

A Development of a Transient Hydrogen Generation Model for Metal-Water Interactions

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Abstract

A transient model for hydrogen generation in molten metal-water interactions was developed with separate models for two stages of coarse mixing and stratification. The model solves the mechanistic equations (heat and mass transfer correlation, heat conduction equation and the concentration diffusion equation) of each stage with non-zero boundary conditions. Using this model, numerical simulations were performed for single droplet experiments in the Argonne National Laboratory tests and for FITS tests that simulated dynamic fragmentation and stratification. The calculation results of hydrogen generation showed better agreement to the experiment data than those of previous works. It was found from the analyses that the steam concentration to be reached at the reaction front might be the main constraint to the extent of the metal droplet oxidized. Also, the hydrogen generation rate in the coarse mixing stage was the higher than that in the stratification stage. The particle size was the most important factor in the coarse mixing stage to predict the amount of hydrogen generation.

Key Words : severe accident, metal-water interaction, hydrogen generation

1. Introduction

During severe accidents of nuclear power plants, the molten fuel called corium may come into contact with the water remained in-vessel or ex-vessel. If the corium falls into the water, the metal-water interaction will occur. A metal-water interaction is a phenomenon where a hot liquid

(molten metal) contacts a cold, more volatile liquid (water), and then the hot liquid rapidly fragments with transferring heat to the cold liquid to generate steam, which possibly leads to a locally high pressure. The rapid steam generation may threaten the containment integrity or other safety-related equipment integrity by local over-pressurization. During this process, the corium can also react with

the steam to generate hydrogen. Moreover, a formation of such combustible gas mixture can pose an additional serious threat via hydrogen burns such as a deflagration or a detonation.

The hydrogen generation in the nuclear power plant containment is, in nature, a sub-physics accompanied by various thermo-hydraulic interactions between high temperature molten metal and the coolant water. Therefore, its prediction should require overall consideration of such interactions of interest although it can be treated in a simplified approach.

Since a simple theoretical model developed by Baker and Just[1] for a molten zirconium metal sphere in water, a number of studies with different approach for molten metal oxidation in metal-water interaction have been reported. Epstein et al. [2] were the first who present sophisticated boundary layer treatment of film boiling around a hot sphere for steam diffusion through steam/hydrogen mixture. Corradini et al. [3] predicted limiting hydrogen generation rates for three different stages of metal-water interaction including steam explosion stage, based on the observation of FITS experiments. They stated that the hydrogen generation would be governed by controlled mechanisms such as solid and gas diffusion. Young et al. [4] improved the model of Corradini et al. with accounting for the effects of radiation heat transfer and oxidation energy, of which the calculation results showed no distinct difference from those of Corradini et al.. Recently Uludogen and Corradini[5] had developed thermo-hydraulic model using a semi-empirical heat transfer correlation and a mass and energy transfer analogy to predict the concentration of the reactants (i.e. steam or metal) at the reaction front. But, as in earlier works, the reaction rates were assumed to be controlled by either of dominant processes between gas and solid diffusion.

To predict an amount of the hydrogen generation under realistic configuration of metal-water interactions, and generalize the hydrogen generation mechanism, Lee and Park[6] have developed a detailed mechanistic model which includes the dynamic mixing of fragmentation process, the semi-empirical heat and mass transfer correlation, and the concentration diffusion equation with the general non-zero boundary condition. Although it gave a reasonable agreement with some of the experiments, the diffusion of the reactants into reaction front, however, was assumed to take place in a quasi-steady at given time scale. In general, this approach can be hardly valid for a problem where rapid variation of thermodynamic quantities can occur or where on very small time scale major quantities have to be traced within the region of interest.

For metal-water interactions of interest, for example, three parts of the model are required. First, the physical processes of coarse mixing and stratification should be treated in tractable ways. Second, it is important to determine the heat and mass transfer rates in film boiling and metal oxide layer. Third, the mechanism of oxidation reaction and treatment of reaction front have to be addressed.

