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Zirconium ignition in exposed fuel channel

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HIGHLIGHTS

- We demonstrate the idea of runaway zirconium–steam reactions in severe accidents in today's LWRs.
- We predict the thermal-hydraulics conditions relevant to cladding oxidation in an exposed fuel channel of a partially uncovered core.
- The Semenov theory of metal combustion is extended to define a criterion for runaway oxidation reaction in fuel cladding.

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ABSTRACT

A theoretical model based on simultaneous solution of the heat and mass transfer equations is developed for predicting the rate of thermo-chemical reaction between zirconium cladding and a hot steam environment. Ignition conditions relevant to cladding oxidation in an exposed fuel channel of a partially uncovered core are predicted based on the theory of metal combustion. A range of decay power, convective heat transfer coefficients, and initial temperatures leading to uncontrolled runaway cladding oxidation is identified. The model could be readily integrated as part of a fuel channel analysis code for predicting possible outcomes of different accident mitigation procedures in light water nuclear reactors under LOCA conditions.

1. Introduction

The recent events at the Fukushima plants have underscored the importance to the overall reactor safety of secondary heat generation sources, such as thermo-chemical reactions at the cladding surface. Realistic analysis of metal oxidation in a partially uncovered reactor core is a complicated numerical computation task, requiring the simultaneous solution of a set of energy balance equations in the fuel elements and their metal claddings along with the mass, momentum and energy equations in the corresponding coolant channels (cf., severe accident codes; MAAP, 1992; MELCOR, 2000). Conservative analysis of cladding integrity is typically accounted for by setting a predetermined critical minimum ignition temperature, which is based on out-of-pile oxidation experiments using small specimens of cladding material (Baker and Just, 1962; Cathcart et al., 1977).

Accurate modeling of metal oxidation during severe accident must account for the time dependent balance between the thermochemical reaction heat release at the cladding surface, the decay power in the fuel and the rate of cooling by the surrounding steam. A step in that direction has been previously described by using a lumped parameters model (Nekhamkin et al., 1998; Hasan et al., 1999; Pickard, 2002) that relies on the Semenov type methodology (Semenov, 1928; Yarin and Hetsroni, 2004; Khaikin et al., 1970; Boddington et al., 1982) to identify critical conditions for runaway clad–steam oxidation reactions. A more realistic cladding oxidation model based on solid combustion theories is described in this paper.

The theory of metal oxidation and combustion has been extensively developed in the last century as part of the technological effort to develop efficient solid propellants and later in conjunction with nuclear reactor safety. Conditions for a runaway thermochemical reaction were analytically derived by Chambré (1952) and Frank-Kamenetskii (1969) by solving the one-dimensional steady-state balance equation in a system of finite size. Based on the theory of thermal explosion, the combination of size, conductivity and ambient temperature at which such solution becomes mathematically impossible was defined as the condition of ignition or inflammation.

An extensive review of the basic theoretical and engineering literature on metal combustion by Yarin and Hetsroni (2004) demonstrates that the rate of metal oxidation in an oxidizing gas environment depends on the thermal-hydraulic conditions in both the solid and the surrounding gas. The idea of runaway metal–steam reactions was introduced by Khaikin et al. (1970) who

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used the Semenov (1928) analysis to derive a conjugate set of heat and mass balance equations for the time evolution of temperature and oxide layer thickness on a small metal particle placed in an oxidizing gas environment of uniform temperature. In the following the basic combustion theories for metal ignition in steam are extended to account for the special characteristic conditions at a partially exposed nuclear fuel rod. In particular the effect of temperature non-uniformity along the oxidizing specimen as well as the effect of stored and decay heats at the inner surface of a cylindrical cladding shell are considered. Heat and mass balance equations are developed to define runaway timing and the thermal conditions leading to uncontrolled oxidation during severe accident. The paper outlines the possibility for integrating the proposed model in a full-scale fuel channel transient analysis.

