Nuclear Engineering and Design 326 (2018) 244–260

Contents lists available at ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

Analysis of deficiencies in current prediction method for hydrogen generated from fuel cladding and potential improvement approaches

Xinghe Ni[a], Yifen Chen[a], Jun Wang[b], Jianxiang Zheng[a,*], Huifang Miao[a], Zijing Huang[a], Ning Li[a]

[a] *Institute for Nuclear Energy, College of Energy, Xiamen University, Xiamen 361102, China*
[b] *College of Engineering, The University of Wisconsin-Madison, Madison, WI 53706, United States*

ARTICLE INFO

Keywords:
Hydrogen generation
Steam oxidation
Oxidation model
CORA

ABSTRACT

The prediction of hydrogen generated from fuel cladding by steam oxidation is significant in severe accident analysis. However, the existing methods and models are difficult to make an accurate prediction of hydrogen generation rate for integrated experiments and reactor core under severe accident conditions. In this work, the current models for steam oxidation of zirconium alloy cladding were reviewed by simulating five past CORA severe fuel damage experiments. A modified model based on the best-estimated temperatures of CORA tests was proposed to improve the prediction of hydrogen generation. Then, hydrogen generation rates predicted by different correlations were compared and analyzed. Among the traditional oxidation correlations for temperatures above 1873 K, the original Urbanic-Heidrick correlation is recommended for steam oxidation of zirconium alloy cladding by this work. The modified model also presents a good performance. This paper ends up with discussions about five significant factors on forecasting precision of hydrogen generated by steam oxidation of zirconium alloy cladding. These factors include: 1) temperature prediction, 2) nodalization schema, 3) inherent conservatism, 4) undue conservatism, and 5) time-delay between hydrogen generated and hydrogen gas released. They indicate several deficiencies in current prediction method for hydrogen generated from fuel cladding by steam oxidation.

1. Introduction

To accurately predict the hydrogen generated and released from the reactor core is important for severe accident analysis. The severe accidents will produce and release an enormous amount of hydrogen (OECD/NEA, 1999; Kim and Hong, 2015) since zirconium reacts with water and/or steam at high ($1173\,K < T < 1773\,K$) and ultrahigh ($T > 1773\,K$) temperatures. The excessive amount of hydrogen will lead to combustion or explosion and then cause hazards to the radiation barriers (e.g. reactor building, containment, etc.) (Fuchigami and Kasahara, 2015; Huang et al., 2015). Hence, steam oxidation of zirconium alloy cladding is a key issue for hydrogen generation prediction.

In the past decades, a lot of experiments and simulations were conducted to study zirconium alloy oxidation. Several famous projects were made to do integrated experiments on severe fuel damage (Haste et al., 2015), such as CORA, QUENCH, Phébus SFD, Phébus FP and so on. These experiments were usually considered as benchmarks to verify the models and codes of severe accidents. The existing steam oxidation correlations were almost the best-fits based on the data collected from separate-effect tests. A great number of separate-effect tests had been done at temperatures below 1800 K, but tests at temperatures above 1800 K were relatively limited (Schanz et al., 2004). Oxidation simulations for temperatures below 1800 K usually showed positive results, while the results for temperatures above 1800 K did not (Schanz et al., 2004). The microstructure and geometry of cladding are dramatically altered at ultrahigh temperatures. Moreover, the early failure of cladding may occur due to the attacks of low melting point materials (Minato et al., 1991; Hering and Hofmann, 1994) and mechanical stresses. Therefore, the correlations fitted from separate-effect tests are still difficult to accurately simulate the cladding oxidation and hydrogen generation. Consequently, it is necessary to develop some more accurate simulation models and methods.