In this study, a transient hydrogen generation model in molten metal-water interactions was developed based on a modification of the Lee and Park[6] model. This model includes the mechanistic concept of each stage, heat and mass transfer, and coupled transient heat conduction and steam concentration diffusion equation with non-zero boundary conditions in reaction domain. Besides, the variation of thermodynamic properties with temperature is considered. With developed model, the calculation results are compared with single droplet experiments in the Argonne National Laboratory (ANL)[1] tests and

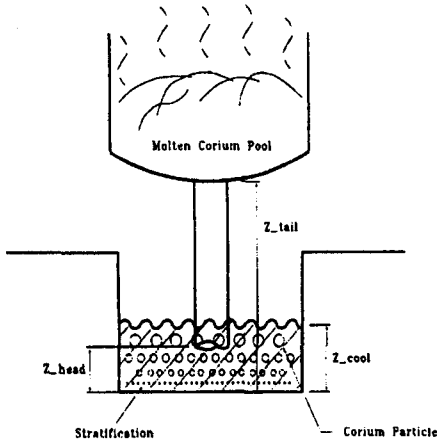


Fig. 1. A Schematic of Physical Transfer

with Fully Instrumented Test Site (FITS)[7] tests that simulated dynamic fragmentation and stratification to estimate the model capability.

2. Model Descriptions

2.1. Physical Process

Fig. 1 depicts the physical process of the metal-water mixing considered in this problem. As were in earlier work[6], we considered only non-explosive case where a coarse mixing is followed by a stratification of the molten metal over the cavity floor, finally resulting in stable coolable debris beds. Therefore, the process can be divided into two stages, coarse mixing and stable stratification. In the coarse mixing, spherical molten metal droplets fall down or are ejected with single terminal velocity in an infinite pool of subcooled or saturated water. Undergoing the fragmentation during the dynamic mixing, over a short time the droplets are encircled with the stable vapor film. Fig. 2 shows the practical representative of this concept, where a prescribed size of the droplet can be modeled by the modified Chu's correlation[8] developed for a water/air

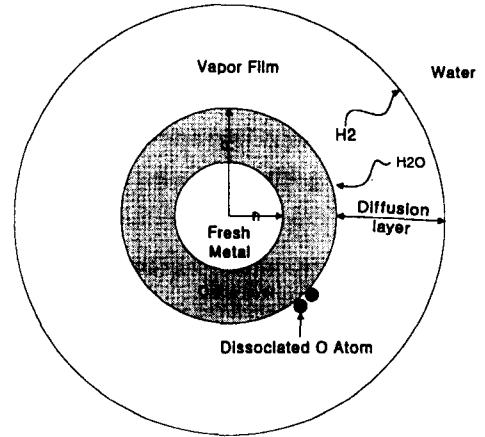


Fig. 2. The Physical Concept of Coarse Mixing Stage

system as,

$$D_f(t) = D_{f0} \exp(-Z) \quad \text{for } z_{Bot} \leq z \leq z_{Pool} \quad (1)$$

where the variables, Z and C_1 , are

$$Z = \left(\frac{C_1 We^{0.254}}{D_{f0}} \right) \left(\frac{\rho_c}{\rho_f} \right)^{1/2} \quad (2)$$

$$C_1 = 0.1232 - 0.149(\rho_c / \rho_f)^{1/2} \quad (3)$$

The fragmentation is limited by minimum droplet diameter proposed by Fauske and Henry[9,10] or Corradini[11].

When fragmented corium falls down the cavity floor, it may begin to be stratified. In the stratification stage where the molten metal can be underlying the water, the reaction is assumed to start after the last part of corium particles falls down the cavity floor.

2.2. Heat and Mass Transfer

The energy generated as a result of exothermic chemical reaction would be transferred by the conduction from the reaction site into the boundary and away from the boundary to the bulk

water by the convection and radiation. Then, the energy balance and related boundary conditions can be established as follow,

$$\rho c_p \frac{\partial T}{\partial t} = \nabla(k \nabla C_v) \quad \text{for } r_i < r < R \quad (4)$$

At the metal droplet surface R,

$$-k \nabla T = h_c(T(R) - T_0) + h_{rad}(T^4(R) - T_0^4) \quad (5)$$

And, a moving interface (or reaction front) r_i ,

$$\begin{aligned} 4\pi r_i^2 a k_s C_f C_v(r_i)(-\Delta H) + 4\pi r_i^2 k \nabla T \\ = \frac{4}{3} \pi r_i^3 \rho_f(r_i) c_p(r_i) \frac{dT(r_i)}{dt} \end{aligned} \quad (6)$$

These governing equations were applied for the geometry of interest; one-dimensional spherical for coarse mixing and rectangular for stratification. These equations could be derived valid for the oxide metal layer from general heat conduction equation in which the convective and radiative heat transfers were implemented into boundary condition of the equation at solid droplet surface. The fresh metal, i.e. unoxidized metal which lies between the center of the metal and reaction front, was treated as a medium of lumped heat transfer (is shown in the right hand side of Eq. (6)) since it has very high Biot number. The first term in left hand side of Eq. (6) represents the exothermic heat determined by the reaction kinetics.

