n)\mathrm{ZrI}_n(s), \tag{3}$$

$$\begin{aligned}&\mathrm{ZrI}_n(s) + (m-n)/(4-m)\mathrm{ZrI_4}(g)\\ &\quad = (4-n)/(4-m)\mathrm{ZrI}_m(s), \quad m > n.\end{aligned} \tag{4}$$

Peehs et al. propose a model [10], based on their own results [10] and others [82,83]. In this model ZrI substrate forms by reactions (1) and (2) and crack propagation in stressed specimens is due to Eq. (3) where $\mathrm{ZrI_4}(g)$ disproportionates and Zr is picked up. This view is discussed below.

$\mathrm{ZrI_4}$ is volatile at cladding temperatures but the lower iodides are not. When iodine reaches a freshly exposed Zr site, ZrI (solid) must be the first compound formed, because Zr + I = ZrI has an equilibrium constant K_p which fixes $p(\mathrm{I})$. This $p(\mathrm{I})$ is less than that fixed by K_p for the next higher iodide which forms next in sequence: ZrI + I = $\mathrm{ZrI_2}$. This means $\mathrm{ZrI_2}$ cannot form on Zr without ZrI intervening. In the same way $\mathrm{ZrI_3}$ and $\mathrm{ZrI_4}$ must form later, also in sequence. This same conclusion is also predicted by the phase rule: Zr and its iodides cannot all co-exist in contact. So, strictly speaking, it should not be said that iodine reacts with Zr to form $\mathrm{ZrI_4}$; iodine will first adsorb and then form ZrI, $\mathrm{ZrI_2}$, $\mathrm{ZrI_3}$ and $\mathrm{ZrI_4}$ layers in strict sequence, on Zr, if sufficient iodine pressure is available. Following this rationale, Peehs et al. [10] give 3Zr + $\mathrm{ZrI_4}$ (g) = 4ZrI (reaction (3) above) as being responsibe for crack propagation: $\mathrm{ZrI_4}$ vapour converts Zr to ZrI (solid) on the Zr surface, which (having little tensile strength) will crack exposing further Zr. But it was later found that radiolytic iodine is highly available (see Section 4.3) and the alternative ZrI-producing reaction Zr + I(g) = ZrI etc. can occur much more strongly to directly convert Zr into the rising sequence of solid iodides.

The radiolytic $p(\mathrm{I})$ is high enough (see Table 1: typically 8.5×10^{-8} bar) to form all these iodides (see Fig. 5) and the highest member, $\mathrm{ZrI_4}$, is a volatile solid which will then diffuse as a vapour from the crack tip to its mouth, thus removing Zr and deepening the crack. Even at lower iodine pressures, since $\mathrm{ZrI_4}$ can exist in gaseous form, it is not necessary to reach the values of $p(\mathrm{I})$ shown in Fig. 5 to produce it. These values are for producing solid $\mathrm{ZrI_4}$ at unit activity, but a gas can be produced at any activity, much less than unity, for example. This is shown in Fig. 6 which gives the $p(\mathrm{ZrI_4})$ available over all the lower iodides (without needing any solid $\mathrm{ZrI_4}$ to be present).

Table 1
Effect of radiation on gas pressures in the fuel-cladding gap in a PWR pin at 650 K in the presence of condensed CsI; 2.9% burn-up; fission products in gap taken as 1% of total fission products in pin; partial pressures in bar. Differing radiochemical assumptions give alternate values shown in one case below. From Ball et al. [89]

p(CsI)	p(Cs)	p(I)	$p(I_2)$
Oxygen potential, RT ln $p(O_2) = -698$ kJ/mol			
Thermodynamic equilibrium			
1.8×10^{-8}	1.6×10^{-2}	1.2×10^{-29}	9.6×10^{-52}
With radiation			
1.8×10^{-8}	1.6×10^{-2}	1.8×10^{-15}	2.6×10^{-31}
1.8×10^{-8}	1.6×10^{-2}	2.5×10^{-17}	1.0×10^{-34}
Oxygen potential $= -400$ kJ/mol			
Thermodynamic equilibrium			
1.8×10^{-8}	4.6×10^{-14}	4.3×10^{-18}	1.2×10^{-28}
With radiation			
1.8×10^{-8}	4.6×10^{-14}	8.5×10^{-8}	2.6×10^{-6}

ZrI_4 is essential to deepen a crack by removing Zr (van Arkel mechanism), but is not essential to cause cracking; iodine will cause cracking by lowering the Zr bond energy.

The time needed to cover a freshly cracked metal surface with iodine will be less than the time for stress relaxation. Calculation of the time to form a monolayer of gas molecules on a surface, using basic gas theory, is possible [10]. The results show the short time (about 15–20 min.) needed for gaseous ZrI_4 to cover a fresh Zr surface when an I:Zr ratio of 2 is exceeded in the substrate around the crack. This model is in good agreement with the experimental threshold time for iodine SCC in laboratory experiments using 1 mbar p(I) at 400°C [10]. A minimum time is required to set up the correct chemistry (ZrI_4 production).

