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Metal Burning in Graphite-Moderated Reactors

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Evaluating the consequences of severe accidents in graphite-moderated nuclear reactors requires predicting the ignition of bulk metal components. Because of insufficient and inconsistent published information on metal ignition, we formulated a simple model to predict ignition and gas-phase burning as a function of local conditions. We incorporated our model into GRSAC, a general safety evaluation code for gas-cooled reactors. Model results compare relatively well with measured out-of-pile burning rates for magnesium-clad simulated fuel.

Introduction

Studies are underway at Oak Ridge to assess the consequences of severe accidents in graphite-moderated reactors, some of which contain metallic uranium fuel and magnesium alloy or aluminum cladding. Combustion of graphite and reactor components can be important for reactor accidents in which air is used to directly cool the core (a discarded practice) or in which the pressure vessel is breached, exposing the overheated core to atmosphere. In such cases, gas-phase burning of the cladding alloy and perhaps the metallic fuel need to be considered along with heterogeneous oxidation of the metals and graphite.

In the Oak Ridge study, we are using the Graphite Reactor Severe Accident Code (GRSAC) to evaluate various types of accident scenarios. GRSAC is a coupled neutronics/thermal hydraulics code for gas-cooled reactors in which damage functions have been added to account for the effects of heterogeneous oxidation of uranium fuel, magnesium and aluminum cladding, and graphite moderator. Previous comparisons of GRSAC results with out-of-pile heating tests conducted on French reactor fuel [1] showed that simple heterogeneous oxidation of the magnesium alloy cladding was inadequate to explain the observed results. Specifically, these earlier simulations could not reproduce the severity of the observed combustion damage.

In reviewing the literature we have been unable to find consistent observations for gas-phase burning near the surface of bulk uranium, magnesium, or aluminum. The so-called “ignition” point and its relationship to gas-phase burning is also unclear. For example, wide ranges are reported for the ignition temperature of bulk magnesium and uranium. Fassel et al. [2] reported a value of 896 K for the ignition temperature of magnesium compared with 1250 K reported by Abbud-Madrid et al. [3]. Also, Baker et al. [4] reported an improbably low ignition temperature for uranium of 873 K, a temperature far below temperatures at which metallic uranium is routinely handled in air.

Because of the lack of consistent observations and a general predictor for bulk-metal ignition, we constructed a simple gas-phase burning model that we could use with GRSAC to simulate graphite reactor accidents. In the following discussion, we describe the simple model and compare model predictions with the French out-of-pile test data.

Specific Objectives

The specific objectives of this paper are to:
(1) review the literature regarding ignition of bulk metals;
(2) propose a simple model for ignition based on gas-phase burning that can be used for reactor accident simulations; and
(3) compare model predictions with available test data.

Results and Discussion

Literature Review

Much of the relevant work on metals burning appears to have been done more than three decades ago. Gordon [5] first suggested that there were five basic categories of behavior, which were elaborated on by Bzustowski and Glassman [6] and Markstein [7]. Each category was defined by the relative metal volatility and the physical properties of the product oxide. Briefly, the five categories are: a) High volatile metals; b) Non-volatile metals; c) Metals with protective oxide films; d) Nonvolatile metals with volatile oxides; and e) Alloys. Category a) includes volatile metals such as magnesium and alkali metals. Metals in a) tend to burn in the vapor phase with the emission of large amounts of smoke. There is conflicting evidence about whether or not aluminum falls in this category. Harrison and Yoffe [8] observed aluminum wires burning in the vapor phase, but Abbud-Madrid et al [3] were not able to ignite aluminum up to 1770 K.

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For our purposes, the most relevant categories are a) and b) which would include magnesium cladding and uranium fuel, respectively. Aluminum cladding might also be included in category a), but we would also consider it a likely candidate for c). For future studies, the appropriate designation of aluminum cladding is likely to become an important concern.