For the convective heat transfer coefficient used in coarse mixing stage, Dhir and Purohit's model[12] for film boiling around a sphere on subcooled water was used in this study because it gave a good prediction of their data over a wide range of subcooled liquid temperatures. In the stratification stage, a modified Berenson's correlation[14] for film boiling on a horizontal flat surface was used.

The governing equation for mass transfer can be

established in a similar approach, but it has to be discussed with a concept of the reaction mechanism which will be explained below.

2.3. Reaction Mechanism

The oxidation reaction was modeled by unreacted-core-shrink model[15]. As the reaction proceeds, the reaction front will move into the interior of the metal droplet. Thus, in order to the steam reach the new front of unreacted core, it must move through the steam/hydrogen mixture around the particle and the porous reacted oxide layer. An approach of Corradini et al.[5] was somewhat similar to this work, but assumed all the steam arrived at the reaction front deems to react with the metal molecules and at last disappear. This assumption arose from the concept that steam concentration is much less compared with that of fresh metal at the reaction front and therefore its concentration is compelled to control the reaction. But this assumption led to overestimated results in hydrogen generation[5]. Instead, this study introduces realistic concept that absolute concentration of the reactants (steam or metal) which has to be determined by counter-current steam/metal diffusion characteristics in the oxide layer, might control the reaction rates with the appropriate reaction kinetics.

A transient counter-diffusion equation with respect to the steam can be written as follows:

$$\varepsilon \frac{\partial C_v}{\partial t} = \nabla(D \nabla C_v) \quad \text{for } r_i < r < R \quad (7)$$

At the metal particle surface R,

$$-D \nabla C_v = k_m(C_v(R) - C_{v,0}) \quad (8)$$

At the moving interface r_i ,

$$D \nabla C_v = a k_s C_f C_v(r_i) \quad (9)$$

$$a C_f \frac{dr_i}{dt} = -D \nabla C_v \quad (10)$$

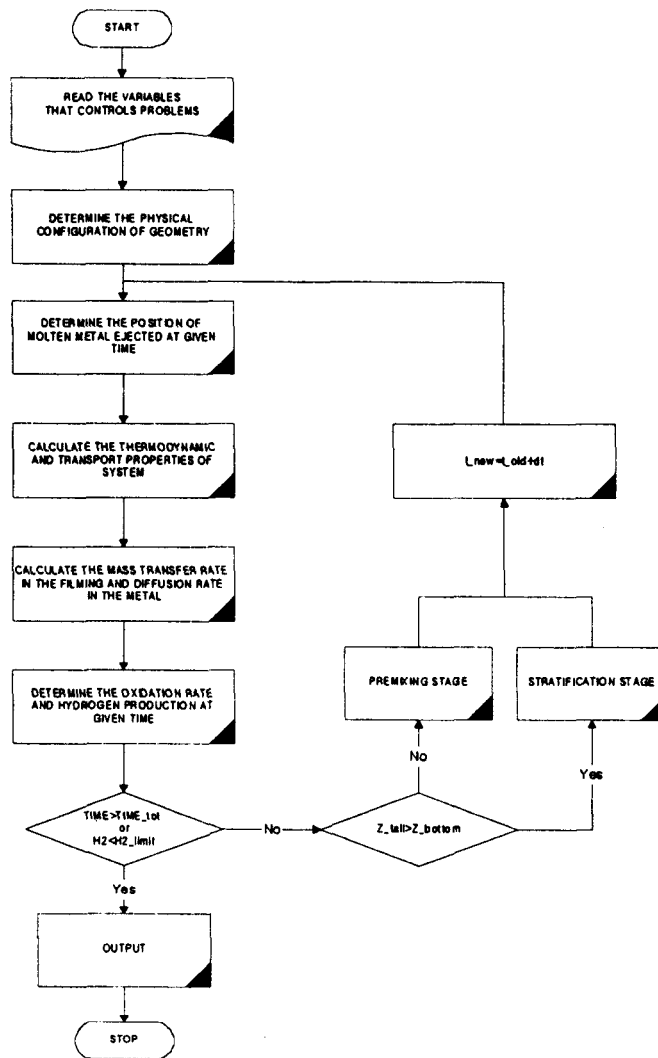


Fig. 3. Numerical Scheme for Hydrogen Generation Prediction

The initial condition is $R = r_1$ at $t=0$. As like in the energy transfer, these equations are applied for each stage through appropriate coordinate.

