THERMOCHEMICAL REACTIONS IN PARTIALLY EXPOSED NUCLEAR FUEL

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ABSTRACT

Oxidation of fuel-cladding during a hypothetical severe accident in light water reactors is theoretically investigated in an attempt to realistically simulate the time dependent heat generation in a partially uncovered reactor core. Two modes of oxidation, heterogeneous and homogeneous, are generally considered. Heterogeneous oxidation refers to chemical reactions with steam at the outer cladding surface in which a dense oxide layer is formed that physically hinders the oxidant from reaching the reacting metal. That mode of oxidation may not fully explain the kinetics of cladding oxidation following severe accident, where thermochemical reactions take place in pores and cracks inside the metal. A theoretical model is, therefore, developed to quantitatively understand the homogeneous oxidation of degraded fuel cladding. A dimensionless cracks' concentration parameter, ψ, is developed in order to study the effect of cracks on the ignition temperature of zirconium. A critical parameter, η_{max}, is identified above which runaway ignition conditions are expected.

Steam temperature and decay power are the main conditions leading to cladding heterogeneous ignition. Cracks density could be important for evaluating homogeneous oxidation of degraded cladding.

INTRODUCTION

Thermo-chemical reactions between fuel cladding and a hot steam environment have to be considered for realistically estimating the thermal-hydraulic behaviour of a nuclear reactor under severe accident conditions. Recent interest in zirconium oxidation has concentrated on the exothermic nature of the reaction and the hypothetical possibility of reaching runaway conditions during a reactor transient. The chemistry and kinetics of the oxidation of zirconium at moderate temperature has been a subject of extensive studies for the past 50 years [1,2]. It seems to be qualitatively agreed-upon that at temperatures below ca 800 ^{o}C oxidation may be considered as a heterogeneous surface phenomenon in which a dense oxide layer is formed that physically hinders the oxidant from reaching the reacting metal. As the oxide layer thickness increases, the rate of additional oxide layer growth varies inversely with the layer thickness (parabolic law) for a given temperature [2,3,4]. For safety evaluation, a predetermined maximum temperature and oxidized layer thickness, based on the parabolic law, are defined to guarantee cladding integrity during design-base accident conditions. Data are typically based on out-of-pile oxidation experiments using small specimens of cladding material [4,5,6]. Major mechanistic severe accident codes [7,8] generally contain empirical models and correlations for conservative estimation of cladding integrity and excess hydrogen generation during quenching following hypothetical severe accident.

NOMENCLATURE

A	[kg^2/m^{4}s]	Parabolic law pre-exponent
a	[m]	Sample half thickness
$C_{1,2}$	[-]	Coefficients
E	[J/mole]	Activation energy
Q	[W/m^3]	Volumetric heat of reaction
R	[W/mole-K]	Gas law constant
T	[K]	Temperature
T_0	[K]	Surface temperature
W	[1/s]	Reaction velocity
x	[m]	Cartesian coordinate
z	[-]	Dimensionless coordinate

Special characters

α	[m^2]	Surface oxide area per unit volume
δ	[m]	Oxide layer thickness prior to ignition
φ	[1/s]	Density rate of reaction
λ	[W/m-K]	Thermal conductivity
θ	[-]	Dimensionless temperature
η	[-]	Dimensionless internal heating
ξ	[-]	Dimensionless temperature gradient
ψ	[-]	Dimensionless cracking parameter

An extensive review of the theory of oxidation [9] demonstrates complex relationships between the rate of metal oxidation in an oxidizing environment and the thermal-hydraulic conditions in both the solid and the surrounding oxidant. Hence, critical conditions for thermal runaway oxidation in metal must rely on simultaneously solving the transient mass and heat balance equations in the oxide layer [3]. That concept has been applied in [10] to determine the necessary channel conditions that could lead to an uncontrolled escalation of the metal temperature and the oxide layer thickness. In both of the latter references an assumed heat transfer coefficient was used parametrically to account for the thermal-hydraulic conditions in the flow channel.