Failure times in ZrI_4 are much less than in iodine [59], which indicates that much of the incubation time may be used in forming a critical ZrI_4 concentration. Some of the lower iodides formed have layer lattices with easy cleavages [84,85] which could provide a micromechanism for transgranular cracking [86], but the absence of striations on fracture faces makes this improbable. Adsorption-induced pseudo-cleavage is a more likely mechanism [2,87].

4.3. Radiolysis

Radiolysis will greatly increase the chemical thermodynamically calculated p(I) values and suggests that I atoms are much more likely to be the active agent for SCC. Radiolysis produces iodine far in excess of the chemical thermodynamic equilibrium dissociation pressure over CsI. Radiolysis is athermal. Konashi et al. [17] calculate $p(I_2)$ over CsI during irradiation is 10^7 times greater than with no irradiation at 600°C inner cladding temperature and an oxygen potential $\{RT \ln p(O_2)\}$ of −418 kJ/mol. Further radiochemical calculations by Konashi et al. [88], which indicate that p(I) rises with temperature, are incorrect due to a units error making their calculated p(CsI) values 10 times too large and this was carried forward to their radiolysis values for p(I). Also, Ball et al. [89] and Burns et al. [90] mention that helium is well known to greatly sensitise the radiolytic decomposition of fission fragments [91], which must also be considered in calculating p(I). Table 1 gives values [89].

SEM photographs of cracks from failed reactor tubes are given by Yaggee et al. [25]. They also report [25] that 6 and 0.6 mg/cm^2 iodine gave similar results on irradiated claddings. 0.05 mg/cm^2 showed increased times to failure [92] on unirradiated claddings. The time to failure is inversely proportional to iodine concentration down to 0.001 mg/cm^2 [81].

4.4. Role of CsI

CsI has a melting point of 626°C and boils at 1280°C. It is the stablest iodide known. CsI crystals have been found in the fuel-Zircaloy gap [93,94]. The thermodynamics of CsI + Zr = ZrI + Cs is unfavourable (very low K_p value) [16]. The fractography of PCI cracks and the small strains to failure are similar to ISCC produced in laboratory tests and are also similar to those produced by other SCC agents like Cd (less likely) [95] and Cs [96].

A simple chemical thermodynamic treatment (but neglecting radiolysis) is as follows.

As shown above, p(I) over a chemisorbed iodine monolayer is 10^{-19} bar at 600 K (normal Zircaloy cladding temperature). Lower pressures are at equilibrium with fractional iodine chemisorption (10^{-22} bar for $x = 0.1$ layer). Calculation is possible of p(I) produced in the fuel-gap from: $CsI(s) + 0.5UO_2(s) + 0.5O_2$ (from fuel) $= 0.5Cs_2UO_4(s) + I(g)$, for which $\Delta G^0 = 25 \pm 14$

$-(0.024 \pm 0.011)T$ kJ [78,97–99] which is about 10.6 kJ at 600 K.

The value of oxygen potential, RT $\ln(pO_2)$, in a typical fuel rod at 600 K is about −410 kJ/mol O_2 and so for 0.5 O_2 205 kJ is added to the above ΔG^0 to obtain 216 kJ and hence at 600 K, $p(I) = 10^{-19}$ bar [16,100]. This $p(I)$ is enough to form a chemisorbed iodine layer. Since K_p for the above reaction is $K_p = p(I)/(pO_2)^{1/2}$ (note all other reactants are solids and so have unit activity as long as any solid at all is present), the $p(I)$ is dependent on the $p(O_2)$ in the fuel. This $p(O_2)$ will increase with rod temperature, i.e. with power, and so $p(I)$ will also rise with power, but depending also on the change of K_p above which varies with temperature.

Calculations by Burns et al. [90] show that the above iodine pressure from chemical thermodynamics, at a fuel-cladding gap of a PWR rod is insufficient to cause a Zr–I reaction but radiolysis of CsI can cause enough iodine pressure for Zr–I reactions and ISCC (Table 1) [89].

As just mentioned, radiolysis will release I from CsI, well beyond the value of $p(I)$ calculated from chemical thermodynamics [101,102]. Laboratory experiments show that CsI does not cause SCC in the absence of radiation [103,104], but see below. Une [68] irradiated Zircaloy-2 for 8–24 h and reported cracking above 1.1 mg/cm^3 critical iodine concentration, but no cracking occurred (within 24 h) in the presence of CsI only. For $2Cs(g) + I_2(g) = 2CsI\ (s)$, $\Delta G^0 = -754$ kJ at 350°C [51,52]. Hence (neglecting radiolysis) $p(I_2) = 10^{-24}$ bar if $p(Cs) = 3 \times 10^{-4}$ bar at 350°C. Wood and Hardy [104] also report no cracking with CsI only, present. Une [68] concludes that metallic Cs and Cs_2O will supress ISCC. The oxide reaction is

$$I_2(g) + Cs_2O(s) = 2CsI(s) + 1/2O_2;$$
$$\Delta G^0 = -465 \text{ kJ at } 350°\text{C}.$$

