Title: Modification of MELCOR for Severe Accident Analysis of Candidate Accident Tolerant Cladding Materials

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Abstract

A number of materials are currently under development as candidate accident tolerant fuel and cladding for application in the current fleet of commercial light water reactors (LWRs). The safe, reliable and economic operation of the nation's nuclear power reactor fleet has always been a top priority for the nuclear industry. Continual improvement of technology, including advanced materials and nuclear fuels, remains central to the industry's success. Enhancing the accident tolerance of light water reactors became a topic of serious discussion following the 2011 Great East Japan Earthquake, resulting tsunami, and subsequent damage to the Fukushima Daiichi nuclear power plant complex. The overall goal for the development of accident tolerant fuel (ATF) systems for LWRs is to identify alternative fuel system technologies to further enhance the safety, competitiveness, and economics of commercial nuclear power. Designed for use in the current fleet of commercial LWRs, or in reactor concepts with design certifications (GEN-III+), to achieve their goal enhanced ATF must endure loss of active cooling in the reactor core for a considerably longer period of time than the current fuel system, while maintaining or improving performance during normal operation. Many available nuclear fuel performance analysis tools are specifically developed for the current UO₂ – Zirconium alloy fuel system. The MELCOR severe-accident analysis code, under development at the Sandia National Laboratory in New Mexico (SNL-NM) for the US Nuclear Regulatory Commission (NRC), is one of these tools. This paper describes modifications made to a version of the MELCOR code by the Idaho National Laboratory (INL) that allows its application to alternate fuel-cladding systems. Preliminary analysis results are presented in this paper for candidate silicon carbide and FeCrAl cladding concepts.

Keywords

1. Introduction

Scoping simulations performed with advanced severe accident computer codes can be used to investigate potential safety advantages that advanced materials might have during severe accident conditions, such as those encountered during beyond design basis accidents (BDBAs), and to identify areas of computer code development needed to evaluate these advanced materials. To this end, in fiscal year (FY) 2012 an effort was initiated at INL to modify the MELCOR computer code by replacing Zircaloy for SiC in the code's reactor core material oxidation and thermal properties routines. The modified version of MELCOR was benchmarked against available experimental data to ensure that present SiC oxidation theory in air and steam were correctly implemented in the code. Additional modifications were subsequently implemented during FY 2013 to 2015 to improve the specificity in defining components fabricated from non-standard materials. This paper provides an overview of these modifications and preliminary analysis results produced during a severe accident scenario.

1.1 Description of MELCOR

MELCOR is the primary code used by US NRC to model and analyze the progression of severe accidents [1]. MELCOR, developed and maintained for the NRC by SNL-NM, is a systems level severe accident analysis computer code that includes the major phenomena of the system thermal hydraulics, fuel heat-up, cladding oxidation, radionuclide release and transport, fuel melting and relocation, etc.

MELCOR was designed for current LWR core material configurations. As such, the code contains material property definitions for UO₂, Zircaloy, ZrO₂, steel, steel oxide, and Inconel for the fuel, cladding, spacer grids, support plates and channel boxes. In the standard code version the user can override the internally defined material oxidation rate equation parameters and thermal properties through user input in an attempt to model other materials. Internally, however, the material heat-of-reaction remains at the assigned value for the original material, the oxidation rate equations must be parabolic (correct for metals) and the allowed materials for a specific core component cannot be modified; for example, the cladding is composed of Zircaloy and/or Inconel but not steel. In addition, a material property change to address one of the core's components, e.g. the cladding, will also change the material properties of all other core structures that contain that same material, e.g. Zircaloy in channel boxes. These assumptions can only be changed by internally modifying the code to consider additional materials for any given core component.

1.2 Initial MELCOR Modifications: Material Substitution

Initial modifications to include SiC as an additional cladding material in MELCOR version 1.8.6 were completed at INL in FY 2012 [2]. INL focused on applying this modified MELCOR code to the Three Mile Island Unit 2 (TMI-2) loss-of-coolant accident (LOCA). The TMI-2 accident was caused by a small-break LOCA in a two-loop Babcock and Wilcox (B&W)

pressurized water reactor (PWR). The MELCOR input model used for this accident analysis is that developed by SNL-NM and Innovative Technology Solutions Corporation, Albuquerque, NM [3].

The initial MELCOR modifications directly replaced SiC for Zircaloy in all of MELCOR's reactor core components. The properties and oxidation behavior of monolithic chemical vapor deposited (CVD) SiC were used in place of Zircaloy in the MELCOR reactor core oxidation and material property routines [4]. These modifications included MELCOR's reactor core oxidation (oxidation in air and steam) and material property routines (properties such as thermal conductivity, specific heat, density, emissivity, and heat of formation). Details of the SiC oxidation model and results of these initial analyses have been summarized in References [4, 5].

Much of what is considered for nuclear applications (cladding or other components) would use SiC-based ceramic matrix composites (CMC) rather than or in addition to monolithic CVD SiC, a brittle ceramic. However, the property data for SiC CMCs, particularly oxidation behavior, is limited. Many of these data gaps have been, or are being, addressed by current research in several Department of Energy programs (e.g., Fusion Materials Program, Fuel Cycle Research & Development Program, and the LWR Sustainability Program). In 2014 Oak Ridge National Laboratory (ORNL) developed a Systematic Technology Evaluation Plan for SiC, defining the additional testing necessary to elevate the technology readiness level (TRL) of SiC for fuel cladding application [6]. Properties for monolithic CVD SiC were applied in the initial studies because property data for the oxidation of SiC CMCs was insufficient at the time this MELCOR modification was benchmarked. However, modified property data can and should be incorporated in future analyses as the data becomes available using the modified MELCOR structure.