2. Metal Ignition Temperatures. The term ignition temperature is often used in a manner that implies an intrinsic property, like melting point. Clearly, however, details of the measurement method effect the result. The common method, used by Fassel et al. [2], Baker et al. [4] and Abdur-Madrid et al. [3], is to ramp the specimen temperature until the heat generated by oxidation exceeds heat losses, at which point there is a distinctive jump in sample heating. The ignition temperature so determined depends on the sample size, apparatus geometry, manner of temperature measurement, and amount of air flow (if any). Also, under quiescent conditions of a laboratory apparatus, adherent oxide films, such as for aluminum, may remain intact resulting in higher measured ignition temperatures than would be exhibited in engineering systems. It is clear that such ignition temperatures can only be used directly in a specific context. This makes application to different reactor designs and flow conditions problematic.

3. Vapor Pressure Theory of Epstein [9]. Epstein proposed a simple ignition rule based on metal vapor pressure. According to Epstein, metals with stable, insoluble oxides ignite at temperatures where the vapor pressure reaches about \(2 \times 10^4\) atm. This prediction leads to the comparisons shown in Table 1. We note from the table that despite a fair match for magnesium (observations of Fassel and Martin), there is frequently poor agreement with reported ignition temperatures.

### Table 1. Predicted ignition temperatures compared with measurements.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Measured Ignition Temperature (K)</th>
<th>Vapor Pressure at reported Ignition Temperature [10] (atm)</th>
<th>Ignition Temperature Predicted by Epstein [9] (K)</th>
<th>Approximate Ignition Temperature from Simple Model (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1250 [3]</td>
<td>0.36 (at 1250 K)</td>
<td>812</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>898-933 [1]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>896 [2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>2327[3]</td>
<td>0.20</td>
<td>1423</td>
<td>2400</td>
</tr>
<tr>
<td>U</td>
<td>873 [4]</td>
<td>(5 \times 10^{-22})</td>
<td>2477</td>
<td>3600</td>
</tr>
<tr>
<td>Zr</td>
<td>1555 [3]</td>
<td>&lt; (2 \times 10^{13})</td>
<td>2983</td>
<td>---</td>
</tr>
<tr>
<td>Fe</td>
<td>1470 [3]</td>
<td>2.6 (\times 10^{-7})</td>
<td>1889</td>
<td>3600</td>
</tr>
<tr>
<td>Ti</td>
<td>1670 [3]</td>
<td>6.1 (\times 10^{-4})</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sn</td>
<td>1156 [3]</td>
<td>1.5 (\times 10^{-4})</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Zn</td>
<td>1060 [3]</td>
<td>0.29</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu</td>
<td>1360 [3]</td>
<td>7.8 (\times 10^{-7})</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

### The Gas-Phase Burn Model

We conclude from our literature review that it would be difficult to construct a simple ignition model capable of generally explaining reported ignition behavior. At least some of the inconsistencies are probably due to differences in the experimental setup and measurement methods among investigators, and the confusion is likely to be resolved only by detailed measurements of local metal vapor concentration and temperature near the solid surface. One particular issue we see is that most experiments did not include an unambiguous measure of actual surface temperature of the metal at the site of combustion.

In order to have some basis with which to proceed with reactor accident simulations, we adopted a modified version of Epstein's ignition theory; i.e., ignition depends on the metal vapor pressure reaching a sufficiently high level that gas-phase combustion becomes more important than heterogeneous combustion. In this approach, we define ignition as the point when metal vaporization rate equals or exceeds the heterogeneous oxidation rate. Our estimates for individual combustion thus depends on determining the relative rates of heterogeneous oxidation and metal vaporization inside reactor flow channels.

Heterogeneous oxidation involves both boundary-layer oxygen transport and chemical reaction at the solid surface. When the surface oxidation reaction is the rate limiting step an expression such as...
\[ R_m = A \exp(-E/RT) P(O_2), \]  
(1)

can be used where \( R_m \) is the surface oxidation rate, \( A \) is a constant, \( E \) is an activation energy, \( R \) is the universal gas constant, \( T \) is absolute temperature at the surface and \( P(O_2) \) is oxygen pressure at the surface. This latter term assumes first order dependence on oxygen pressure.