However, the tubes used by Une [68] were irradiated only for 24 h and his tests were for a maximum of 24 h and although ISCC is said to occur within a 24 h period, it may be unrealistic to use only 24 h pre-irradiated Zircaloy and to limit testing to 24 h. The above conclusions that CsI only cannot cause ISCC may not be correct. Many experiments have failed to show SCC with unirradiated and irradiated CsI [5,68,104–108]. There may be a ‘window’ in which CsI will not cause SCC. Cox et al. [109] reports laboratory SCC experiments with 10% solutions of CsI in molten nitrates.

Also Une [68] reports that Cs reacts with UO_2, with cladding components and with other fission products, causing pin swelling and corrosion at higher oxygen concentrations. Some phase diagram studies are available [110–113]. Small, possibly molten, globules of Cs–U–O compounds are reported [3,34,59,107,114–118]. It is reported [109] that Cs^+ ions in the absence of iodine do not cause SCC.

Ohuchi [119] gives the following empirical equation for the weight w (mg Cs/cm^2) deposited inside cladding as a function of burnup B (GW d/t U): $w = 0.00019B(F + 1)$, where F = fission gas release %.

The report that CsI itself does not cause SCC also conflicts with previous work on hot salt SCC [120–123]. But covering of the metal surface by molten salt is a pre-requisite for SCC, and this condition may not occur with the small quantity of iodine available. SCC caused by CsI has longer times to failure than SCC by iodine vapour [109], which suggests that radiolysis of CsI is important.

The transport of cesium and iodine within the fuel occurs at different rates [14]. Analyses showed that iodine migrates slightly faster than Cs [14], Fig. 7. Cs is partly dissolved in the fuel matrix. The iodine concentration is highest in the fuel-cladding gap [14]. Post-irradiation analyses show iodides of Cs, Ba, Mo, Mn and Ag in the fuel-cladding gap [14].

Lysell and Schrire [15] report the fission product distribution and concentrations in fuel rods and that a surplus of iodine over cesium could reach the cladding during a power ramp. Gamma scans showed iodine and cesium from pellet centres were concentrated at the PCI.

The chemical thermodynamics of UO_2 + CsI reactions forming Cs_2UO_4 and $Cs_2U_4O_{12}$ is given by Götzmann [80]. For normal operating temperatures of about 360°C, $p(I)$ for equilibrium between CsI and UO_2 at an oxygen potential of −350 kJ is just below the SCC criterion. Götzmann [80] also considers Mo (fission product) in possible CsI, Mo, O reactions which could increase $p(I)$. But radiolysis will modify the results of chemical thermodynamic calculations and thermody-

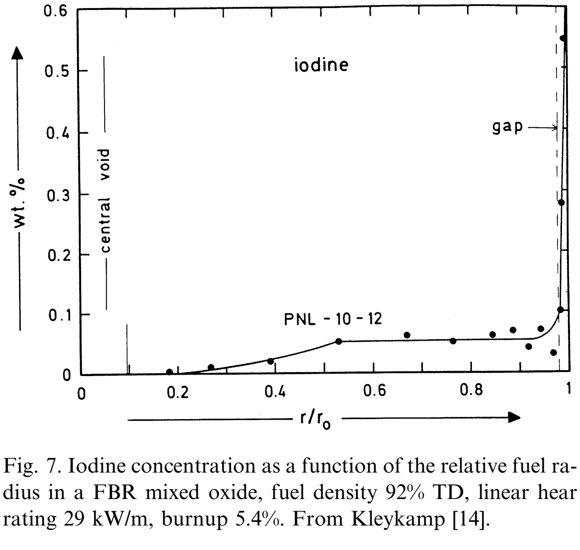

Fig. 7. Iodine concentration as a function of the relative fuel radius in a FBR mixed oxide, fuel density 92% TD, linear hear rating 29 kW/m, burnup 5.4%. From Kleykamp [14].

namic predictions alone will be unreliable and likely to be incorrect by a large factor. Direct radiolysis of CsI will increase $p(\mathrm{I})$. Götzmann [80] considers that in a fuel rod, the iodine carrier is not free iodine nor ZrI_4 and can only be CsI. Wood suggests FeI_2 [56]. Götzmann [80] suggests $p(\mathrm{I}) =$ about 10^{-10} bar. At 360°C, $p(\mathrm{CsI}) = 10^{-7}$ bar over pure condensed phase CsI.

Tasooji et al. [18] (discussion) report that free iodine was detected in irradiated oxide fuels, perhaps due to: $4CsI + O_2 \rightarrow 2Cs_2O + 2I_2$. But it would also be due to radiolysis.