1.3 Additional MELCOR Modifications: Definition of New Materials

Following the initial study that directly substituted CVD SiC for Zircaloy in the PWR simulation, additional work was completed to allow the user the ability to define both SiC and SiO₂ as unique cladding materials, in addition to Zircaloy, ZrO₂, and Inconel, in both the core physics and thermal material property data packages. These modifications also allow the user to apply the properties of CVD SiC and its oxide (silica), or to override these properties with more appropriate values for their application. In this version, the user controls the mass of SiC in the cladding for each core volume (see Appendix B in Ref. [4] for new user instructions). The logic for this modified MELCOR assumes SiC to be the outermost material on the cladding surface in a specific core volume, or the entire cladding composition if no other cladding material is specified by the user, such as Zircaloy. This allows the user to model the SiC as a single cladding material, or as a coating or wrap on the base metallic cladding, without affecting the Zircaloy in any other core component or any other core volume of a user's model. When SiC is present as a composite cladding material, the rod failure criterion is changed from that of Zircaloy to the decomposition temperature of SiC (3150 K). For SiC-coated or wrapped cladding, the code reverts back to Zircaloy oxidation equations and failure and candling criteria if the SiC is lost from the surface (e.g. by oxidation in steam). Upon rod failure, the SiC in that core volume enters the debris field in the adjoined user specified coolant volume, where it continues to undergo further oxidation by steam. This modification required considerable

changes to MELCOR's material oxidation logic and oxidation routines.

A second modified version of MELCOR was initiated in FY 2014 for materials that exhibit only parabolic oxidation behavior with both air and steam. This version uses FeCrAl as a cladding material option. Like the SiC version, the user can model FeCrAl as a single cladding material or as a cladding coating for any given region of the core through user input. If the user desires to use a different cladding material option, then the FeCrAl material and oxidation properties can be overridden, except for heat-of-reaction, through user input as long as the oxidation process for this new material is parabolic. The material properties used for FeCrAl are provided in Appendix A of Ref. [4]. Material properties for FeCrAl oxide were not available when this code version was developed, but these properties are being investigated by researchers at ORNL. Hence, the initial FeCrAl version applies the properties of stainless steel oxide as listed in the MELCOR theory manual [1] to simulate FeCrAl oxide. Unlike the SiC version, which must track a much more complicated steam oxidation process (described in the following two sections), the FeCrAl version of MELCOR is able to make use of MELCOR's standard oxidation routines while still allowing use of both Zr-alloy and FeCrAl in the reactor core materials. The adopted FeCrAl cladding and coating failure temperature is that of the melting temperature of its oxide, taken here as the value for stainless steel oxide (1870 K) given in the MELCOR code. If FeCrAl is the only cladding material in a core zone, then reaching this temperature is the rod failure criterion. If Zircaloy is present in the cladding of the same core volume, then the rod failure and candling criteria revert back to those for Zircaloy after exceeding the FeCrAl failure criterion.

2. Detailed Material Modeling

The following sections provide detailed modeling information used to describe the oxidation behavior of SiC and FeCrAl in the INL modified version of MELCOR. Ceramic SiC materials exhibit parabolic oxidation in air, but they undergo a more complex process in a water-vapor environment. FeCrAl demonstrates parabolic oxidation behavior in both air and water-vapor environments, similar to the oxidation behavior of Zirconium alloys. Note that the analyses described here for both SiC and FeCrAl cladding only replace the cladding material; all other core components (e.g. fuel, cladding, spacer grids, support plates and channel boxes) remain the standard materials in the TMI-2 design. This assumption is consistent with the ATF program goal to identify and evaluate alternative fuel system technologies to further enhance the safety, competitiveness, and economics of commercial nuclear power without requiring additional design modifications to the existing fleet.

2.1 Silicon Carbide Oxidation

Oxidation of SiC in air at high temperatures follows the chemical equation:

As reported by Fox [7], this reaction exhibits a parabolic oxidation rate after a very short ($\ll 1$ h) period of linear oxidation. For this type of reaction, the square of the thickness of the silica scale formed (x) is proportional to exposure time (t) as:

$$x^2 = k_p t, \quad (2)$$

where the k_p ($\mu\text{m}^2/\text{h}$) is the parabolic rate constant. This rate constant can be described by the usual Arrhenius type relationship as follows:

$$k_p = k_{p,o_2}^o e^{-E_a \cdot o_2 / RT} (p_{O_2} / p_{o_2}^m)^n, \quad (3)$$

where k_{p,o_2}^o is the a pre-exponential constant ($\mu\text{m}^2\text{-SiC/h}$), R is the universal gas constant (J/mol-K), E_a is the activation energy (J/mol), and p_{O_2} is oxygen gas pressure (Pa) with m representing the oxygen gas pressure at which k^o was derived, and $n = 1/2$ as proposed by Fox [7]. Based on his experimental data, Fox determined the activation energy to be 190 kJ/mol and the pre-exponential constant to be 6.478×10^{-5} ($\text{kg}^2\text{-SiC/m}^4\text{-s}$).

For all oxidation reactions, MELCOR determines the heat-of-reaction based on the sum of the heat-of-formation of the products, times their mole fractions, minus the sum of the heat-of-formation of the reactants, times their mole fractions, at 298 K. This value is then corrected for the enthalpy change of the products and reactants from 298 K to the temperature at which the SiC is oxidizing. Based on the heats-of-formation for the products and reactants given in Ref. 8, the heat-of-reaction for Eq. 3 at 298 K is -2.4×10^7 J/kg-SiC, which is an exothermic reaction.