For required mass transfer coefficient, the heat and mass analogy[13] was used under the assumption that the physical properties are constant for very small time step and the mass transfer rate is small. In the metal water interaction, actually the physical properties of steam and water with vapor film are assumed to

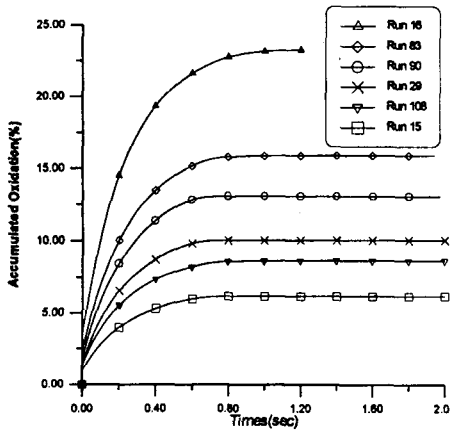
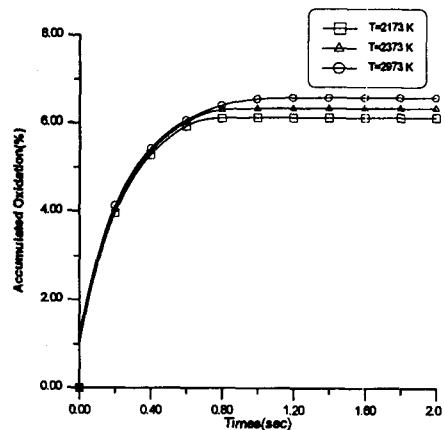
be at saturated condition, and mass transfer rate is generally very low. Besides, this analogy has been confirmed experimentally for a number of flow systems[13].

3. Calculation Method

The numerical method to solve a set of coupled differential equations [[4] to [6] and [7] to [10]] consists of converting differentials into difference,

Table 1. Calculation Results Compared with ANL Tests

Run	Exp. Conditions			Results			
	Mean Particle Diameter (μm)	Metal temp ($^{\circ}\text{C}$)	Appearance of Residue	Exp. Results		Cal. Results	
				Percent Reaction	H2 Gen.(g)	Percent Reation	H2 Gen.(g)
15	2040	1900	Spherical	9.0	0.1096	6.1	0.0743
108	1680	2100	Spherical	14.8	0.1007	8.7	0.0592
29	1500	1852	Spherical	7.9	0.0383	10.0	0.0485
90	1290	1852	Spherical	19.7	0.0607	13.1	0.0404
83	1180	2200	Spherical	14.8	0.0349	15.9	0.0375
16	980	2700	Spherical	17.1	0.0231	23.2	0.0313

**Fig. 4. The Calculated Metal Oxidation Rates****Fig. 5. The Effect of Initial Metal Temperature (reference Case : Run 15)**

choosing a proper relationship between independent parameter increments for the computational convenience. Because of the metal-water interaction with varying the properties and very small particle size in the coarse mixing, to obtain a stable solution is most important. By using fully implicit formulation of Euler method, the set of partial differential equations was transformed into the difference equations. And iteration method with under-relaxation was used to solve the equations.

For the simulation of ANL tests, the reaction

occurs only premixing stage since the molten metal is a single particle with constant size. The coolant pool is divided finely below 1.0×10^3 nodes and the transient analysis is conducted each time step dividing the mesh into more fine sub-mesh. When the metal particle enters new mesh of the coolant pool it is assumed that the unreacted surface is exposed and surrounded by the steam reactant. And, the thermodynamic and transport properties, heat and mass transfer rate was calculated in each time step. The calculation is conducted only non-explosive test cases.