The needle- and rod-like picture of CsI by [124] (their figs. 2–4(c) and (d), pp. 2–8), indicates vapour deposition of CsI into this morphology.

Tasooji et al. [18] also mention irradiation causing dissociation and a fluxing mixture which could dissolve CsI and provide easy ionic transport for I^- ions, like 'hot salt cracking' of Ti alloys which has also been demonstrated with Zircaloy using KI in mixed nitrate melts. If an ionic transport route exists for iodide ion to reach a crack tip, then cracking may be possible by 'hot salt cracking'; for chloride ion, cracking occurs with only 1 μg, but there are no data for iodide ions. Low melting fission compounds may produce a suitable salt melt at cladding temperatures. Tasooji et al. [18] (discussion) also reports that pure CsI does not cause SCC but cesium uranate and molybdate may do so. They give 9.5×10^{-7} g/cm^2 as the minimum external iodine concentration for SCC (value of I_{IG} for 448 MPa hoop stress in the SCCIG model) and this value depends on the applied stress. Below 448 MPa failure is intergranular and above this is transgranular and at iodine concentrations below I_{IG} [18]. An iodine concentration of 9.5×10^{-6} kg/m^2 is produced at the inner tube wall by a burnup of about 5 MWd/kg U, assuming 1% fission gas release [18]. Cs_2O will form preferentially to CsI [67]. Bouffioux et al. [67] shows $p(\mathrm{CsI})$ vs. T.

4.5. Other reactions

Ohuchi [119] reports that fuel-cladding deposits contain Ag, Cd, Te, I, Cs, Ba, O and U. The Cs:I ratio is 1:1. The Cs:Te ratio is 2:10 in tiny nodules and 2:1 in more massive deposits ($CsTe_2$) [119]. Kleykamp [14] reports 960 ppm of Cs after 1% burnup and 1 year cooling time. He lists 24 metals and Te, I and inert gases as fission products and describes phase diagram studies. Isothermal (1300°C) release measurements of cesium and iodine from highly irradiated LWR fuels show a higher fraction of iodine [125]. Mild transients on pre-irradiated FBR fuel showed iodine completely released but Cs only negligibly changed. Preferential iodine attack is reported at Fe inclusions [92,117,124].

Thermodynamic calculations [53,126] are reported to show that no free iodine or bromine can be expected in Zircaloy clad fuel rods. But this statement is not correct because iodine can exist as a vapour, even below its boiling point of course and it can exist in thermodynamic equilibrium with any iodide.

5. Attack by iodine

5.1. General

The failure strain in iodine is much lower than that for the presence of Cd, which suggests that ISCC is more relevant to PCI failures than is Cd cracking [95].

Gartner and LaVake [9] report Cs and iodine diffusing out of the UO_2; iodine migration began at 300 W/cm linear heat rating and increased with power but was independent of fuel burnup. The release of fission gas followed the square root of time, for high burnup fuel for hold times above 10 min, which indicates diffusion. Since bulk (lattice) diffusion of I in Zircaloy is very slow ($D = 1.6 \times 10^{-19}$ m^2/s at 450°C [127], it is likely that surface diffusion and adsorption are rate controlling [18].

Iodine reacts rapidly with Zr at 340°C producing pits [83]. Gaseous ZrI_4 decomposes increasingly to Zr and iodine at increasing temperatures (van Arkel) and so it can ferry Zr from a crack tip (cooler, near water) where it forms some ZrI_4, to a crack mouth (hotter, near fuel) where it thermally decomposes, dumping Zr and forming iodine gas which goes down to the crack tip again to form more ZrI_4 cyclicly. This micromechanism also explains why iodide-forming impurities like Fe are also dumped at crack mouths, being also concentrated there by a similar van Arkel process for impurities also having volatile iodides which preferentially decompose in hotter regions. Impurities at crack mouths may thus be formed this way rather than pre-existing the cracking process. Another mechanism (now abandoned) involved formation and brittle cracking of a solid reaction product, but no evidence could be found.

For V-bent specimens, pit numbers are greatest at high tensile stress regions, perhaps due to cracks in oxide films. Pits line up in bands, boat-shaped in stressed regions. Localised attack is found at intermetallic particles, especially with bent specimens [7,92]. But the first step in SCC is usually selective corrosion of grain boundaries, with maximum rate perpendicular to stress and only occurring above the threshold stress. Preoxidised Zr took weeks to start reacting with iodine, if unstressed and unstrained. If strained but exposed unstressed, pits began in oxide cracks [83]. There were 3 cm^3 of air present in the laboratory experimental setup, which caused oxidation.

It is often assumed that iodine cannot penetrate such oxide films nor films normally found inside the cladding tubes of reactors (but see later). Thus, strain induced oxide film cracking is an essential step for SCC. This occurs at strains below 0.5% [92]. For unirradiated annealed Zircaloy 2, the threshold SCC stress needs a 10% strain at 340°C; in this case, oxide cracking occurs before the SCC threshold is reached. For hard Zircaloy and irradiated material, the strain at the SCC threshold stress is much less and so oxide cracking may be a critical event.