For further development, an analysis of the deficiencies in current simulation method is carried out in this work. In the following, a significant cause of conservative for traditional correlations is reviewed, and a modified model is proposed for better simulation. Five past out-of-pile CORA experiments are conducted as the benchmarks. The rate and total weight of generated hydrogen are employed as the two key indexes for model verification. Moreover, a past MELCOR simulation (Wang et al., 2015) of CORA13 is reviewed. Finally, several impact

---

[*] Corresponding author.
E-mail address: zwu@xmu.edu.cn (J. Zheng).

https://doi.org/10.1016/j.nucengdes.2017.11.012
Received 30 August 2017; Received in revised form 1 November 2017; Accepted 3 November 2017

Table 1
Published correlations for weight gain rate of zirconium reacted.

Names	Expressions $K_{Zr}(T)$ ($kg^2 \cdot m^{-4} \cdot s^{-1}$)
Baker and Just (1962)	$3330 \cdot \exp(-22910/T)$ $1373\,K \le T \le 2473\,K$
Urbanic and Heidrick (1978)	$29.6 \cdot \exp(-16820/T)$ $1323\,K \le T \le 1853\,K$$87.9 \cdot \exp(-16610/T)$ $1853\,K < T \le 2123\,K$
Ballinger et al. (1976)	$31.0 \cdot \exp(-16802.6/T)$ $1144\,K \le T \le 1755\,K$

factors on prediction precision of hydrogen generated from cladding oxidation are discussed.

2. Models and methods

2.1. Hydrogen calculation approaches

The chemical equation of zirconium-steam reaction is

$$Zr + 2H_2\,O \rightarrow ZrO_2 + 2H_2 \tag{1}$$

Thus, the predicted weight of hydrogen produced by zirconium oxidation is

$$W_{H_2} = \frac{4}{123.22} W_{ZrO_2} = \frac{4}{91.22} W_{Zr} = \frac{4}{32} W_O \tag{2}$$

where, W_{ZrO_2} is the weight of ZrO_2, W_{Zr} is the weight of zirconium reacted, W_O is the weight of oxygen uptake.

It is best to know the ZrO_2 weight in order to calculate the weight of generated hydrogen. However, none of previous researches had obtained such a type of data. In addition, the measured thickness data of ZrO_2 layer is not applicable for accurate prediction of the weight and rate of generated hydrogen. It is because the breakaways, out-growth and in-growth of oxide scale will take place during oxidation. Therefore, the weight of zirconium reacted and oxygen uptake are relatively suitable and convenient for using.

However, there exists a α-Zr(O) layer, and a part of zirconium is used for forming the α-Zr(O) layer. The total amount of zirconium reacted is considered to include the zirconium in ZrO_2 and α-Zr(O) layers, thus a correction factor ϕ_{Zr} is defined in Eq. (3). The ϕ_{Zr} is defined as the lineal weight proportion or atomic ratio of zirconium in ZrO_2 layer relative to the total zirconium in ZrO_2, α-Zr(O) and β-Zr layers.

$$W_{H_2} = \phi_{Zr} \cdot \frac{4}{91.22} \widehat{W}_{Zr} \tag{3}$$

where, $0.0 < \phi_{Zr} \leqslant 1.0$, $\widehat{W}_{Zr} \geqslant W_{Zr}$. The default condition is $\phi_{Zr} = 1.0, \widehat{W}_{Zr} = W_{Zr}$.

Similarly, a part of oxygen is absorbed in α-Zr(O) layer, and a correction factor ϕ_O is employed in Eq. (4). The ϕ_O is defined as the lineal weight proportion or atomic ratio of oxygen in ZrO_2 layer relative to the total oxygen in ZrO_2 and α-Zr(O) layers.

$$W_{H_2} = \phi_O \cdot \frac{4}{32} \widehat{W}_O \tag{4}$$

where, $0.0 < \phi_O \leqslant 1.0$, $\widehat{W}_O \geqslant W_O$. The default status is $\phi_O = 1.0$, $\widehat{W}_O = W_O$.

