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Zirconium Ignition in an Exposed Fuel Channel

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INTRODUCTION

The recent events at the Fukushima plants have underscored the importance of secondary heat generation sources, such as thermo-chemical reactions, to the overall safety of the reactor. The theory of metal oxidation and combustion has been extensively developed in the last century as part of the technological effort to develop efficient rocket propellants and later in conjunction with nuclear reactor safety. Extensive review of the basic theoretical and engineering literature is given in [1, 2]. This paper aims at surveying some of the classical models available for predicting the threshold ignition temperature related to *Zr* oxidation and outlines the possibilities for integrating chemical oxidation models in a full scale fuel channel transient analysis.

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 ten degrees higher than that of the coolant, i.e. about 330-350 $^{\circ}$C. The oxidation rate at that temperature is generally low with minimal heat release. However, if the cooling deteriorates and the critical heat flux is exceeded in the core, the clad temperature could increase by several hundred degrees. At temperatures above about 900 $^{\circ}$C, clad oxidation rate begins to significantly increase, leading to release of heat and formation of hydrogen, as expressed by the following chemical equation [4, 5]:

$$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 + \text{Heat} \; ; \quad Q = 140 \text{ kcal/mole}$$
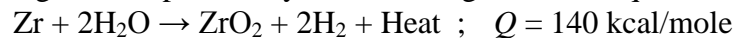
The heat of reaction, Q, is 6500 kJ/kg of Zr reacted (1540 kcal/kg) and the stoichiometric volume of hydrogen generated is 0.5 m^3. Generally, the reaction rate depends strongly on the metal temperature, T, and on the rate of oxygen diffusion through the oxidized layer, of thickness, δ, which is formed on the outer surface of the metal. Thus, predicting the necessary conditions for ignition calls for simultaneous solution of heat and mass transfer equations. This conjugate problem was effectively approached by Khaikin et al. [3] as an extension of the classical theory of thermal explosion of a small metal sphere. Their model is slightly modified here to describe the ignition of a thin metal slab simulating the fuel cladding. A lumped parameter heat balance over a slab introduced instantaneously into a gaseous oxidizer yields,

$$mc_p \frac{dT}{dt} = \rho Q S \frac{d\delta}{dt} - hS(T - T_0) \tag{1}$$

Where m and S are the mass and surface area of the metal; ρ and c_p are its density and specific heat, h the heat transfer coefficient, δ is the thickness of the oxide film at the surface, Q is the heat release per gram oxide multiplied by the oxide/metal density ratio, and T_0 is the ambient gas temperature. Equation (1) can be further manipulated by expressing the particle volume and surface area in terms of its initial thickness, a_0, and by defining the heat transfer coefficient in terms of the Nusselt number and the metal conductivity, λ, ($h = Nu\lambda / a_0$), resulting in,

$$\rho c_p a_0 \frac{dT}{dt} = \rho Q \frac{d\delta}{dt} - \frac{\lambda}{a_0} Nu(T - T_0) \tag{2}$$

Various oxidation laws for $\delta(\tau)$ have been theoretically investigated by Khaikin et al. [3], the simplest takes the form,

$$\frac{d\delta}{dt} = \frac{A_\delta}{\delta^n} \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where E is the activation energy, R the universal ideal gas constant and A_δ is a pre-exponent coefficient, which accounts for the oxidizer concentration at the surface. The parabolic law ($n=1$) will be used here as it coincides with the Baker-Just [4] model, which is broadly used in estimating Zr oxidation rate in nuclear reactors. We further adopt the following dimensionless variables,

$$\eta = \frac{\delta - \delta_i}{\delta_i} \; ; \; \tau = t \frac{Q}{c_p} \frac{E}{RT_0^2} \frac{A_\delta}{a_0 \delta_i} \exp\left(-\frac{E}{RT_0}\right) \; ; \; \chi = \frac{Q\rho}{\delta_i} \frac{E}{RT_0^2} \frac{a_0}{Nu\lambda} A_\delta \exp\left(-\frac{E}{RT_0}\right) \; ;$$