Oxidation of SiC in a water-vapor environment is a more complicated process than in oxygen because the silica (SiO_2) that forms on the surface of the SiC also undergoes a chemical reaction with steam to form a vapor at the silica surface. The chemical equations for these reactions are:

As demonstrated by Opila [9], the kinetics for these reactions that produce a silica layer thickness, x (μm), through which H_2O must diffuse to react with the base SiC, can be modeled by the parabolic oxidation process in Eq. 4, described by a rate constant, k_p ($\mu\text{m}^2\text{-SiO}_2/\text{h}$), and a linear volatilization process in Eq. 5, described by a rate linear constant, k_l ($\mu\text{m-SiO}_2/\text{h}$), combined as follows:

$$\frac{dx}{dt} = \frac{k_p}{2x} - k_l. \quad (6)$$

The growth of this layer is initially parabolic, but at long times or high volatility rates, a steady state is achieved where oxidation is controlled by the linear volatilization process. Under these conditions, there is a limiting or equilibrium silica layer thickness, x_L (μm), given as:

$$x_L = \frac{k_p}{2k_l}. \quad (7)$$

As is the case for SiC oxidation in a gaseous oxygen atmosphere, a parabolic rate constant for SiC oxidation in steam can be specified by the Arrhenius relationship (Eq. 3). We adopted values for this relationship proposed by Opila [9], which are k_{p,H_2O}^o of 6.915×10^{-9} ($\text{kg}^2\text{-SiO}_2/\text{m}^4\text{-s}$), E_{a,H_2O} of 35 (kJ/mol-K) and n of 1 for this reaction.

In this MELCOR modification, the linear silica volatilization process is assumed to proceed in chemical equilibrium at the silica surface and to be controlled by the rate at which orthosilicic acid $[\text{Si}(\text{OH})_4]$ gas can diffuse away from this surface through the steam boundary layer that develops adjacent to the silica surface based on steam flow conditions, defined as follows:

$$k_{l_{\text{Si}(\text{OH})_4}} = k_D (\rho_{\text{Si}(\text{OH})_4}^S - \rho_{\text{Si}(\text{OH})_4}^B), \quad (8)$$

where k_D is a mass transport coefficient (m/s) and $\rho_{\text{Si}(\text{OH})_4}$ is the $\text{Si}(\text{OH})_4$ vapor density (kg/m^3) at the silica surface (S) and in the steam bulk flow (B).

The $\text{Si}(\text{OH})_4$ vapor density in Eq. 8 can be obtained from the ideal gas law if the $\text{Si}(\text{OH})_4$ gas pressure, $p_{\text{Si}(\text{OH})_4}$ (Pa), at the silica surface is known. According to Hashimoto [10], the equilibrium constant, k_{eq} (Pa^{-1}), for the chemical reaction in Eq. 5 can be determined from the following relationship:

$$\ln(k_{eq}) = \ln(p_{\text{Si}(\text{OH})_4} / p_{H_2O}^2) \approx -\Delta H_r^o / RT + \Delta S_r^o / R, \quad (9)$$

or

$$p_{\text{Si}(\text{OH})_4} \approx p_{H_2O}^2 \exp(-\Delta H_r^o / RT + \Delta S_r^o / R), \quad (10)$$

where, according to Hashimoto [10], this approximation can be derived by combining van't Hoff isotherm and Gibbs-Helmholtz equations, ΔH_r^o is the standard enthalpy change (J/mol), and ΔS_r^o is the standard entropy change (J/mol-K). Hashimoto [10] measured a standard enthalpy and entropy change of 56 kJ/mol and -66.2 J/mol-K to give k_{eq} in atm^{-1} . However, as explained in References [4, 6], the standard enthalpy change of 172 kJ/mole and entropy change of 16.36 J/mol-K were required to match oxidation data from Robinson [11], designated as “Rich Burn” gas conditions. Since the “Rich Burn” parameters gave the largest oxidation rate found in literature at that time [2], these parameters were adopted until more suitable values can be derived for prototypical severe accident conditions in LWRs.

To predict the $\text{Si}(\text{OH})_4$ gas mass transport coefficient, k_D in Eq. 8, MELCOR employs an analogy between heat and mass transfer known as the Sherwood analogy. The Sherwood analogy is as follows:

$$Sh = Nu Sc^{1/3} / Pr^{1/3}, \quad (11)$$

where Nu and Pr are the Nusselt and Prandtl numbers for convective heat transfer, respectively, and Sc is the Schmidt number for diffusive mass transfer.

Once the Sherwood number is determined by MELCOR from its convective heat transfer package, the mass transfer coefficient, k_D (m/s), is calculated as follows:

$$k_D = Sh \frac{D}{L_c}, \quad (12)$$

where D (m²/s) is the binary gaseous diffusion coefficient, and L_c (m) is the heat structure characteristic dimension.

In deriving a relationship to fit experimental data for the linear rate constant, k_l , Terrani [12], adopted the following heat transfer correlation applicable for laminar gas flow over a flat plate:

$$Nu = 0.664 Re^{1/2} Pr^{1/3}. \quad (13)$$

After substituting Eqs. 11, 12, and 13 and the definitions for Reynolds and Schmidt numbers into Eq. 8, Terrani [12] derives the following relationship for the linear rate constant:

$$k_{l_{Si(OH)_4}} = 0.664 \left(\frac{\rho L_c V}{\mu} \right)^{1/2} \left(\frac{\mu}{\rho D} \right)^{1/3} \frac{D}{L_c} (\rho_{Si(OH)_4}^S - \rho_{Si(OH)_4}^B) \quad (14)$$

By assuming that the bulk $Si(OH)_4$ density is negligible, Eq. 14 becomes:

$$k_{l_{Si(OH)_4}} = 0.664 L_c^{-1/2} \rho^{1/6} V^{1/2} \mu^{-1/6} D^{2/3} \rho_{Si(OH)_4}^S \quad (15)$$