Assuming that oxygen transported from the free stream to the surface is completely consumed, then the mass-transfer-controlled heterogeneous oxidation rate may be approximated by

\[ R_m = n h_m [O_2], \]  
(2)

where \( R_m \) is the heterogeneous oxidation rate, \( \text{mol(L}^2\text{-t)} \); \( n \) is the number of oxide molecules produced per \( O_2 \); \( h_m \) is the mass transfer coefficient, \( \text{L/t} \); and \( [O_2] \) is the oxygen concentration in the free stream, \( \text{mol/L}^3 \).

For laminar flow in long, cylindrical ducts, \( h_m \) depends primarily on the diffusivity of oxygen in air, therefore on temperature. In such cases, the Graetz or Nusselt solution may be used (constant Nusselt number) to determine \( h_m \). The nature of this solution is such that \( h_m \) does not depend on free stream velocity but does increase with temperature due to the increase of oxygen diffusivity. In turbulent flow, models in GRSAC use the Reynolds analogy to determine \( h_m \) using estimated roughness and Reynolds number to determine the friction factor. Complex flow cross-sections require use of the hydraulic mean diameter for determination of the Reynolds number. In turbulent flow, \( h_m \) is directly velocity dependent. But for a given mass flow rate, the increase in \( h_m \) with temperature due to reduction in density is exactly compensated by the reduction in oxygen concentration. Therefore, a feature of oxygen mass transfer control in turbulent flow is that it is not temperature dependent at constant mass flow.

If we assume that metal vaporization is also limited by boundary-layer transport, the rate of metal vapor transport from the surface to the gas bulk is given by,

\[ R_g = h_m [M] \], \]  
(3)

where \( R_g \) is the gas-phase burning rate, \( \text{mol(L}^2\text{-t)} \); \( h_m \) is the mass transfer coefficient for metal vapor to the free stream, \( \text{cm/min} \); and \([M]\) is the concentration of the vaporized metal at the surface, \( \text{mol/L}^3 \).

Values of \([M]\) depend on the vapor pressure of the metal and may be approximated for present purposes by the ideal gas law. Unlike Epstein's theory, this model considers the mass-transfer coefficient of metal vapor, which is highly temperature dependent in the laminar regime but dependent primarily on the gas velocity in turbulent flow. For estimating vapor diffusivities in air we use a method based on the Gilliland equation. Specifically, metal vapor diffusivities are obtained from the diffusivity of oxygen in nitrogen, multiplied by a parameter ratio that depends on molecular masses and atomic volumes. The result for magnesium is,

\[ D(Mg,T) = 0.0949 (T/298)^{1.5}, \]  
(4)

where \( D \) is in units of \( \text{cm}^2/\text{s} \). Equation (4) yields a lower diffusivity for Mg relative to oxygen because of its larger atomic volume. At 298 K, the estimated value is 0.0949 \( \text{cm}^2/\text{s} \) compared to 0.181 for oxygen.

![Fig. 1. Metal Oxidation regimes for fixed cooling rate.](image)

Figure 1 illustrates the transition from burning dominated by heterogeneous oxidation to gas-phase-dominated burning as surface temperature increases. The horizontal line shows the rate when dominated by the mass transfer of oxygen to the surface, assuming turbulent flow in the free stream. The curve, "chemical rate," shows the steep increase with temperature typical of an Arrhenius rate expression. The "metal-vapor-transfer" curve also rises steeply with temperature due to increasing vapor pressure of the metal. Below \( T_1 \), in the chemical control regime, there is ample oxygen delivery to the surface and oxidation is limited by the intrinsic surface reaction rate. Metal vapor transfer to the air is low due to low vapor pressure. Above \( T_1 \) (but below \( T_2 \)), the oxidation rate is restricted by oxygen transfer to the surface and, therefore, remains approximately steady with increasing temperature. Ignition occurs above \( T_2 \), when metal vapor transfer to the free stream exceeds surface reaction rate. Combustion is no longer limited by oxygen transport.
because metal vapor is being conveyed in large quantities into the bulk gas. Estimated values for \( T_2 \) are listed in Table 1 for magnesium, aluminum and uranium. These temperatures agree fairly well with the ignition measurements of Abbud-Madrid [3] for magnesium and aluminum.