$$\beta = \frac{RT_0}{E} \; ; \; \Theta = \frac{E}{RT_0^2}(T - T_0) \; ; \; \Theta_i = \frac{E}{RT_0^2}(T_i - T_0) \; ; \; \gamma = \frac{a_0}{\delta_i} \frac{c_p RT_0^2}{EQ} \tag{4}$$

where c_p is the Zr specific heat and the index i refers to initial conditions. Equations (2) and (3) are then reduced to

$$\frac{d\Theta}{d\tau} = (\eta+1)^{-1} \exp\left(\frac{\Theta}{1+\beta\Theta}\right) - \frac{\Theta}{\chi}$$

$$\frac{d\eta}{d\tau} = \gamma(\eta+1)^{-1} \exp\left(\frac{\Theta}{1+\beta\Theta}\right) \tag{5}$$

$$I.C. : \quad \tau = 0, \quad \eta = 0, \quad \Theta = \Theta_i$$

The solution of (5) is determined to a considerable extent by the parameter γ in the second equation. In most cases relevant to cladding oxidation $\gamma \gg 1$ is a realistic condition. In fact, Khaikin et al. [3] have estimated the value of γ to be in the range of 10^2 to 10^5. At values $\gamma \gg 1$ the system behavior depends on the exponent term in (5). To define the ignition conditions for $\gamma \gg 1$, Khaikin et al. [3] used the following change of variables in (5)

$$\frac{d\Theta}{d\tau'} = \frac{1}{z} \exp\left(\frac{\Theta}{1+\beta\Theta}\right) - \frac{\Theta}{\Omega}$$

$$\frac{dz}{d\tau'} = \frac{1}{z} \exp\left(\frac{\Theta}{1+\beta\Theta}\right) \tag{6}$$

$$z = \frac{\delta}{a_0} \frac{QE}{c_p RT_0^2} \; ; \; \tau' = \frac{\tau}{\gamma} \; ; \; \Omega = \frac{\chi}{\gamma}$$

$$I.C. : \quad \tau' = 0, \quad z = \frac{1}{\gamma}, \quad \Theta = \Theta_i$$

The set of equations (6) was numerically solved for $\beta=0.0873$ and initial Zr thickness of $a_0=0.57$ mm, which corresponds to a PWR fuel cladding. The initial oxide thickness was 10 nm, resulting in $\gamma=430$. Figure 1 shows the Zr dimensionless temperature vs. time for two values of the parameter Ω. It is seen that, in the studied range, a small variation of Ω dramatically changes the temperature profile. The value of Ω corresponding to the abrupt temperature change is termed 'critical'. At $\Omega = \Omega_{cr}$ the oxidation heat generation exceeds the rate of convection cooling leading to rapid metal temperature escalation. The thickness of the oxide layer change significantly during the heating process, as shown in Fig. 2.
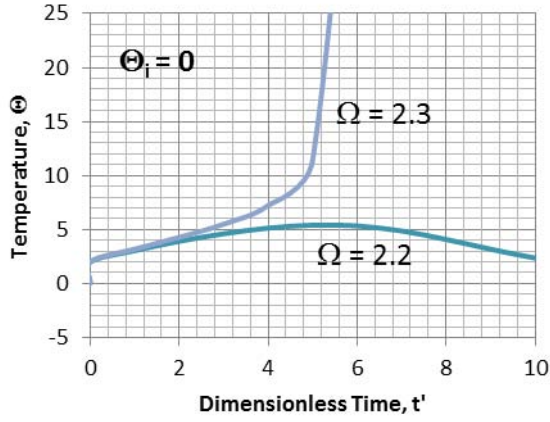
Fig. 1 Dimensionless temperature vs. dimensionless time for two values of Ω
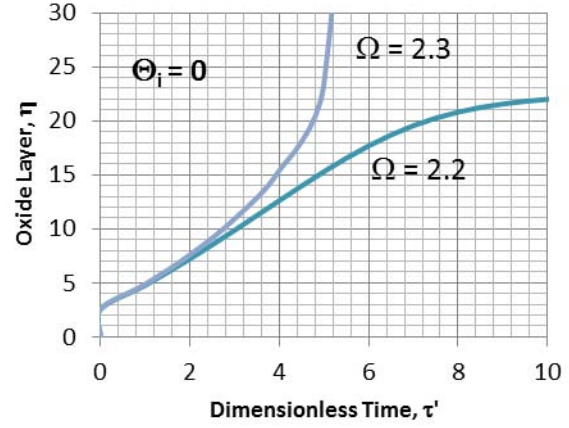