Applying the ideal gas law ($P = \rho RT/M$) for both the steam and $Si(OH)_4$ densities, results in:

$$k_{l_{Si(OH)_4}} = 0.664 L_c^{-1/2} \left(\frac{PM_{H_2O}}{RT} \right)^{1/6} V^{1/2} \mu^{-1/6} D^{2/3} \frac{P_{Si(OH)_4} M_{Si(OH)_4}}{RT} \quad (16)$$

Finally, by using the relationship between $Si(OH)_4$ and steam pressures given in Eq. 10, gives:

$$k_{l_{Si(OH)_4}} = 0.664 M_{Si(OH)_4} M_{H_2O}^{1/6} L_c^{-1/2} (RT)^{-7/6} V^{1/2} \mu^{-1/6} D^{2/3} P^{13/6} P_{ref}^{-1} \exp(-\Delta H_r^\circ / RT + \Delta S_r^\circ / R) \quad (17)$$

Eq. 17 is only applicable to flat plates. In order to implement this model in a more general way in MELCOR, Eqs. 8 and 10 must be used directly. To achieve this, the physical constants of standard enthalpy change (ΔH_r°) and standard entropy change (ΔS_r°) of the silica-steam chemical reaction (note Eq. 10) must be derived not only by matching experimental data [12], but by including property relationships used by the MELCOR code when deriving these constants. Adopting the following expressions for D and μ given by the kinetic theory of gases (see Ref. 13):

$$D = \frac{3}{16} \sqrt{\frac{2}{\pi} \left(\frac{1}{M_{H_2O}} + \frac{1}{M_{Si(OH)_4}} \right)} \frac{(RT)^{3/2}}{N_A P \sigma_{AB}^2 \Omega_{D,AB}}, \quad (18)$$

$$\mu = \frac{5}{16\sqrt{\pi}} \frac{\sqrt{M_{H_2O} RT}}{N_A \sigma^2 \Omega_{\mu}}. \quad (19)$$

For simplicity, substituting the following temperature dependent power law fits to tabular data in reference [14] for collision integrals: $\Omega_{D,AB} = 9.59 T^{-0.305}$ and $\Omega_{\mu} = 16.67 T^{-0.359}$ (accurate within 0.3% over the temperature range 1100-1600°C), along with the constants $M_{H_2O} = 0.018$ kg/mol, $M_{Si(OH)_4} = 0.096$ kg/mol, $\sigma = 2.641 \times 10^{-10}$ m, $\sigma_{AB} = 3.9455 \times 10^{-10}$, and $P_{ref} = 101325$ Pa, gives:

$$k_{l_{Si(OH)_4}} = 4.08 \times 10^{-10} L_c^{-1/2} V^{1/2} p^{3/2} T^{-0.106} \exp(\Delta S_r^o / R - \Delta H_r^o / RT), \quad (20)$$

where the constant 4.08×10^{-10} has units $\text{Pa}^{-1/2} \text{m}^{-1} \text{s}^{3/2} \text{K}^{0.106}$.

We use a nonlinear-least-squares method in the *R* statistical program [15] to fit data from Ref. 12 to the form of Eq. 20 to obtain a standard enthalpy and entropy. As was the case for Ref. 12, in order match the entire range of data with Eq. 20, we developed two data matched equations, one each for the low pressure (digitized from figure 14 in Ref. 12) and high pressure (calculated from tables II and III in Ref. 12) data. The resulting values are $\Delta H_r^o = 183.27$ kJ/mol and $\Delta S_r^o = 39.20$ J/mol-K for high pressure ($L_c = 0.04$ m) as shown in Eq. 21, and $\Delta H_r^o = 81.82$ kJ/mol and $\Delta S_r^o = -51.28$ J/mol-K for low pressure ($L_c = 0.018$ m) data as shown in Eq. 22. The results in the form of Eq. 20 are:

$$k_{l_{Si(OH)_4}} = 2.04 \times 10^{-9} V^{1/2} p^{3/2} T^{-0.106} \exp\left(\frac{39.20[J/mol-K]}{R} - \frac{183.27[kJ/mol]}{RT[K]}\right), \text{ and} \quad (21)$$

$$k_{l_{Si(OH)_4}} = 3.04 \times 10^{-9} V^{1/2} p^{3/2} T^{-0.106} \exp\left(\frac{-51.28[J/mol-K]}{R} - \frac{81.82[kJ/mol]}{RT[K]}\right), \quad (22)$$

where the pre-factors 2.04×10^{-9} and 3.04×10^{-9} have units $\text{Pa}^{-1/2} (\text{m/s})^{-3/2} \text{K}^{0.106}$. Figure 1 shows the re-fitted forms alongside the digitized experiment data from Ref. 12. This fit is to the data directly versus the log of the data. Hence, it does not give inappropriate weighting to any particular data point.

Figure 1. Data fit to oxidation data found in Ref. 12.

Terrani [12] also derived a parabolic oxidation rate relationship for the SiC-steam reaction with a k_{p,H_2O}^o of 3.424×10^{-2} ($\text{kg}^2\text{-SiO}_2/\text{m}^4\text{-s}$), an E_{a,H_2O} of 238 (kJ/mol-K) and $n=1$ (note Eq. 3) for their SiC-steam oxidation data at temperatures ranging from 1200 °C to 1600 °C and a steam pressure of 0.1 MPa. These parameters give oxidation rates that are ~3 times lower than that proposed by Opila [9] at 1200°C and ~10 times higher at a temperature of 1600°C.