2. Ignition of metal particles

Thermo-chemical reaction between steam and zirconium in the fuel cladding could become an important heat source under accident conditions. During normal operation of power reactors, the cladding temperature is about 10° above the coolant temperature, i.e., about 330–350 °C, with low oxidation rate and minimal heat release. However, if cladding is partially exposed, because of core coolant loss, the clad temperature could increase by several hundreds degrees. At cladding temperatures above about 900 °C, clad oxidation rate begins to significantly increase, leading to release of heat and formation of hydrogen, according to the following chemical reaction for Zr (Baker and Just, 1962; Whitmarsh, 1982):

$$\mathrm{Zr} + 2\mathrm{H_2O} \rightarrow \mathrm{ZrO_2} + 2\mathrm{H_2} + \mathrm{Heat}$$

The heat of reaction, Q_0, is 140 kcal/mole (6500 kJ/kg of Zr reacted or 1540 kcal/kg) and the volume of hydrogen generated is 0.5 m^3 (at STP conditions) per 1 kg of reacting Zr.

Generally, the rate of oxidation depends on the metal temperature, T, and on the rate of oxygen diffusion through the oxidized layer, which is formed on the outer surface of the metal. Thus, predicting the necessary conditions for ignition calls for simultaneous solution of the heat and mass balance equations at the cladding surface. At certain conditions, heat generation by the oxidation reaction may exceed the cooling rate, which leads to an accelerated or runaway oxidation. In the following, a threshold criterion for runaway oxidation is derived for three representative cases: uniform temperature approximation; decay power effect and a general one-dimensional system.

2.1. Uniform temperature approximation

To gain a better physical insight into the diffusion and thermal processes taking place during metal oxidation, we consider first a simplified case of a thin walled planar zirconium specimen with initial temperature $T_{\mathrm{C,i}}$ instantaneously introduced into an infinite steam environment with a constant and uniform temperature, T_0. As proposed by Khaikin et al. (1970) ignition conditions in this case are determined by considering a balance between the rate of heat release by the oxidation reaction and the rate of heat transfer from the metal to the ambient steam. For a thin walled zirconium metal (low Biot number), a lumped parameters heat balance equation is given by,

$$m_{\mathrm{Zr}} C_{\mathrm{Zr}} \frac{dT_{\mathrm{C}}}{dt} = \rho_{\mathrm{Zr}} Q_0 S \frac{d\delta}{dt} - hS(T_{\mathrm{C}} - T_*) \quad (1)$$

where m_{Zr} and S are the mass and surface area of the zirconium metal; ρ_{Zr} and C_{Zr} are its density and specific heat, h the heat transfer coefficient, δ is the thickness of the oxide film at the surface, Q_0 the heat release per unit mass of oxidized metal and T_{C} is the zirconium temperature. The exact definition of the characteristic temperature, T_*, depends on the physical problem solved. In this first case the characteristic temperature is conveniently taken as a constant that equals the ambient steam temperature, i.e., $T_* = T_0$. In Eq. (1) it is assumed that the metal mass remains constant. This holds for the initial stage of the process when the thickness of the oxide film is insignificant.

For a planar zirconium slab of unit width, height L and initial thickness a_0, Eq. (1) can be further manipulated by expressing the slab volume and surface area in terms of its initial dimensions,

$$\rho_{\mathrm{Zr}} C_{\mathrm{Zr}} a_0 \frac{dT_{\mathrm{C}}}{dt} = \rho_{\mathrm{Zr}} Q_0 \frac{d\delta}{dt} - h(T_{\mathrm{C}} - T_*). \quad (2)$$