Heterogeneous surface reactions may not fully explain the kinetics of cladding oxidation under severe accident conditions. It was established that the quenching could cause reheating of the rod, enhanced oxidation and a sharp increase in hydrogen production, which might threaten the containment integrity. While detailed mechanisms of are not well established, clad heating and enhanced hydrogen generation may well be related to a number of physiochemical phenomena, such as cracking, decomposition, melting and swelling typically accompanying metal oxidation during severe accident [1,2]. The mechanical behavior of hot cladding during quenching was experimentally shown to depend on both the quench temperature and the extent of oxidation prior to quenching [11]. A multitude of through-cladding crack formations have been observed, which could not be accounted for by the surface oxidation models of intact cladding [11]. It is thus hypothesized that under certain conditions relevant to severe accident conditions, thermo-chemical reactions may take place in pores and cracks inside the metal volume. Volume oxidation may proceed violently in an uncontrolled manner leading to ignition or thermal explosion of the oxidizing specimen. Full quantitative understanding of degraded metal oxidation is still at large, yet it could be mathematically described by existing models of homogeneous oxidation.

The theory of homogeneous thermal explosion was first introduced by Semenov [12]. Assuming uniform temperature in the solid, he defined a critical temperature above which a steady-state solution cannot exist, i.e., if the reactant temperature exceeds the critical value, the material self-heats and thermal explosion results. Frank-Kamenetzky [13] and later Chambre [14] extended the theory of ignition by postulating that a critical homogeneous runaway condition is reached when the amount of heat developed by the chemical reaction in the volume is just equal to the amount lost to the surroundings. Their model avoids the use of the concept of heat transfer coefficient by assuming that the loss of heat to the walls, which must be in balance with the chemical heat generation, takes place entirely by conduction within the volume interior. The critical ignition condition requires the solution of the nonlinear Poisson-Boltzmann differential equation. A closed form analytical solution was derived [13,14] by resorting to an approximation of the heat generation term, which is valid when the ratio between the metal and the boundary temperatures is close to unity. An exact solution to the one-dimensional steady-state energy equation for slab was obtained in [15] using the Arrhenius internal heat generation law in terms of the unknown mid-plane temperature. The solution showed that the ignition process may be explained as a stability problem. The exact solution was originally developed using boundary conditions of the first kind (specified surface temperatures) and later extended to other more practical types of boundary conditions involving temperature gradients [16,17].

In the following the theory of homogeneous oxidation will be utilized to study the oxidation kinetics of a degraded fuel cladding. Since temperature variations across the relatively thin fuel cladding are expected to be small, the approximate solutions of [13] and [14] are deemed to be appropriate for determining a criterion for thermal explosion. The ignition model is described in the next section followed by numerical example related to typical nuclear reactor fuel cladding.

THE IGNITION MODEL

We consider thermal ignition in a section of fuel-rod cladding self-heated volumetrically by thermochemical oxidation reactions, which may also be heated on its inner surface by the decay products in the nuclear fuel and cooled by steam at its outer surface. Since clad thickness is typically small relative to its diameter, the sample may be described as a plane parallel thin plate. The one-dimensional steady-state heat conduction equation with an exothermic heat generation term for a one dimensional solid in Cartesian coordinates is,

$$\lambda \frac{d^2T}{dx^2} = -Q \cdot W \quad -a \leq x \leq a \tag{1}$$

where $T(x)$ is the metal temperature, $2a$ the sample thickness, Q the heat of reaction, λ the thermal conductivity and W the reaction velocity. As the oxidation reaction in steam follows zeroth-order Arrhenius law, then

$$W = \varphi \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where φ is the density rate of thermochemical reactions, E the energy of activation and R is the gas constant. Equation (1) becomes,

$$\frac{d^2T}{dx^2} = -\frac{Q}{\lambda} \varphi \exp\left(-\frac{E}{RT}\right) \tag{3}$$