Table 1 contains a list of the oxidation parameters compiled, or derived, for the current effort. The SiC oxidation experiments conducted in Ref. 12 are the most applicable to LWR severe accidents at the time this paper was completed. However, it should be pointed out that the standard enthalpy change, ΔH_r^o , and the standard entropy change, ΔS_r^o , for the silica-steam reaction are physical constants that should not change with pressure. Ref. 12 did not address this point in their paper; but, by examining Figs 16 and 19 of Ref. 12, it can be seen that there is a dramatic change in the structure of the silica layer with pressure. This change was also pointed out by Ref. 16. Since we have yet to find a satisfactory way to incorporate this pressure effect in to our steam oxidation equations, Eqs. 21 and 22, the correlations adopted in Ref. 2, as highlighted in Table 1, remain those used in the analyses appearing in this paper.

The heat-of-reaction for the SiC oxidation by water vapor, Eq. 4, was calculated to be -4.15×10^6 J/kg-SiC at 298 K based on heat-of-formation data given in Ref. 8. The heat-of-reaction for SiO₂ reacting with H₂O was based on the heat-of-formation for SiO₂ given by Ref. 5, and the heat-of-formation for Si(OH)₄ given by Ref. 17. At 298 K, the heat-of-reaction for Eq. 5 is estimated to be -1.02×10^6 J/kg-SiO₂, which demonstrates that this is an exothermic reaction at room temperature.

Table 1. SiC oxidation correlation parameters compiled for this modification effort.

Parameter Source	Gas	Pre-factor	Activation energy/standard enthalpy change (KJ/mol)	Standard entropy change (J/mol-K)	Pressure dependence “n” $(p/p^m_o)^n$
	Parabolic rate constant (kg ² -SiO ₂ or SiC/m ⁴ -s)				
Fox [7]	Oxygen	6.478 × 10 ⁻⁵	190	-	1/2
Opila [9]	Steam	6.915 × 10 ⁻⁹	35		1
Terrani [12]		3.424 × 10 ⁻²	238		
	Linear rate constant (kg-SiO ₂ /m ² -s)				
Hashimoto [10]	Steam	Calculated by MELCOR. Flow conditions and geometry dependent.	56	-66	2
Robinson “lean” [11]			123	-24	
Robinson “rich” [11]			172	16	
Curve fit to Terrani low pressure data [12]			82	-51	
Curve fit to Terrani high pressure data [12]			183	39	

2.2 FeCrAl Oxidation

Oxidation of FeCrAl in air or steam exhibits a parabolic reaction and can be modeled in straightforward manner by Eqs. 2 and 3. Pint et al. [18] recently produced parabolic oxidation data for Kanthal’s Advanced Powder Metallurgy Tube (APMT[®]) alloy for both air and steam. This FeCrAl alloy contains 69% Fe, 21.6 % Cr, 4.9 % Al, plus other minor constituents. Figure 5 of Ref. 18 provides air and steam oxidation data for various materials, including CVD SiC and APMT. Pint did not derive values for the pre-exponential and activation energy for APMT reactions in air and steam for Eq. 3. For the current application, the APMT curves for air and steam were digitized from Pint’s data and fit to determine a $k_{p,air}^o$ of $6.6998 (\text{kg}^2\text{-FeCrAl}/\text{m}^4\text{-s})$ and an $E_{a,air}$ of 294 (kJ/mol-K) for air and a k_{p,H_2O}^o of $5.213 \times 10^{-1} (\text{kg}^2\text{-FeCrAl}/\text{m}^4\text{-s})$ and an E_{a,H_2O} of 260 (kJ/mol-K) for steam; these values were adopted for this MELCOR modification.

Measured heat-of-reaction for FeCrAl oxidation in air or steam could not be found in the literature at the time this work was completed. In estimating these quantities, the approach used by the SNL-NM MELCOR developers for stainless steel was applied. This approach is to mole-weight the heat-of-reaction of the constituent elements (Fe, Cr and Al) to determine a heat-of-reaction for the alloy. Using this method results in a heat-of-reaction of $\sim 7.808 \times 10^6$ (J/kg-FeCrAl) and $\sim 1.278 \times 10^6$ (J/kg-FeCrAl) for air and steam at 298 K, respectively. However, Ref. 19 demonstrates that the oxide layer that forms on FeCrAl is primarily Al_2O_3 (60% to 90% Al) and not an oxide with the same composition of oxides (FeO, Cr_2O_3 and Al_2O_3) as the composition of oxidizing elements of the base metal (70% Fe, 23.5% Cr and 5.8% Al). If this is the case, then the heat-of-reaction would be more like that of aluminum reacting with air and steam, which are $\sim 3.016 \times 10^7$ (J/kg-FeCrAl) and $\sim 1.518 \times 10^7$ (J/kg-FeCrAl) at 298 K, respectively. These numbers are ~ 4 and ~ 12 times higher than those from the weighted approach.

However, if the scale is really mostly alumina, then its melting temperature is likely closer to that of alumina (2323 K) instead the adopted value 1870 K of stainless steel oxide. The current approach implemented the weight-averaged approach for the FeCrAl heat-of-reaction, as is assumed in MELCOR for stainless steel.

3.0 Application of the Modified MELCOR to the TMI Event

The INL-modified MELCOR code was used to examine the potential safety advantages associated with replacing Zircaloy cladding with SiC or FeCrAl cladding or coatings on fuel rods in LWRs while maintaining the same fuel rod geometry (e.g. rod outer diameter and cladding thickness). Note that in each case only the cladding material was modified to the proposed ATF material (e.g. SiC or FeCrAl); all other structural materials in the core remained Zircaloy. The evaluation presented in this paper is for the Three Mile Island Unit 2 (TMI-2) loss-of-coolant accident (LOCA). The TMI-2 accident was caused by a small-break LOCA in a two-loop Babcock & Wilcox (B&W) Pressurized Water Reactor (PWR) [20]. Unaware of the small LOCA caused by a stuck-open pilot-operated relief valve (PORV), throughout the first 300 minutes of this event the reactor operators manually overrode the system to operate the Emergency Core Cooling System (ECCS). This action injected water into the reactor pressure vessel (RPV) to cool the reactor core while simultaneously draining the primary cooling system by way of the coolant letdown system in an attempt to prevent the primary system from becoming incompressible (that is, becoming completely filled by water).