The thickness of the oxide film, $\delta(t)$, has been theoretically investigated (Baker and Just, 1962; Khaikin et al., 1970). The simplest diffusion model takes the form,

$$\frac{d\delta}{dt} = \frac{k_{\mathrm{r}}}{\delta^{\mathrm{n}}} \exp\left(-\frac{B}{T}\right) \quad (3)$$

where B is the activation energy ($B = 22{,}900$ K) and $k_{\mathrm{r}} = 3.968 \times 10^{-5}$ m^2/s is a pre-exponent reaction rate, which accounts for the oxidizer concentration at the surface (Baker and Just, 1962). A parabolic law ($n = 1$) will be used here as it is broadly used for estimating zirconium oxidation rate in nuclear reactors (MAAP, 1992; MELCOR, 2000 codes). Thus, in order to derive an ignition criterion for metal oxidation it is necessary to solve Eqs. (2) and (3) jointly subject to the following initial conditions, $\delta(t = 0) = \delta_{\mathrm{i}}$ and $T_{\mathrm{C}}(t = 0) = T_{\mathrm{i}}$. Eqs. (2) and (3) are first reduced into the following dimensionless form,

$$\frac{d\theta}{d\tau} = \frac{1}{\eta} \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \frac{\theta}{\omega} \quad (4a)$$

$$\frac{d\eta}{d\tau} = \frac{1}{\eta} \exp\left(\frac{\theta}{1 + \beta\theta}\right) \quad (4b)$$

with the following initial conditions,

$$\mathrm{I.C.}: \text{at } \tau = 0 \; \eta = \eta_i, \; \theta = \theta_{\mathrm{i}}.$$

The following dimensionless variables and parameters are adopted in Eqs. (4a) and (4b),

$$\eta = \frac{\delta}{\delta_*}; \; \theta = \frac{B}{T_*}\left(\frac{T_{\mathrm{C}}}{T_*} - 1\right) = \frac{1}{\beta}\left(\frac{T_{\mathrm{C}}}{T_*} - 1\right); \; \tau = \frac{t}{t_*}; \; \delta_* = \frac{C_{\mathrm{Zr}}\, a_0\, \beta\, T_*}{Q_0};$$
$$\beta = \frac{T_*}{B}; \; t_* = \frac{\delta_*^2\, e^{1/\beta}}{k_{\mathrm{r}}}; \; \omega = \frac{1}{h}\left(\frac{Q_0}{\beta T_*}\right)^2 \frac{\rho_{\mathrm{Zr}}\, k_{\mathrm{r}}\, e^{-1/\beta}}{a_0 C_{\mathrm{Zr}}} = \frac{1}{h}\frac{a_0\, C_{\mathrm{Zr}}\, \rho_{\mathrm{Zr}}}{t_*}. \quad (5)$$

The right hand side of (4a) expresses a balance between the oxidation exponential heat generation in the specimen and the rate of convective cooling by the steam (θ/ω). The parameter, ω, specifies the ratio between the average rate of heat accumulation in the metal (over a characteristic time, t_*), and that transferred to the ambient steam. The initial value of the dimensionless oxide layer in Eq. (4b) is typically small ($\eta_{\mathrm{i}} \approx 0$). In the following, the effect of the initial temperature difference, θ_{i}, will be studied parametrically.

In order to demonstrate the utility of the model for predicting zirconium ignition conditions, Eqs. (4a) and (4b) were integrated numerically for a wide range of characteristic temperatures using an initial thickness of $a_0 = 0.57$ mm, which corresponds to typical PWR fuel cladding. As an example, in Figs. 1 and 2 the characteristic temperature, T_*, and the initial cladding temperature, T_{C}, were arbitrarily taken as 800 K, yielding $\theta_{\mathrm{i}} = 0$ and $\beta = 0.035$. Also, following Khaikin et al. (1970) we use $\delta_{\mathrm{i}} = 10$ nm resulting in $\eta_{\mathrm{i}} = 1.46 \times 10^{-3}$.

Fig. 1 is a typical example showing the evolution of the dimensionless temperature, θ vs. dimensionless time, τ for two values of the parameter ω. It is noticed that there exists a critical minimum value, $\omega = \omega_{\mathrm{cr}}$, above which the temperature escalates dramatically.