Fig. 2 Dimensionless oxide thickness vs. dimensionless time for two values of Ω

The critical condition in a slab, could be expressed as a function of ambient temperature as,

$$\Omega_{cr} = A_\delta \left(\frac{QE}{RT_{0.cr}} \right)^2 \frac{\rho}{Nu\,\lambda\,c_p\,k} \exp\left(-\frac{E}{RT_{0,cr}} \right) \tag{7}$$

where $T_{0,cr}$ is the ignition temperature, i.e., the oxidizing gas temperature corresponding to metal ignition. Figure 3 shows Ω_{cr} vs. $T_{0,cr}$ using Nu=2 according to [3]. The exact value of Nu must be determined according to accident conditions.

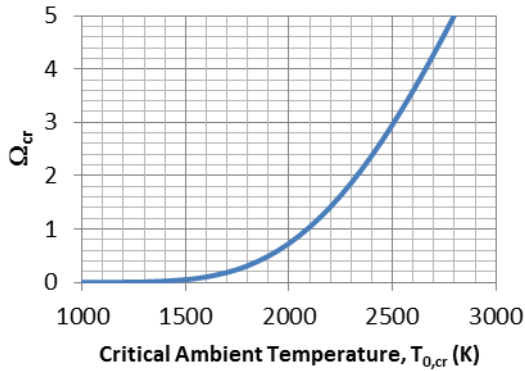
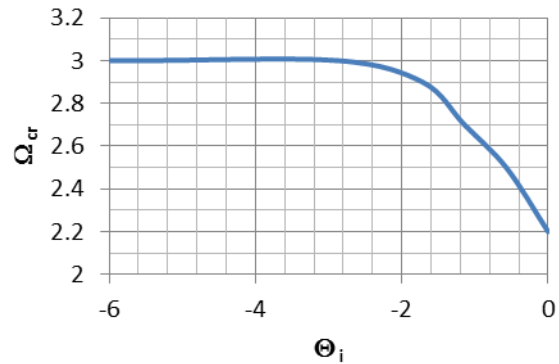Fig. 3 Critical ignition parameter, Ω_{cr}, vs. temperature for Zr oxidation

Fig. 4 Critical ignition parameter, Ω_{cr}, vs. initial Zr temperature

Using the data of Fig. 1, the value of Ω_{cr} is 2.3 for Θ_i=0. Therefore, from Fig. 3, the ignition temperature is estimated as 2400 K. It is noted that the exact value of Ω_{cr} depends on the initial condition as shown in Fig 4.

CONCLUSIONS

A theoretical model based on simultaneous solution of the heat and mass transfer equations is developed for estimating the ignition temperature of Zr cladding subject to heating and oxidation in hot steam environment. The present solution will be integrated as part of a channel code for predicting the anticipating possible outcomes of different accident mitigation procedures in light water nuclear reactors under LOCA conditions.

REFERENCES

[1]. L. P. Yarin and G. Hetsroni, "Combustion of Two-Phase Reactive media", Springer-Verlag Berlin, 2004.

[2]. Y. Nekhamkin, V. Rosenband, D Hasan, E. Elias, E. Wacholder and A. Gany, *Oxidation and Heat Transfer Considerations in Degraded Core Accident*, TOPSAFE98, Valencia, April 1998.

[3]. B. I. Khaikin, V. N. Bloshenko and A. G. Merzhanov, "On the Ignition of Metal Particles", UDC 536.46-662.215.1, Translated from Fizika Goreniya i Vzryva, No. 4, pp. 474-488, October-December, 1970, also in Combustion, Explosion, and Shock Waves, Vol. 6, No. 4 (1970).

[4]. Louis Baker, Jr. and Louis C. Just, "Studies of Metal-Water Reactions at High Temperatures", Argonne National Lab. ANL 6548, May 1962.

[5]. C. L. Whitmarsh, "Review of Zircaloy-2 and Zircaloy-4 Properties Relevant to N.S. SAVANNAH Reactor Design", ORNL-3281, 1982.