Two reactor coolant system (RCS) pumps were operated during the first 100 minutes of this event, providing adequate core cooling; however, increasing pump vibration caused by two-phase water entering these pumps forced the operators to stop RCS pump operation. At ~140 minutes, the operators became aware of the LOCA and terminated this loss of coolant by closing the appropriate electromatic relief valve (ERV) block valve. However, by this time the core had become uncovered and heated up, causing spacer grid loss by melting, cladding ballooning, control rod meltdown, fuel rod oxidation, hydrogen production, cladding melting, melt candling, fuel melting, molten fuel/cladding pool formation, and a portion of this molten pool pouring into the RPV lower head.

Figure 2 illustrates the predicted RPV pressure during the TMI-2 accident based on the actual core structural and fuel materials. Also noted in this figure are the times when the RCS pumps were tripped in both cooling loops of the reactor (RCP A and RCP B) due to excessive pump vibration, the ERV was closed, and a single pump in the B loop was restarted.

Figure 2. MELCOR-predicted RPV pressure during a TMI-2 accident.

3.1 SiC Performance during the TMI Event

As mentioned previously, the MELCOR model used the Zircaloy cladding model developed by SNL-NM and Innovative Technology Solutions Corporation, Albuquerque, NM, as the base case for this study [3]. This model was used as received from SNL-NM. Figure 3 presents a comparison between the predicted peak-cladding temperature for the TMI-2 accident for Zircaloy and SiC cladding (peak occurs at the top-center region of the core). For the first 100 min of this accident, cladding cooling was maintained by the RCPs in spite of the loss of reactor coolant inventory created by both the LOCA and operator action of draining water from the RCS through the letdown system. According to the MELCOR prediction, the RPV water level drops below the top of active fuel height 100 min into the accident, and the uncovered fuel rod cladding starts to heat up due to fuel decay heat in what is now a slow moving steam environment produced by boil-off of remaining core water inventory. By 125 min, the Zircaloy cladding case reaches temperatures where oxidation heating produced by the steam/Zircaloy reaction starts to accelerate the cladding temperature rise. Cladding failure is predicted to occur at ~145 min, producing a loss of cladding and core geometry in this core region. In the MELCOR code, this failure criterion is purely a temperature set point based on experimental data and modeling experience, which coincides with the melting temperature of a $\text{UO}_2\text{-ZrO}_2$ eutectic (~2500 K) [1]. Upon exceeding this failure criterion, MELCOR transfers the rod's fuel and cladding into a debris field in the coolant channel, where channel blockage and debris heating accelerates damage in this region of the core. In contrast, the simulated SiC cladding case reaches a peak cladding temperature of 1830 K, which is below the melting temperature of the SiC silica protective scale (~1873 K), and well below the SiC decomposition temperature (~2900 K). Temperatures begin to decrease after ERV isolation even under the low makeup water being injected at this time in the accident. Large decreases are seen when a pump in loop B restarts (at ~175 min), and ECCS high pressure injection (HPI) is restored (at ~195 min).

Figure 3. Comparison of MELCOR-predicted maximum cladding temperature during a TMI-2 accident sequence.

A primary reason for the stark difference in Zircaloy and SiC cladding temperature during this accident analysis is that the SiC oxidation heating is approximately two orders of magnitude less than that for Zircaloy, as can be seen in the predictions shown in Figure 4. In addition, because of lower temperatures, MELCOR analysis predicted that SiC cladding would produce more than 10 times less combustible gas during this accident scenario than Zircaloy (see Figure 5).

Figure 6 presents a comparison for the peak cladding temperature predicted by the modified MELCOR for an all SiC-cladding option (shown in Figure 3) and a SiC (0.2-mm thick) coated, or wrapped, Zircaloy (0.47-mm thick) cladding option. As can be seen, the results are nearly identical during the core dryout phase of the accident (100 to 150 min). During this phase the core's cooling water boils off, leaving the upper part of the fuel rods exposed to low-flow, high-temperature steam cooling. There are noticeable differences in the quenching phase of the accident (after 150 min) when ECCS water injection occurs. This divergent quench behavior has not been fully investigated at this time.

Figure 4. Comparison of MELCOR-predicted cladding oxidation heating produced during a TMI-2 accident sequence.

Figure 5. Comparison of MELCOR-predicted combustible gases produced during a TMI-2 accident sequence.

Figure 6. Comparison of MELCOR maximum cladding temperature for SiC and SiC-coated Zircaloy during a TMI-2 accident.

3.2 FeCrAl Performance during the TMI Event

Figure 7 presents a comparison of the predicted maximum cladding temperature for Zircaloy and FeCrAl cladding during the TMI-2 accident. The FeCrAl cladding thickness was taken as that for the Zircaloy in the MELCOR TMI-2 input model. Actual thickness of FeCrAl cladding in fuel design may be less than that of Zircaloy (~0.67 mm) to accommodate the higher neutron absorption cross section and taking advantage of the higher strength of FeCrAl relative to Zircaloy [21]. As noted for SiC, because the oxidation rate for FeCrAl is much lower than that of Zircaloy, the predicted cladding temperatures are primarily a result of decay heat from the fuel. Like the SiC cases, the core configuration is predicted to survive intact. Unlike SiC, however, the FeCrAl cladding is predicted to come close to its assumed failure criteria. Having already achieved complete melt of the FeCrAl at this core location, the temperature remains tenuously below the adopted melting temperature for FeCrAl oxide of 1870 K. A higher level of confidence for FeCrAl cladding remaining intact during this event can only be obtained by determining if the melting temperature of FeCrAl oxide is closer to that for alumina instead of that for steel oxide, and if the oxide “holds” the fuel and molten FeCrAl in place at these high temperatures and during the subsequent rod quench.