**Limitations of the Model.**

Our model implicitly assumes a Reynolds-like analogy between metal vapor transport and oxygen transport in the gas-phase boundary layer. This is obviously an oversimplification, but, as we show below, appears to give reasonable results when implemented in the GRSAC code. In some cases, one might expect that the analogy would break down; for example, when the metal vapor is very unreactive (flame thickness >> boundary layer thickness) and must travel far out into the bulk before it is consumed. Also, unique chemical and physical properties of the product oxides could strongly affect the release rate of the metal vapor at the surface. Finally, in some cases, the rate of vaporization could be controlled by heat transfer in the solid, so that transport through the boundary layer is not the rate limiting step. Such deviations from our “ideal” picture may explain the results shown in Table 1. As shown, aluminum, magnesium, and zinc have sufficiently high vapor pressure for significant gas phase burning at the measured ignition temperature. However, vapor pressures for titanium, zirconium, tin, iron and copper are extremely low at the measured ignition temperature.

**Comparison of Magnesium Vapor Phase Burning Rates with Observations of Martin et al. (1962).**

In 1957 a channel fire occurred in the French G-1 reactor, which was a graphite moderated reactor containing natural uranium metal fuel clad in a magnesium alloy and cooled by once-through air flow [11]. Out-of-pile tests, described by Martin et al. [1], sought to elucidate the conditions under which such a fire may occur. (Some early reactors used air cooling for simplicity. The practice was abandoned due to the fire hazard.) Nuclear heating of a fuel element was simulated by enclosing an electrical resistance heater in a uranium tube of 2-mm wall thickness. The heaters were capable of generating a 12-W/cm² heat flux, representative of the G-1 reactor power density, and had an upper limit temperature of 1050°C. The uranium cylinder was placed in a magnesium can simulating the cladding. An 18 fin cladding was used. The length of the elements ranged from 30 to 60 cm. They were placed in graphite tubes measuring 40 to 80 cm in length. Temperatures were measured on the cladding, the uranium, and the resistance heater. Tests were conducted at progressively higher air flow rate, resulting in progressively more rapid cladding oxidation.

Oxidation was monitored photographically and by post test weight changes. For safety reasons, an iron rod was substituted for uranium at the highest air flow rate, which simulated 60% of full flow conditions.

Table 2 summarizes the test data and the GRSAC simulation using the gas-phase burn model described above. It was found that best results were achieved when the temperature used for evaluating the vapor pressure was increased above the measured bulk temperature, i.e., the following modification to Eq. (3) was used in this comparison:

\[
R_g = h_m \frac{P_r(T + \Delta T_{HS})}{R_i} T
\]

where \( \Delta T_{HS} \) is the temperature augmentation. The subscript denotes hot spots, as were observed on the cladding during the heating tests. The comparisons shown in the table used a value for \( \Delta T_{HS} \) of 300 K.

**Table 2. Comparison with French Channel Fire Test Data of Martin (1962)**

<table>
<thead>
<tr>
<th>Flow</th>
<th>3%</th>
<th>15%</th>
<th>60%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed magnesium oxidation rate (cm/min)</td>
<td>2</td>
<td>2.3</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Calculated magnesium oxidation rate(( \Omega )) (cm/min)</td>
<td>5.7</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>Observed peak temperature (°C)</td>
<td>1050</td>
<td>790</td>
<td>1200</td>
</tr>
<tr>
<td>Calculated peak temperature(°C)</td>
<td>1650</td>
<td>1650</td>
<td>1450</td>
</tr>
<tr>
<td>Observed uranium oxidized (g)</td>
<td>66</td>
<td>16</td>
<td>d</td>
</tr>
<tr>
<td>Calculated uranium oxidized(g)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td></td>
</tr>
</tbody>
</table>

a. The 15% flow case was reported to be pulsating.

b. Linearized rate from 20% to 100% magnesium oxidation.

c. At test termination, when 100% magnesium oxidation occurred.

d. Test used steel rod instead of uranium.