Sejnoha and Wood [58] report that surface pitting increases with iodine concentration. They also found that notches did not induce iodine SCC, but sharp cracks did propagate, which shows the importance of crack tip geometry. Cracking of stress-relieved Zircaloy occurred away from surface scratches in iodine vapour at 573 K, but in contrast, cracks always nucleated at scratches in methanol–iodine at 293 K [58]. This does not mean K_{ISCC} for methanol–iodine cracking is less than in iodine vapour because tests showed K_{ISCC} to be slightly more in methanol–iodine solution than in iodine vapour [47]. Instead, it is concluded [58] that in iodine vapour, irregularities such as intermetallic precipitates or slip steps either raised the stress or subtly controlled the local chemistry to give favourable SCC conditions in iodine vapour.

5.2. Role of oxide layer

The reaction of iodine with Zircaloy is rapid unless a protective oxide is present. But iodine can penetrate thin oxides [128]. Pits were observed in unstressed unoxidised Zircaloy in iodine, showing that iodine can penetrate thin air-formed oxide films [129], but these isolated pits do not correlate with iodine-induced crack nuclei. Roberts et al. [129] suggest that iodine cannot rapidly penetrate oxides (>0.5 μm) on inside surfaces of irradiated fuel cladding unless mechanical rupture occurs. Hence the cladding must attain sufficient strain to do this. 1 and 3 μm thick oxides were cracked when unirradiated Zircaloy was given a total (elastic plus plastic) strain of above 0.4% at reactor operating temperatures [129]. The threshold stress of 280 MPa for ISCC was unaffected by preoxidation, which means that oxide penetration (although necessary) does not imply that SCC will actually occur: penetration is not the critical step in ISCC.

Fig. 8 shows the results of calculations on iodine attack [7]. Fig. 9 [39] shows iodine and ramp conditions for Figs. 10 and 11 [9]. Fig. 9 is a model where cladding temperature, hoop stress and iodine concentration rise for 0.6 h and simple fracture and experimental chemical calculations [21,81] are used to calculate the crack growth, but an assumption that iodine attack of the cladding cannot occur until its inner oxide film has cracked at an arbitrary 135 MPa may be incorrect because hot corrosion studies on gas turbine alloys show that a pre-oxidised metal shows instant cracking of surface oxide films when NaCl vapour is introduced [130].

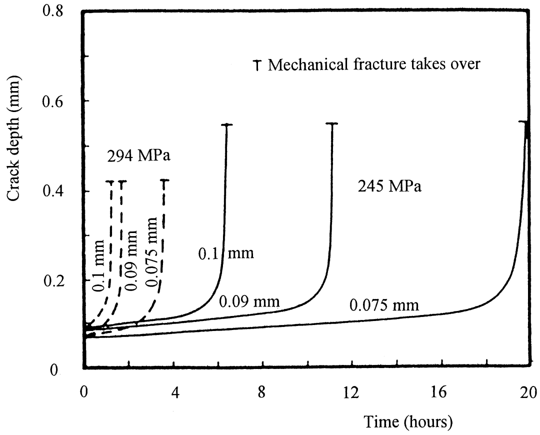

Fig. 8. Crack propagation as a function of time for recrystallized Zircaloy-2 at 340°C and with 3 mg iodine per cm^3. The curves apply for the three different depths of starting defects shown, having a length of five times the indicated depth. From Videm and Lunde [6].

From these calculations, Fig. 10 shows ISCC on unirradiated cladding and Fig. 11 on irradiated cladding [39]. For the unirradiated cladding (Fig. 10), crack growth starts at 0.2 h and continues during the ramp (Fig. 9), but never reaches the critical length a_c for starting cleavage and fluting. So no failure occurs. But for the

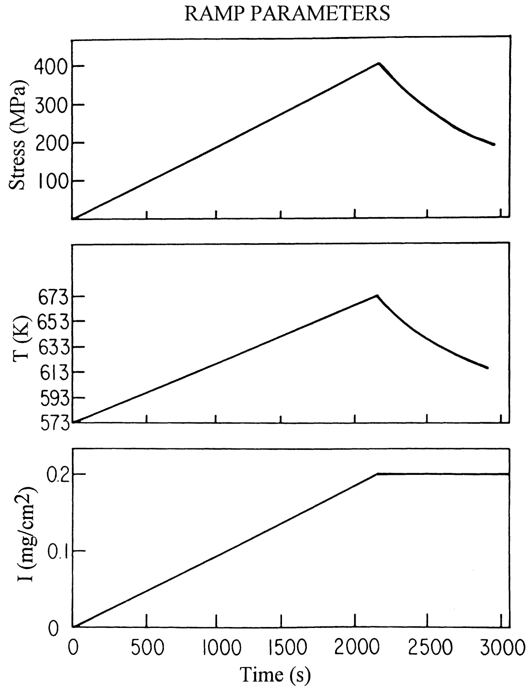

Fig. 9. Ramp parameters for Figs. 10 and 11. From Yaggee et al. [39].