Table 2. FITS Series Experimental Conditions and Results

Test	Fuel Mass Deli.	Water Mass	Mass Ratio	Water Temp	Ambient Pressure	Water Side Dime.	Water Depth	Melt Entry Vel.	Metal Oxidation (%)	
	kg	kg	m_c/m_l	K	MPa	m	m	m/s	FeO	Fe ₂ O ₃
FITS0D	17.8	182.9	10.3	368	0.085	0.61	0.51	5.9	29	19
FITS2D	19.0	95.37	5.0	289	1.103	0.38	0.66	7.3	24	16
FITS2DR	18.7	95.3	5.1	299	1.103	0.38	0.66	7.3	30	20
FITS3D	18.9	86.6	4.6	401	0.70	0.76	0.15	5.7	97	67
FITS5D	19.5	21.3	1.1	368	0.083	0.38	0.15	7.3	24	16
FITS8D	19.5	21.3	1.1	367	0.083	0.38	0.15	6.9	31	21

For the simulation of FITS tests, it is assumed that the cylindrical column of the molten metal determined by the vessel rupture size and the falling velocity, is poured into the coolant pool. The calculation during coarse mixing stage begins with the molten metal contact coolant water and ends if last single or fragmented particles touch the cavity floor. Next, the calculation for stratification continues until saturated reaction rate reaches. In the coarse mixing stage, because the position of particles varies with time and the radius of particles varies with height, it is not easy to treat numerically the particle fragmentation and heat and mass transfer at the same time. For this study, it was taken numerically that the metal particles might be fallen down exactly one mesh during one time step and the radius of particles change with the representative value for each mesh of coolant pool by Eq. (1). Fig. 3 is the flow chart for the calculation of hydrogen generation.

4. Results and Discussion

The prediction capacity of numerical model was tested by comparing its results with two experimental observations. First, the calculations were conducted for several tests among ANL experiments[1] which showed non-explosive interaction. As specified in Section 3, the size of

the droplet was assumed to be constant all over the time of the simulation, so that the droplet did not undergo the fragmentation. Table 1 summarizes the effects of droplet diameter and metal temperature for the six tests of ANL experiments which have spherical liquid metal. The relative error of total amount of hydrogen generation is about -41% to +35%. Considering the instrument errors on experimental measurements and the deformation of metal droplet surface, it is expected that this uncertainty range can be reasonable. It should be noted that a prediction of the surface area to be reacted is very important for the hydrogen generation. Actually, in the experiment, liquid zirconium wire was used so that a shape of the droplet might vary during the experiment. Also, there exists the uncertainty on material properties under very high temperature conditions.

Fig. 4 shows a variation of the hydrogen generated as a function of time. As expected, the amount of oxidation was highly affected by the particle size.(see Run No. 16) The oxidation rate was decreased as the time elapsed and the oxidation mostly ceased at 1 second, arriving at the isothermal state. Fig. 5 represents the effect of initial metal temperature in metal-water interaction. The amount of oxidized metal was increased with increasing the initial metal

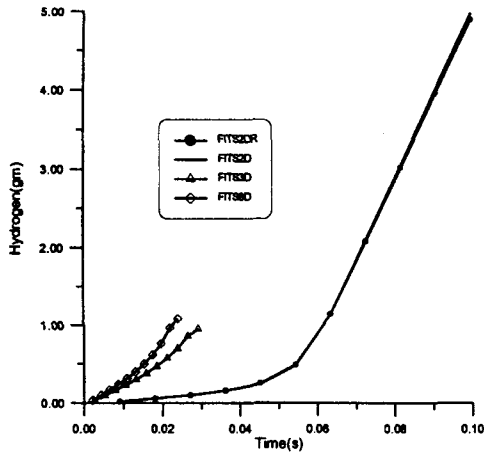


Fig. 6. Calculation Results of FITSD Series (Coarse Mixing Only)

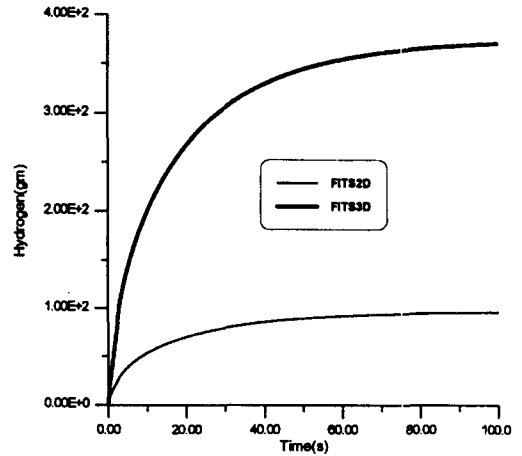


Fig. 7. Calculation Results of FITS2D & FITS3D (Coarse Mixing + Stratification)