**GRSAC Model Setup**

The reference case GRSAC model of the French channel fire experiments feature a small core with a test channel consisting of 10 axial nodes. The simulated 60-cm long test section consists of either 5 axial nodes at the outlet end of the active core, or a single node. The axial power inputs are tailored to provide for heating the inlet gas to the test section, and to optionally provide simulated electrical heating for the fuel rods.
Fuel and cladding oxidation is suppressed in all except this test section, and graphite oxidation is assumed nil.

While the French experiments used an oven and electrical resistance heating to heat the test fuel element mockups, in the GRSAC test we have the flow to the experiment node(s) heated by the upstream nodes. Some electrical heating is also assumed in the test element section. The air cooling flow rate is set manually via the interactive screen, as is the heating input. The procedure used for these runs was to pre-set the power and flow values to give reasonable heat-up rates for the three experimental cases (3, 15, and 60 g/s test element flows).

GRSAC Model Results

The algorithm for gas-phase burning is activated (for magnesium) and added to the expression for the heterogeneous oxidation. Other than accounting for oxygen depletion, no rate limiting of the gas-phase burning is assumed.

There are two options available for activation of the fuel oxidation process: the first is to allow fuel oxidation to occur if either the cladding exceeds the melting temperature or if the cladding oxidation is 90% complete, whichever occurs first; the second option is to allow fuel oxidation to occur only when the cladding is >90% oxidized.

The results for the second oxidation option with the reference 5-node test section model and the low air flow (3 g/s) showed very rapid oxidation of the cladding occurring in successive spurts. Ignoring the "dead time" periods, the total time for completion of the cladding oxidation was ~12 min, giving an approximate burning rate of ~5 cm/min, compared to the observed value of ~2 cm/min.

The "spurts" (periodic burns) seen in these results are assumed to be an artifact of the model, which does not include such effects as axial radiant heat transport between nodes, which would help to reduce the granularity of the predicted oxidation pattern. In the experiment, it was also observed that there was very little oxidation of the uranium fuel rod, while the simulation results showed substantial fuel oxidation taking place in the periods where cladding oxidation does not dominate.

Using the GRSAC alternative 1-node test section model (vs. 5 nodes), the peak temperature for the 3g/s low-flow case is ~1650°C (Fig. 2), which is closer than the 5-node model predictions were to the observed value of 1050°C; however, the predicted burn rate is faster, ~7 cm/min vs. the observed value of ~2 cm/min.

Results were also obtained for the first oxidation model option, where fuel oxidation is assumed to occur beginning either when 90% of the cladding has been oxidized or when the cladding melts (which generally occurs first). The rapid oxidation of the cladding takes place over about the same time period (9 min), but there is more uranium oxidation predicted, which is contrary to the observations. In all cases, it is assumed that the experiment is terminated just after the cladding burns.

Model improvements that are needed include allowing variation in bulk oxygen concentration through the channels and more accurate evaluation of radiative, convective and conductive heat transfer from the cladding surface.

Conclusions

It appears that our simple model for metal ignition and gas-phase burning in a graphite reactor gives reasonable results in simulating the behavior of magnesium cladding in out-of-pile tests. With further benchmarking, we expect that this model can be effectively used with the GRSAC code to study graphite reactor accident scenarios. Studies of extremely severe accidents may also require improved burning models for the uranium fuel and graphite moderator as well. Clearly, additional basic studies of bulk metal ignition are needed to provide a more reliable basis for predicting the outcome of such accidents.

A general observation we can make from our simulation studies is that the final outcome of any accident scenario depends very much on the details of the initial conditions assumed. Slight changes in the starting conditions and details of cladding integrity can totally change the severity of the predicted damage. This illustrates the importance of having a more complete understanding of bulk metal ignition.

References


Fig. 2. Results of French Experiment Simulation - One-node model; low-flow case (3 g/s). Fuel oxidation allowed only if the cladding oxidation is >90% complete. Clad (maximum) temperature and oxidation rates during gas-phase burn period.