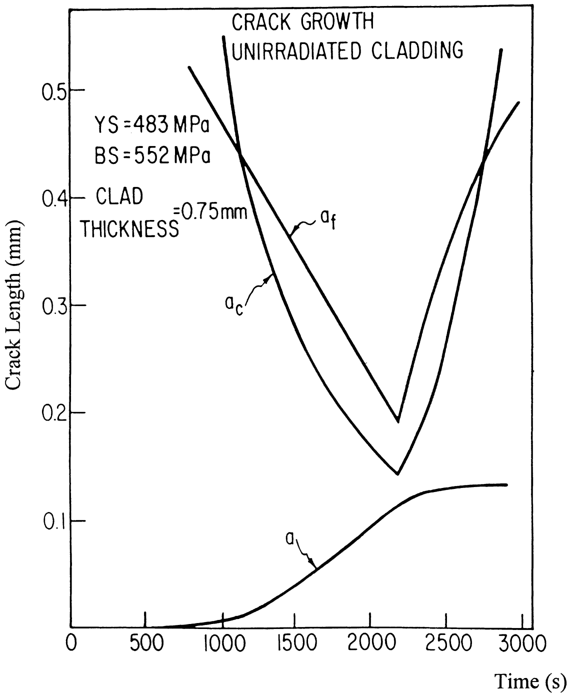

Fig. 10. Change in crack length, a, with time in unirradiated Zircaloy cladding for the power ramp conditions shown in Fig. 9; a_c = critical crack length where cleavage and fluting start; a_f = critical crack length where failure occurs by stress rupture; $\sigma_{ys} = 483$ MPa, $\sigma_B = 552$ MPa, cladding thickness = 0.75 mm.

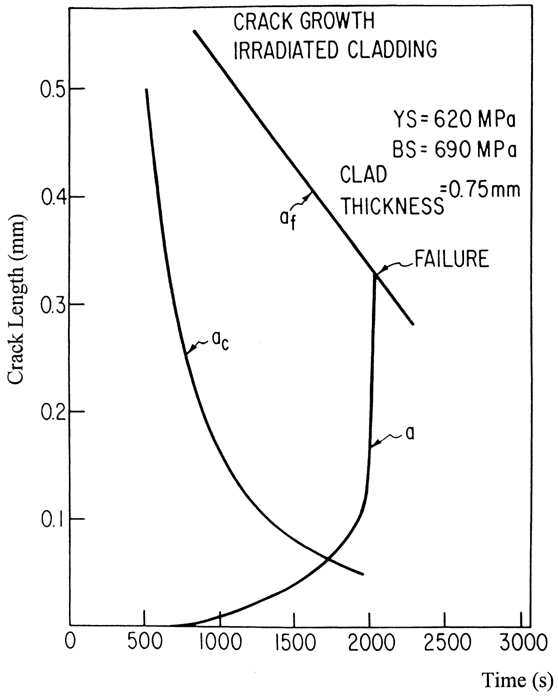

Fig. 11. Change in crack length, a, with time in irradiated Zircaloy cladding for the power ramp conditions shown in Fig. 9; a_c = critical crack length where cleavage and fluting start; a_f = critical crack length where failure occurs by stress rupture; $\sigma_{ys} = 620$ MPa, $\sigma_B = 690$ MPa, cladding thickness = 0.75 mm.

irradiated cladding, a_c is reached at 0.48 h (a intersects a_c) and failure occurs soon after by rapid crack growth by cleavage and fluting (intersection of a and a_f, stress rupture). In this example, 85% of the time to failure is chemical growth to less than 10% of the cladding thickness.

Oxide growing in an iodine environment will thicken up to several μm but incorporation of iodine during growth prevents it from being protective and hence irradiated tubing cannot be assumed less susceptible to ISCC due to its thicker oxide. Oxide films on ex-reactor tube interiors are observed to be 1–20 μm thick [8,12,39,131–133].

Against the above comments on the effect of oxide films, Yaggee et al. [25] report that Zircaloy tubes with thick oxide inhibit ISCC by a simple barrier effect by the compressive stress due to the volume (Pilling–Bedworth) ratio of oxide to metal for ZrO_2. This stress must be overcome before SCC can occur. Thick, high quality unbreached oxide is an important factor in ISCC susceptibility [124], providing an iodine barrier up to moderate fluences of about 10^{21} neutrons/cm^2. Tube claddings from reactors with such oxide were found to have a high threshold stress for SCC of about 280 MPa; this is about the same as that for unirradated stress-relieved cladding [92]. ISCC occurred only after such oxide was mechanically breached [124]. Loss of ductility at fracture of Zircaloy-4 is greater when iodine is admitted in vacuum than in air [134]. However, an oxide film should not be relied on as a long-term method for protection against ISCC.