This is a nonlinear steady-state differential equation whose solution yields the steady-state temperature profile in the self-heating slab. Following [13,14] we analyse an approximate form of eq. (3) by expanding the exponent term on the right-hand side as a series of the ratio $(T-T_0)/T_0$, where T_0 is the surface temperature, and neglecting powers higher than the first. Equation (3) is then rendered dimensionless by replacing the space coordinate x with $z = x/a$, where the plate's thickness, $2a$, is used as the significant geometric dimension of the sample, and defining a dimensionless temperature as,

$$\theta = \frac{E}{RT_0^2}(T - T_0) \tag{4}$$

The following dimensionless Poisson-Boltzmann equation is obtained,

$$\frac{d^2\theta}{dz^2} = -\eta e^\theta \quad -1 \leq z \leq 1 \tag{5}$$

where the dimensionless internal heating parameter is given by,

$$\eta = \frac{Q}{\lambda} \frac{E}{RT_0^2} a^2 \varphi \exp\left(-E/RT_o\right) \tag{6}$$

It is worthwhile to note that the approximation, eq. (5), is valid only for values of T/T0 close to unity, i.e., thin Zr cladding. Also, because of the steady state basis of eq. (5), reactant depletion is not considered. This is justified by the observation that runaway commences when a small percentage

of the reactants has been consumed, which requires that the reactants have not been depleted by being maintained in a temperature near the critical for long periods of time. The effect of diminishing reaction rates was studied by [19].

The original solution of eq. (5) [13] is modified here and used to study cladding ignition and to predict the maximum boundary temperature, which a self-heating solid can experience without undergoing accelerated decomposition. It was shown [13] that a steady state temperature profile could not exist in the slab when the characteristic parameter, η, exceeds a certain constant value. This can be readily explained by presenting the analytical solution of eq. (5) as,

$$\theta(z) = \ln\left\{\frac{c_1}{2\eta}\left[1 - \tanh^2\left(\frac{\sqrt{c_1}}{2}(c_2 + z)\right)\right]\right\} \quad (7)$$

The appropriate boundary conditions necessary for determining the coefficients, c_1 and c_2 depend on the physical conditions of the problem. For the analysis of thermal explosion of combustible material in a plane-parallel vessel, Frank-Kamentzky and Chambré [13,14] used boundary conditions of the first kind (specified temperature at the surface), which for the current problem of cladding oxidation may describe, e.g., a dislodged cladding section exposed to steam on its inner and outer surfaces,

$$z = 0, \qquad \frac{d\theta}{dz} = 0 \text{ (symmetry)}$$
$$z = 1, \qquad \theta = 0 \qquad (8)$$

From the first boundary condition one gets $c_2 = 0$ while the second boundary condition yields:

$$1 = \frac{c_1}{2\eta}\left(1 - \tanh^2\left(\frac{1}{2}\sqrt{c_1}\right)\right) \quad (9)$$

The functional relationship (9) between η and c_1 is plotted in Fig. 1, showing that η reaches a maximum value (at a critical c_1) above which the conduction equation has no solution. In Fig. 1 the maximum value of η for which a solution is possible is $\eta = 0.87846$ at $c_1 = 5.757$, which defines a criterion for thermal explosion.
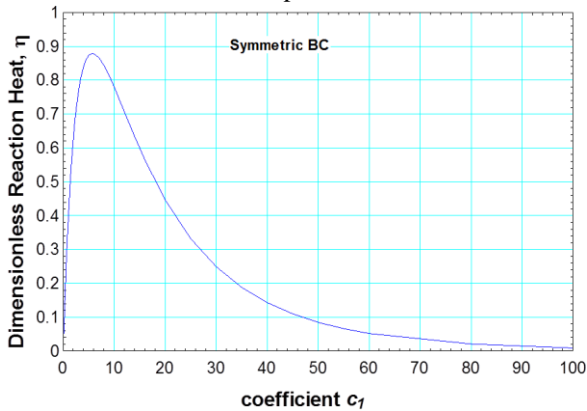
Figure 1 Relationship between η and the coefficient c_1: Symmetric boundary conditions