Table 3. Calculation Results Compared with FITS Tests

Test	Mass of hydrogen Generated		
	Measurement(gm)	Calculated (gm)	
		Coarse Mixing	Stratification
FITS2D	91	4.97 (0.18) *	90.98 (183) *
FITS3D	355	0.95 (1.09) **	365 (132.2) **

Note) *: the calculated result of Corradini et al.[3]
 **: the calculated result of Lee and Park.[6]

temperature, but the difference was very small. This result is quite a different from those in previous works in which there was significant increase in the oxidation rate. This is because of the material characteristics used in the simulations. Whereas more volatile aluminum composites had used in previous works[5], this work simulated with zirconium metal where there was no significant variation of zirconium thermodynamic properties with temperature in the liquid phase.[16] The second simulation was performed for FITS experiments that are typical of fuel-coolant interaction experiment. Among series of FITS

experiments, This study selected FITS-D series aimed at investigating the effects of various initial conditions on the hydrogen generation. Table 2 shows the experimental conditions and results of the successful FITSD series, which used iron/alumina composites and are non-energetic interactions.

Fig. 6 represents the calculated amounts of hydrogen generation in the coarse mixing stage for some selected tests. The hydrogen generation rate is increased over time due to the dynamic fragmentation which increases the total droplet surface. The FITS2D and FIT2DR showed much

more hydrogen generation than FITS3D and FITS8D tests. This result can be explained by following reason. In FITS3D and FITS8D cases, the coolant depth is the smaller so that there exist less chance of the dynamic fragmentation to affect overall hydrogen generation.

Fig. 7 shows the amount of hydrogen generation for FITS2D and FITS3D tests with time. Table 3 summarizes the portions of the hydrogen generated from each stage. Most of the hydrogen was generated in stratification stage since the time interval of coarse mixing was much shorter than that of stratification. But the hydrogen generation rate was much larger in the coarse mixing than in the stratification. This result confirms, when the fuel-coolant interaction occurs somewhere in nuclear power plant, that the hydrogen concentration can rise rapidly up to the flammable level. In the case of FITS3D test, the metal is oxidized completely. Comparing the experiment conditions between FITS2D and FITS3D test, the difference of water subcooling and the system pressure may cause the difference of the amount of hydrogen generation between FITS2D and FITS3D test.

For FITS2D test shown in Table 3, calculated result in this study showed that a total of 95.95 gm was generated all over the time. Comparing with those of the previous works, this result gave much closer to the experimental measurement. Despite the inherent uncertainties on the problem and limited case study, it can be stated that this model can predict the better agreement with experiment, precisely capturing rapid transition on very short time interval.

5. Conclusions

A transient hydrogen generation model was developed to analyze the hydrogen generation during metal-water interaction. Coupled with

improved thermodynamic property data, the model was applied for two major experiments. For the case of applied for limited non-energetic metal-water interaction, the calculation results showed better agreement to the experiment data than those of previous works.

The general findings from this study can be listed below;

- (1) The steam concentration to be reached at the reaction front is the main constraint to the extent of the metal droplet oxidized.
- (2) The hydrogen generation rate in the coarse mixing stage is higher than that in the stratification stage. The particle size is the most important factor in the coarse mixing stage to predict the amount of hydrogen generation.
- (3) The metal ignition which the reaction rate in aluminum composites can increase rapidly over some elevated high temperature, did not take place in zirconium simulation.

The applicability of this model on metal-water interaction may be improved if the mechanistic model for energetic interaction, i.e. steam explosion is additionally developed.

Nomenclature

a	= stoichiometry
C	= concentration
C_1	= empirical constant in Eq. (2)
c_p	= specific heat of metal
D	= diameter, diffusion coefficient
H	= enthalpy
h	= heat transfer coefficient
k	= thermal conductivity
k_m	= mass transfer coefficient
k_s	= reaction rate constant
m	= mass

R	= radius of particle
r	= radial coordinate
T	= temperature
t	= time
We	= Weber number
Z	= nondimensional axial falling distance
z	= axial position
ϵ	= surface emittance
ρ	= density

Subscripts

c	= coolant, convection
f	= metal or fuel
0	= initial
v	= vapor, steam

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