6. Role of metal iodides [135]

6.1. General

SCC of Zircaloy-2 by FeI_2, AlI_3 and ZrI_4 is reported [30,115]. SCC of Zircaloy-4 by ZrI_4, TeI_4 and I_2O_5 (iodine pentoxide) is reported [129]. ZrI_4 was found to be the main gaseous iodine species by [136]. Reactions involving iodine and 15 metal iodides in Zircaloy tubing at 400°C with internal Ar pressurization to a hoop stress of 293 MPa, were studied by [66].

Nagai et al. [135] give ΔG^0 for the reaction $(4/x)MI_x + Zr \rightarrow ZrI_4 + (4/x)M$, where M = element. They show that all those reactions with negative ΔG^0 rapidly caused SCC, while those with positive values caused no SCC, but no correlation was found for the aggressiveness of attack. SEM showed pits on all SCC specimens and the shorter the time to failure, the more pits existed, which suggests chemical reaction is a controlling factor in SCC susceptibility [135]. The lowest time to failure was with ZrI_4 vapour but a much greater time is needed for ZrI_4 solid in contact. This suggests that ZrI_4 produced by a reaction between another metal iodide and Zr may cause SCC, rather than the other metal iodide itself directly [135].

Traces of Fe, Cr and Ni in Zircaloy occur as precipitated compounds. The iodine reaction rate with Fe and Ni was much higher than with Zr at in-reactor temperatures and so precipitated phases will react with excess iodine to form metal iodides and thus supply ZrI_4 locally [135].

6.2. Effect of impurities

Other fission products (besides iodine) can cause SCC [96]. SEM studies of capsule experiments in which Zircaloy reacts with ZrI_4 vapour showed that the sites which reacted most contained impurities like Fe, Si and Ti [16]. The mixed iodides ($ZrMI_x$) may be more stable than ZrI or perhaps the kinetics is faster [16]. Iodine is incorporated into Zircaloy containing impurities. Cracking is more likely near impurities and then propagation starts. Residual stress and cladding texture are other factors. Iron and other impurities may act as microgalvanic couple generators in the presence of a molten salt electrolyte.

ISCC crack sites are found near high local impurity concentrations (Fe, Cr, Si, Al, etc.) [29,34,92,137], especially Fe. In one report Fe was all near the Zircaloy inner surface and when a 60 μm layer was removed, ISCC tests showed a 20-fold improvement [138]. Brittle iron-rich grain boundary inclusions also crack at small strains [139]. But tubing regions containing impurities (Ti,Fe, etc.) have never been found in Chalk River CANDU cladding and yet ISCC occurs.

Zones up to several hundred μm size, containing a few % Fe, Al, Si, etc., were found at crack origins [34,92]. This may mean a defect in quality control methods (see below); one problem is that SEM, EDX, etc. are unsuited to inspecting large areas, while eddy current and ultrasonic methods will not detect chemical inhomogeneities. Chung et al. [140] give an opinion that eddy current tests show that there are no such defects present. But in fact they can be detected (in retrospect) by SCC itself, at SCC cracks. ISCC becomes less as the size of such impurity sites decreases [34]. Fe acts as an ISCC catalyst [56].

The presence of Fe concentrations at ISCC crack sites may be compared with the well-known observation that low sputtering yield species are often found on surfaces after prolonged sputtering [141,142], i.e. Fe could be 'distilled' and concentrated there from the removed crack material (mentioned above). Such deposits [34] are often associated with extensive intergranular attack at the start of cracking.

Tasooji et al. [143] have exposed large areas of (unirradiated) Zircaloy claddings to dilute radioactive iodine solution at zero applied stress. They found that iodine is preferentially adsorbed at chemical inhomogeneities. Autoradiography detected widely separated sites up to 2.5 mm size and these were then analysed by SEM. A correlation was found that resistance to SCC rises substantially as inhomogeneity falls, even if the texture is kept constant [143]. A correlation was later found between these sites and aqueous corrosion [143]. Tasooji et al. [143] speculate that as ZrO_2 and H are formed in aqueous corrosion, absorption of H by Zircaloy occurs and grain structure discontinuities provide hydride nucleation sites since the volume expansion (11 to 23%) can be accommodated there [144,145]. Chemical inhomogeneities are a type of discontinuity. $ZrFe_2H_{0.2}$ and $ZrCr_2H_{3.6}$ are stable to high temperatures [146] and are used as materials for H storage. Tasooji et al. [143] develop this theory to explain Zircaloy aqueous corrosion effects. They also show that chemical inhomogeneities are not formed during tube reduction processes but earlier at much higher temperatures [143]. Zircaloy having low chemical inhomogeneity content has better PCI resistance in reactor ramp tests and so the effect probably carries over to irradiated Zircaloy [146].