It is noted from Fig. 1 that at any values of η below its maximum, the solution (7) bifurcates into two stable temperature distributions as shown in Fig. 2, plotted for an arbitrary value of $\eta = 0.4$. Ignition problem becoming bifurcation problem is noted in e.g., [12,18] in the context of determination of critical ignition conditions in non-premixed counter-flows, as well as in explaining auto-ignition kinetics in time-evolving homogeneous systems. Realistic steady-state solution during heating generally follows the lower branch while the higher branch may be obtained during cooling from high temperature.
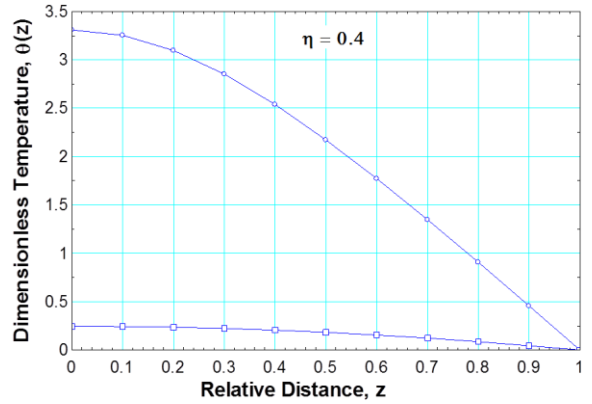
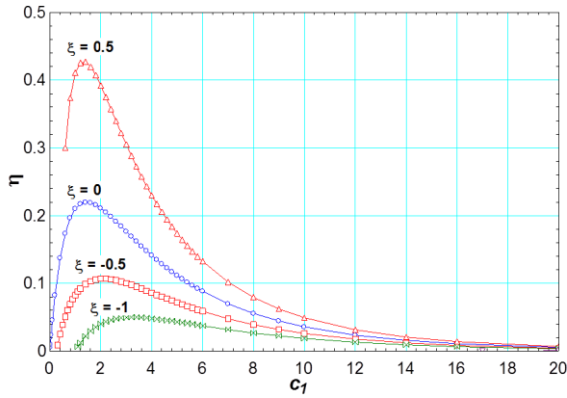**Figure 2** Dimensionless temperature distribution in the Zr for $\eta = 0.4$

When considering the oxidation of fuel cladding it is recognized that boundary conditions of the first kind, as in eq. (8), are not always realistic. During hypothetical severe accident conditions, the fuel cladding may be cooled by steam at its outer surface ($z = 1$) and heated by decay power at its inner surface ($z = -1$). An appropriate set of boundary conditions, in that case is,

$$z = -1, \qquad \frac{d\theta}{dz} = \xi$$
$$z = 1, \qquad \theta = 0 \qquad (10)$$

where ξ is a dimensionless temperature gradient at the inner cladding surface, which is related to decay heat flux at $z = -1$. Substituting θ from eq. (7) in eq. (10) results in two transcendental non-linear equations,

$$1 = \frac{c_1}{2\eta}\left\{1 - \tanh^2\left[0.5\sqrt{c_1}(c_2 + 1)\right]\right\}$$
$$\xi = -\sqrt{c_1}\tanh\left[0.5\sqrt{c_1}(c_2 - 1)\right] \qquad (11)$$

For a given temperature gradient, ξ, eqs. (11) have 3 unknowns, namely η, c_1 and c_2. Figures 3 and 4 demonstrate the solution of η vs. c_1 and c_2 vs. c_1 for a given ξ. Note that positive values of ξ indicate hypothetical cooling at $z = -1$ (an unrealistic condition in nuclear core) while $\xi \leq 0$ indicates insulated or heated left boundary. Solution for c_2 vs. c_1 is shown in Fig. 4 for with ξ as parameter.

Figure 3 Dimensionless chemical heat, η vs. coefficient c_1 from eq. (11)