Figure 7. Comparison of MELCOR-predicted peak-cladding temperature during a TMI-2 accident sequence for Zircaloy and FeCrAl cladding.

Figure 8 shows a comparison between the predicted hydrogen generation for Zircaloy and FeCrAl cladding. Like SiC, the predicted hydrogen generation is much lower than that for Zircaloy, producing only 4.2 kg of hydrogen. Unlike SiC, FeCrAl does not produce the additional combustible gas of carbon monoxide.

Figure 8. Comparison of MELCOR predicted combustible gases produced during a TMI-2 accident.

Figure 9 shows the predicted maximum temperatures for a FeCrAl-coated Zircaloy cladding and FeCrAl-only cladding. As mentioned earlier, the Zircaloy-only cladding

thickness in the TMI model is ~0.67-mm thick. For this comparison, the FeCrAl coating thickness was assumed to be 0.2-mm thick, leaving 0.47-mm of Zircaloy. MELCOR analyses predict that FeCrAl-coated Zircaloy cladding may experience a slightly higher cladding temperature than the FeCrAl-only cladding. The coating layer is predicted to melt and continue to rise in temperature to the point at which the oxide begins to melt. The oxide from the coated cladding case did not completely melt prior to rod quench, as was the case for the FeCrAl-only cladding. Rod failure was not predicted to occur for either the pure FeCrAl or the FeCrAl-coated Zircaloy options. However, an understanding of the coating's behavior near its melting temperature is needed to determine the accuracy of this result.

Figure 9. Comparison of MELCOR maximum cladding temperature for FeCrAl and FeCrAl-coated Zircaloy during a TMI-2 accident.

Given the uncertainty associated with modeling the TMI-2 event, coupled with the fact that this modified version of MELCOR predicts that a FeCrAl coating would melt during this accident, a final parametric case was examined. In this initial case the heat-of-reaction of FeCrAl oxidation in steam was set equal to that for aluminum oxidation in steam. As can be seen in Figure 10, for this case the added heating, even at the very low oxidation rate of FeCrAl, would melt and fail the coating. The consequence of losing the FeCrAl coating at temperatures this high is very rapid oxidation of the base Zircaloy and predicted rod cladding failure within one minute. However, if the FeCrAl oxide really is alumina, then it would not melt until it reaches a temperature of 2323 K, which brings us back to the same conclusion reached several times in this paper: the properties for FeCrAl oxide need to be determined to make a firm conclusion regarding FeCrAl's full safety benefit as a cladding or coating material during the TMI-2 event.

Figure 10. MELCOR-predicted maximum cladding temperature for FeCrAl-coated Zircaloy during a TMI-2 accident sequence with the base heat-of-reaction estimate compared to that with alumina heat-of-reaction.

3.0 Summary and Conclusions

This work has resulted in a numerical capability that can be used to estimate the performance of candidate ATF cladding materials, specifically SiC and FeCrAl, under severe accident conditions. Separate versions of MELCOR were developed for SiC and FeCrAl because of SiC's complicated oxidation processes. The modifications to the core physics and materials properties data packages are not specific to pressurized or boiling water reactor designs, and therefore applicable to accident analyses for both reactor concepts. Analyses performed to date provide preliminary characterization of the potential safety advantages of SiC and FeCrAl over Zircaloy as cladding materials for fuel rods during LWR severe accident conditions.

Modified versions of the MELCOR code were developed to allow the MELCOR user to add SiC and FeCrAl as possible cladding materials in MELCOR's core oxidation and material data property routines. As with standard MELCOR, these code versions also allow the user to define (override) the cladding material data base and define the cladding material composition based on user supplied mass of Zircaloy, Inconel, and either CVD SiC or FeCrAl for the cladding of a core region. Also, as with standard MELCOR, if more than one material is selected by the user in the cladding definition, then this modified MELCOR evaluates the thermal properties of the composite cladding material by mass weighting material enthalpy and volume weighting material thermal conductivity. The surface oxidation routines in this version of MELCOR assumes that either SiC or FeCrAl precedes Zircaloy in oxidation order (i.e., these materials are applied as a wrap or coating on the external surface of the Zircaloy) if either material is included in the cladding material definition, and reverts back to Zircaloy

failure criteria once these material coatings fail. The SiC version of MELCOR was successfully benchmarked against experimental data to ensure that present SiC oxidation theory in air and steam were correctly implemented in the code. Additional SiC data is now available, but benchmarking of the modified MELCOR against this experimental data has not been completed. The same is true for the FeCrAl modified version of MELCOR.

In summary, these modified versions of MELCOR allow evaluation of coated zirconium alloys, SiC/SiC, SiC wrapped zirconium alloys, advanced zirconium-based alloys, and engineering metallic alloys. The modified versions of the code may be used to evaluate the potential performance of additional candidate materials if sufficient data is available, where the material oxidation behavior will determine which code version should be used as a starting point. Materials exhibiting parabolic oxidation behavior (similar to Zircaloy and FeCrAl) should employ the FeCrAl version of the code, simply modifying the FeCrAl properties to that of the new candidate material via user interface. This approach allows inclusion of both Zircaloy and the new material as cladding in a user specified core region, unlike the standard version of MELCOR that would apply the material change to all core components. Materials exhibiting parabolic oxidation and linear volatilization (similar to SiC) should employ the SiC version of the MELCOR code as a starting point. Key materials data required for evaluation as candidate cladding materials include oxidation reactions (oxidation rate, heat-of-reaction, reaction products, etc.), the Arrhenius relationship for the parabolic oxidation rate behavior, and properties of the base material and its oxide (melting temperature, eutectic formation, thermal conductivity, specific heat, density, emissivity, etc.), as a function of temperature and irradiation. However, to date, user override of the heat-of-reaction defined internally to the code is not available.