2.2. Traditional model and correlations

Steam oxidation of zirconium alloy cladding keeps to the parabolic rate law if the oxidation is controlled by solid-state diffusion. It is found that the parabolic law is used in MELCOR (Gauntt et al., 2000), MAAP (Wang et al., 2014), ASTEC (Coindreau et al., 2010), and SCDAP/RELAP5 (USNRC, 1997a). The parabolic law is expressed as

$$\frac{d(X^2)}{dt} = K(T) \tag{5}$$

is the reaction rate; X refers to the thickness of α-Zr(O), ZrO_2 or (α-Zr(O) + ZrO_2) layers as well as the total weight of oxygen uptake, zirconium reacted or ZrO_2 per unit area.

The Arrhenius equation is effective enough to reflect the effects of temperature on the reaction rates of varied metals (Grosse, 2012; Schanz et al., 2004). It can be written as

$$K(T) = A \cdot \exp\left(-\frac{B}{R \cdot T}\right) \tag{6}$$

A is the pre-exponential factor, B is the activation energy constant, R is the universal gas constant ($8.314\,J \cdot mol^{-1} \cdot K^{-1}$), T is the temperature of cladding surface.

In Table 1, three correlations for the weight gain rate of zirconium reacted were acquired by previous steam oxidation experiments of Zircaloy-4. Meantime, the correlations for the weight gain rate of oxygen uptake are listed in Table 2. The Urbanic and Heidrick (1978) correlation has been applied more widely to severe accident analysis codes, such as MELCOR, MAAP, ASTEC, SCDAP/RELAP5, etc. The Urbanic-Heidrick's rate is lower than that of Baker-Just.

The Cathcart-Pawel (Pawel et al., 1979) fits well with the separate-effects tests at temperatures below 1773 K (Schanz et al., 2004; USNRC, 1997b) and is often employed in MAAP, ASTEC and SCDAP/RELAP5. Similarly, Leistikow and Schanz (1987) proposed a correlation. The rate of Leistikow-Schanz is a little lower than that of Cathcart-Pawel. Researchers had made great efforts to separate-effect oxidation tests at temperatures below 1773 K. On the contrary, few publications about separate-effect tests at temperatures above 1773 K were issued, e.g. only Baker and Just (1962), Urbanic and Heidrick (1978), Prater and Courtright (1987) for temperatures above 1773 K. Volchek et al. (2004) made a re-evaluation of the data ranging from 1800 K to 2400 K. In addition, Sokolov et al. (1993) recommended a correlation for Zr-1%Nb alloy, the alloy was used in VVER.

With the above elementary correlations, ten options are enumerated in Table 3 for oxidation calculation from low temperature to ultrahigh temperature. Options 1–4 are used for directly computing the weight of zirconium reacted, and Options 5–10 are employed directly to calculate the weight of oxygen uptake. According to the weight of zirconium reacted or oxygen uptake, the rate and weight of generated hydrogen can be predicted. A linear interpolation is employed in most cases for the transition region. Urbanic and Heidrick (1978) believed that the

Table 2
Published correlations for weight gain rate of oxygen uptake.

Names	Expressions $K_O(T)$ ($kg^2 \cdot m^{-4} \cdot s^{-1}$)
Urbanic-Heidrick (Schanz et al., 2004)	$3.64 \cdot \exp(-16847.2/T)$ $T \le 1800\,K$ $10.82 \cdot \exp(-16630.6/T)$ $T > 1800\,K$
Cathcart-Pawel (1979)	$36.22 \cdot \exp(-20111/T)$ $1173\,K \le T \le 1773\,K$
Leistikow and Schanz (1987)	$52.42 \cdot \exp(-20962/T)$ $1273\,K \le T \le 1773\,K$
Prater and Courtright (1987)	$3295 \cdot \exp(-26440/T)$ $1783\,K \le T \le 2673\,K$
Best-fit (Volchek et al., 2004)	$2.8866E8 \cdot \exp(-48665/T)$ $1800\,K < T < 1900\,K$$2.8484E3 \cdot \exp(-26822/T)$ $1900\,K < T < 2400\,K$
Sokolov et al. (1993)	$159.0 \cdot \exp(-23040/T)$ $T \le 1763\,K$$98.25 \cdot \exp(-20800/T)$ $T > 1783\,K$