It is noted from Fig. 3 that the maximum values of η, which define the critical ignition temperature, depend on the dimensionless temperature derivative (related to the decay heat), ξ, at the inner surface at $z = -1$. Higher absolute value of decay heat flux at the inner surface (negative ξ) decreases η_{max} as shown in Fig. 5. As discussed in the following section, the value of η_{max} defines the limiting ambient steam temperature above which oxidation proceeds in an explosive or runaway manner.
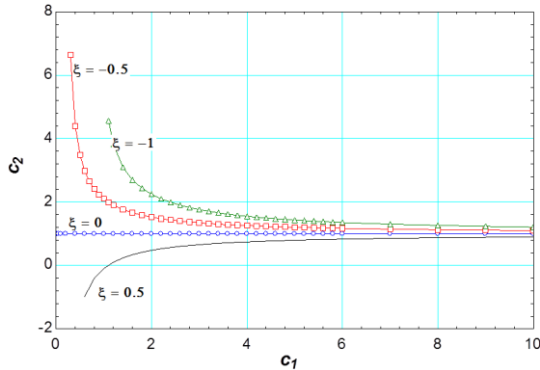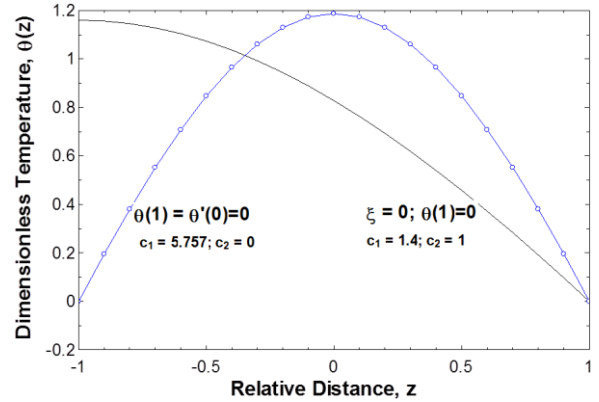

Figure 4 coefficient c_2 vs. c_1 from eq. (11)
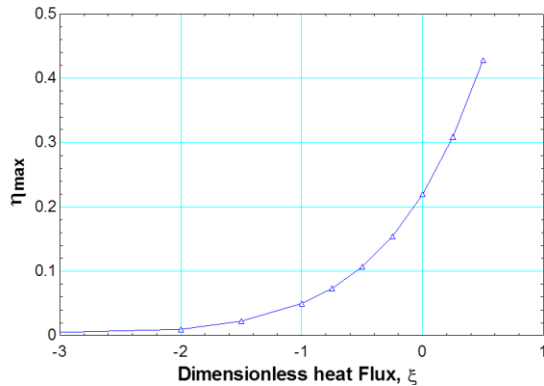
Figure 5 Maximum η vs. dimensionless heat flux at the left surface, ξ

Figure 6 compares the temperature distribution in the metal for two cases; insulated left surface, $\xi = 0$, and centerline

symmetry conditions, $\theta(1) = \theta'(0) = 0$. The high temperature at the left side of insulated metal is noticeable.

Figure 6 Temperature distribution in the metal for insulated left surface, $\xi = 0$, and centerline symmetry conditions,

ZIRCONIUM OXIDATION

The maximum value of η in eq. (6) basically defines critical conditions at ignition, namely thermal explosion. To demonstrate the utility of η for estimating ignition conditions in a typical fuel cladding, we must first define the density rate of thermochemical reactions, φ, and the effective thermal conductivity of the cracked zirconium. The thermal conductivity may be approximated by adopting a simplified porous material model [20], neglecting the steam conductivity relative to the solid's conductivity and assuming low porosity, resulting in, $\lambda \approx \lambda_{ZrO_2}$.

To estimate the reaction density rate, φ, we realize that in degraded cladding, oxidation basically takes place on the large effective surface of the cracks inside the metal. Hence, the parabolic reaction rates for Zircaloy [7,21] may still be utilized for deriving φ in eq. (2). However, since the oxidation area is not *apriori* known in a cracked cladding we introduce here a new specific area parameter, α, defined as the surface area of oxide per unit volume of the metal specimen. The volumetric pre-exponential rate coefficient in eq. (2) becomes,

$$\varphi = \alpha \frac{A}{2\delta \cdot \rho_{ZrO_2}\left(M_{Zr}/M_{ZrO_2}\right)} \quad kg/m^3 \cdot s \qquad (12)$$

where δ is the oxide layer thickness prior to ignition, ρ its density, $M_{Zr}/M_{ZrO_2} = 91/123$ is molecular mass ratio and $A\,[kg^2/m^4 \cdot s]$ is parabolic law pre-exponent [4]. Using eq. (12) the parameter η in eq. (6) becomes,

$$\eta = \frac{Q}{\lambda}\frac{E}{RT_0^2}a^2\,\varphi\,exp\left(-E/RT_o\right) =$$
$$= \frac{Q}{\lambda}\frac{E}{RT_0^2}\psi\,exp\left(-E/RT_o\right); \qquad \psi \propto a^2\frac{\alpha}{\delta} \qquad (13)$$