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References

1. R. O. GAUNTT, et al., "MELCOR Computer Code Reference Manuals," NUREG/CR-6119, Vol. 2, Version 1.8.6, September (2005).
2. B. J. MERRILL, "MELCOR SiC Modifications for Severe Accident Analysis Applications," Idaho National Laboratory Report, INL/LTD-12-27961, December (2012).
3. R. O. GAUNTT, K. ROSS, and K. WAGNER, "MELCOR 1.8.5 Simulation of TMI-2 Phase 2 With an Enhanced 2-Dimensional In-Vessel Natural Circulation Model," 10th International Conference on Nuclear Engineering, Arlington, Virginia, USA, April 14–18, Vol. 3, pp. 487-494, American Society of Mechanical Engineers (2002).

4. B. J. MERRILL, S. M. BRAGG-SITTON, and P. W. HUMRICKHOUSE, "Status Report on Advanced Cladding Modeling Work to Assess Cladding Performance Under Accident Conditions," Idaho National Laboratory Report, INL/EXT-13-30206 Rev. 2, August (2015).
5. B.J. MERRILL and S.M. BRAGG-SITTON, "SiC Modifications to MELCOR for Severe Accident Analysis Applications," in proceedings of the LWR Fuel Performance Meeting, Top Fuel 2013, Charlotte, NC, September 15-19, 2013, paper 8546.
6. Y. KATOH, K. A. TERRANI, and L. L. SNEAD, "Systematic Technology Evaluation Program for SiC/SiC Composite-based Accident-Tolerant LWR Fuel Cladding and Core Structures," Oak Ridge National Laboratory Report, ORNL/TM-2014/210, May (2014).
7. D. S. FOX, "Oxidation Behavior of Chemically-Vapor-Deposited Silicon Carbide and Silicon Nitride from 1200° to 1600°C," *Journal of the American Ceramic Society*, **81**(4), (1998), pp. 945-950.
8. R. C. WEAST and M. J. ASTLE, *Handbook of Chemistry and Physics*, CRC Press, 60th Edition, 1980, B-234.
9. E. J. OPILA, "Oxidation and Volatilization of Silica Formers in Water Vapor," *Journal of the American Ceramic Society*, **86**(8), (2003), pp. 1238-1248.
10. A. HASHIMOTO, "The effect of H₂O gas on volatilities of planet-forming major elements: I. Experimental determination of thermodynamic properties of Ca-, Al-, and Si-hydroxide gas molecules and its application to the solar nebula," *Geochimica et Cosmochimica Acta*, **56**, October (1991), pp. 511-532.
11. R. C. ROBINSON and J. L. SMIALEK, "SiC Recession Caused by SiO₂ Scale Volatility under Combustion Conditions: I, Experimental Results and Empirical Model," *Journal of the American Ceramic Society*, **82**(7), (1999), pp. 1817-1825.
12. K. A. TERRANI, B. A. PINT, C. M. PARISH, C. M. SILVA, L. L. SNEAD, and Y. KATOH, "Silicon carbide oxidation in steam up to 2 MPa," *Journal of the American Ceramic Society*, **97**(8), (2014), pp. 2331-2352.
13. R. B. BIRD, W. E. STEWART, and E. N. LIGHTFOOT, *Transport Phenomena* (Second Edition), John Wiley & Sons, New York, 2001.
14. J. R. WELTY, C. E. WICKS, and R. E. WILSON, *Fundamentals of Momentum, Heat, and Mass Transfer* (Third Edition), John Wiley & Sons, New York, 1984.
15. R DEVELOPMENT CORE TEAM, *R: A Language and Environment for Statistical Computing*, R Foundation for Statistical Computing, Vienna, Austria (2014), <http://www.R-project.org>.
16. P. F. Tortorelli and K. L. More, "Effects of High Water-Vapor Pressure on Oxidation of Silicon Carbide at 1200°C," *Journal of the American Ceramic Society*, **86** [8], (2003), 1249-1255.
17. M. D. ALLENDORF, C. F. MELIUS, P. HO, M. R. ZARCHARIAH, "Theoretical Study of the Thermochemistry of Molecules in the Si-O-H System," *Journal of Physical Chemistry*, **99**(41), (1995), pp. 15285-15293.
18. B. A. PINT, K.A. TERRANI, M. P. BRADY, T. CHENG, and J. R. KEISER, "High

temperature oxidation of fuel cladding candidate materials in steam–hydrogen environments,” *Journal of Nuclear Materials*, **440** (2013) 420–427.

19. C. BADINI and F. LAURELL, “Oxidation of FeCrAl alloy: influence of temperature and atmosphere on scale growth rate and mechanism,” *Surface and Coatings Technology*, **135**, 2001, 291-298.
20. R. E. HENRY, *TMI-2: An Event in Accident Management for Light-Water-Moderated Reactors*, American Nuclear Society, La Grange Park, Illinois (2001).
21. Y. YAMAMOTO, B. A. PINT, K. A. TERRANI, K. G. FIELD, Y. YANG, and L. L. SNEAD, “Development and property evaluation of nuclear grade wrought FeCrAl fuel cladding for light water reactors,” *Journal of Nuclear Materials*, **467**(2) (2015) 703-716.