Cox et al. have studied the SCC of Zr alloys by methyl iodide and the deleterious effect of sealing materials in the form of 'O'-rings and PTFE is discussed [109]. But silicone grease was accidentally found to 'getter' iodine vapour and prevent ISCC. Hence siloxane coatings were developed for preventing ISCC and give a better performance [3] than graphite CANLUB coatings [3,147] but there are some adverse aspects.

Rowland et al. [148] tabulate failure data. Foster and Leasure [149] also describe graphite-lined Zircaloy tubes which have better fracture resistance, perhaps partly due to a physical barrier effect preventing core iodine reaching the cladding easily. There may be a beneficial stress-distributing cushion effect. ISCC was found to begin at Fe-rich precipitates at grain boundaries [150], cracking increasing with their volume fraction and correlating with a ductility decrease with rising Fe content from 260 to 630 ppm. $Zr_6I_{12}C$ cluster compounds have been suggested as an iodine getter [3].

High purity Zr cladding liners were tested and none failed in severe conditions and high burnups [148]; such Zr liners, co-extruded with the Zircaloy tube, to prevent ISCC have also been reported by other workers [4,151–156]. Some problems using Zr sponge liners with oxygen content above 500 ppm have been mentioned [152].

Strasser [157] cites three parameters of pure Zr liners which need investigation:

1. The liner thickness (nominally 75 μm) has no non-destructive testing (NDT) method to verify thickness along the tube. Etching during manufacture (to remove microfissures from the tube reduction process) may not be uniform.
2. The soft Zr liner deforms differently, during manufacture, from the Zircaloy tube. Defects produced may impair its ISCC resistance.
3. The liner is soft to resist PCI but oxygen uptake can harden it during manufacture, which cannot be checked.

Inhomogeneities in Zircaloy cladding tubes, along the tube length have been noted, from waterside corrosion [157].

7. Conclusion

The factors causing ISCC in unlined Zircaloy tubes are a minimum strain rate, a minimum iodine concentration and a minimum time. Stress relaxation can occur, preventing ISCC, if a minimum strain rate is not reached; the ISCC stress threshold is so high that tubes slowly deform at this stress. Closure of the UO_2-fuel-Zircaloy-cladding gap, which occurs soon after a new tube is put into service, causes a strain rate which is high enough to start ISCC, in a power ramp which is steep enough. Both I and ZrI_4 cause ISCC. Radiolytic I far exceeds chemical thermodynamic value of $p(I)$/CsI. A minimum iodine concentration is needed to cause the van Arkel vapour transport of Zr as Zr vapour, out of cracks in the zirconia scale which occur due to the strain. A minimum time is needed to allow this iodine concentration to appear and short-lived iodine fission products (created in a power ramp) play a significant part in this. After a ramp is over, most of the free iodine produced is gettered by unstressed Zircaloy areas away from likely crack sites and so for a subsequent ramp to cause ISCC a further minimum time period is needed to re-establish again the necessary iodine pressure.

The function of the involatile solid iodides (ZrI, ZrI_2, ZrI_3) is to protect the crack sides: the classic stress corrosion cracking mechanism; the volatile iodide, ZrI_4 (with vapour pressure about 0.4 bar at 680 K cladding inner wall temperature), then forms by iodine reacting with fresh Zr at the crack tip, which is exposed by the stress concentration there cracking any protective cover. For $Zr + 4I = ZrI_4\ (g)$, the chemical equilibrium constant K_p is 1044 at 680 K.

As discussed by Cox et al. [1], many laboratory experiments do not simulate the correct in-reactor conditions for ISCC and so their results may not be applicable to reactors. A conclusion drawn from these, that CsI does not cause ISCC, thus seems invalid. More important is the effect of radiolysis on $p(I)$ over CsI (see Table 1) which generates many orders of magnitude more iodine pressure than chemical thermodynamic calculations predict.

Zirconia protective scale on the inner Zircaloy wall will crack at fuel crack ends due to: (a) sudden fuel thermal expansion in a power ramp; (b) a sudden rise in $p(I)$ arriving at the end of a crack in the UO_2 pellet: the sudden cracking of oxides by halide vapours has been demonstrated [130].

When a pit caused by a chemical van Arkel mechanism has deepened to about 70–100 μm, stress-intensity control of cracking can take over, although there is some disagreement about the critical crack depth for this [6,21,26,34,40]. Once catastrophic cracking begins, it is reported to advance at about 9 μm/s, which means a 600 μm tube wall would fail in about 70 s.

Considering the foregoing, some prevention methods are apparent:

1. Use of a softer fuel, to prevent hard gap closure – a small niobium oxide content in the UO_2 fuel, for example, gives this effect.
2. Having a hole in the centre of the UO_2 fuel pellets reduces the gap closure force, but it allows less fuel per rod.
3. SCC is usually confined to alloys and does not affect pure metals. This classic way of stress corrosion cracking prevention is in current use – a pure Zr cladding on the inside of the Zircaloy tube. Coating methods are reviewed by Hocking et al. [158].

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