Here ψ is a dimensionless parameter that depends on the clad thickness, the degree of cracking and the initial thickness

of oxide layer prior to ignition. Figure 7 demonstrates the effect of the cracking parameter, ψ on the ignition temperature using the following data from Ref. 7 corresponding steam oxidation of zirconium and its oxide, zirconia,

$A = 29.6 \ kg^2 / m^4 \cdot s$; $\rho_{ZrO_2} = 5600 \ kg / m^3$;

$\lambda_{ZrO_2} = 8 \ W / m \cdot K$; $E / R = 16820 \ K$; $Q = 5817 \ kJ / kg - Zr$
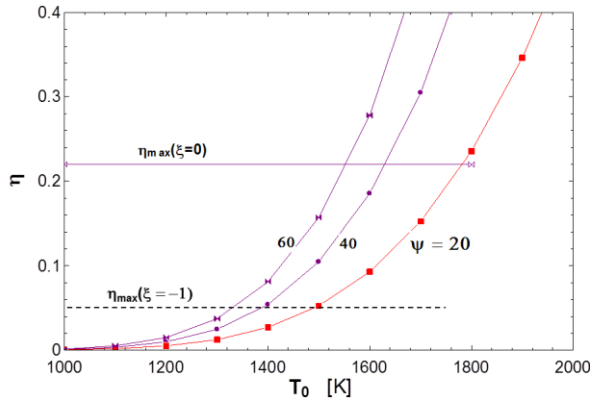
Figure 7 Parameter η vs. right surface temperature for dimensionless cracking parameters in the range, $20 \le \psi \le 60$

The critical values of η_{max} for an insulated ($\xi = 0$) and heated ($\xi = -1$) left surface are indicated in Fig. 7 by horizontal lines. Clearly the ignition temperature due to volumetric self-heating decreases as the dimensionless cracking parameter, ψ, increases. For example, for a $\psi = 20$ ignition due to volumetric oxidation may commence at a right surface temperature of about 1800 K whereas at $\psi = 60$ ignition may occur below 1600 K.
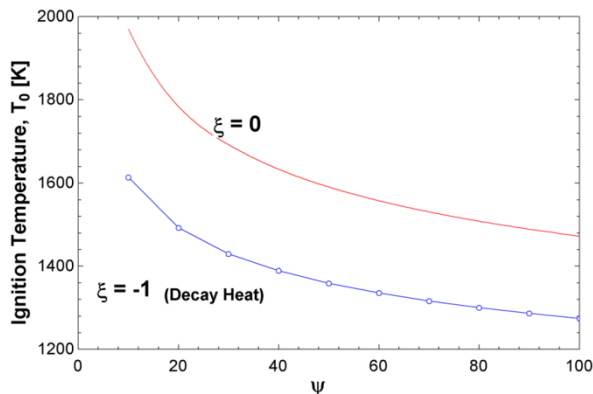
Figure 8 Ignition temperature as a function of ψ for a specimen with ($\xi = -1$) and without ($\xi = 0$) decay heat at inner surface

Figure 8 depicts the ignition temperature as a function of cracking parameter for a clad specimen with negligible decay heating at inner surface, $\xi = 0$ and one with decay heat, $\xi = -1$.

It is noted that at small ψ values, i.e., insignificant cracking, the volumetric heating due to oxidation on the inner cracks surface has little effect on ignition. Runaway conditions in that case may be determined by the classical parabolic law [4,10]. However, large ψ values indicate extensive cracking with no or thin oxide layer on the inner surfaces. In that case volumetric oxidation may be the main contributor to runaway reaction at relatively low temperatures.

CONCLUSION

The effect of volumetric oxidation on the critical ignition temperature of zirconium was investigated. Volumetric chemical reactions may be important in the oxidation of degraded fuel cladding during severe accident in nuclear reactors. The analysis was based on an extension of the original Frank-Kamenetzky [13] approximate solution, which dealt with homogeneous thermochemical reactions. The present approximation is valid for oxidation in thin metal slabs.

A new dimensional parameter, ψ, was defined to specify the cracks density and the thickness of oxide layer on the inner area of the cracks. It is shown that the critical temperature for thermal explosion decreases as ψ increases.

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