



# A simplified computational model of the oxidation of Zr/Al multilayers



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## ABSTRACT

A computational model is developed to describe the oxidation of nanolaminates comprising Zr/Al bilayers. The model is developed in light of recent experimental observations of reactive multilayers ignited in air. These suggest that at early stages following the completion of the formation reaction, the oxidation process is more closely described using a surface-reaction controlled growth regime; however, as the oxide layer thickens, transition to the diffusion controlled growth occurs. A simplified computational model is consequently developed that incorporates both regimes of oxide growth. The evolution of the foil temperature is described using an energy balance equation that takes into account the oxidation heat, oxygen intake and radiative heat loss. The computations are implemented to estimate the oxidation heat release rates and the temperature of the oxidizing foil, and to analyze the impact of radiative heat losses. The temperature measurements are then exploited to characterize the transition from the surface-reaction controlled growth regime to the diffusion-limited growth regime.

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## 1. Introduction

Reactive nanolaminates have invoked a great deal of interest owing to their ability of releasing a large amount of heat in a localized fashion. This has in particular motivated wide areas of applications, including soldering, brazing, sealing, and ignition of secondary reactions [1–9]. Examples of reactive nanolaminates include sputter deposited multilayers alternating between elements that mix exothermically [7,10–22], such as Ni and Al. Numerous computational studies pertaining to such reactive multilayered systems have aimed at characterizing the properties of self-propagating fronts that can be initiated in these systems and their dependence on foil composition and microstructure [23–32].

For many compositions, the heat released by intermetallic formation reaction is sustained for very short duration (milliseconds or smaller), owing to short consumption timescales and/or large velocities of the self-propagating fronts [13,33–36]. As a result, these multilayered systems would not be suitable for applications that require a much longer duration of heat release. The present work is a part of a collaborative effort to develop a new class of nanocomposites that are tens of micrometers thick and still capable of sustaining heat release over periods of several seconds.

Recently, Joress et al. explored the possibility of achieving extended duration of heat release in metallic multilayered systems in [37]. For this purpose, sputter-deposited [36] nanolaminate foils comprising Ni/Al and Zr/Al in different molar ratios were reacted in air. Foil surface temperature during the reaction was measured using a fiber-coupled, two-color ratio pyrometry technique. The pyrometer calibration is estimated to be accurate within 100 K. Further details on foil fabrication and temperature measurement are provided in [37]. For Zr/Al multilayers with 50:50 composition, the experiments in [37] revealed the occurrence of an extended temperature plateau following the completion of the anaerobic ZrAl formation reaction (see Fig. 1). The analysis also showed that the oxidation of zirconium in the intermetallic led to an extended time duration during which the reacted multilayer remains at high temperature. The oxidation process leads to the formation of a zirconium dioxide (ZrO<sub>2</sub>, zirconia) layer at the surface of the foil. Depending on the application being pursued, the presence of this ceramic layer may constitute an important factor governing the foil utilization.

The present work is motivated by a desire to use Zr/Al multilayers as heat sources for sublimating a biocidal agent. Specifically, it aims at developing a simplified computational model that can be used to compute the evolution of oxide layer, reproduce recent observations, and provide insight into the nature of oxidation process and the kinetics of oxide layer growth. As outlined in Section 2, our approach exploits the observed disparity between the timescales of the formation  $\mathcal{O}(10^{-3}$  s) and oxidation reactions

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## Nomenclature

$\Delta H_f(\text{O}_2)$	heat of formation of $\text{O}_2$ , kJ/mole	$d$	instantaneous thickness of the depleting inter-metallic core (Fig. 3), m
$\Delta H_f(\text{ZrAl}_2)$	heat of formation of $\text{ZrAl}_2$ , kJ/mole	$D_o$	diffusivity pre-exponent, $\text{m}^2/\text{s}$
$\Delta H_f(\text{ZrAl})$	heat of formation of $\text{ZrAl}$ , kJ/mole	$d_o$	total foil thickness, m
$\Delta H_f(\text{ZrO}_2)$	heat of formation of $\text{ZrO}_2$ , kJ/mole	$E_a$	activation energy, kJ/mole
$\Delta H_{ox}$	heat of oxidation of $\text{ZrAl}$ , kJ/mole	$m$	instantaneous number of $\text{ZrAl}_2$ and $\text{ZrO}_2$ moles per unit volume, $\text{m}^{-3}$
$\epsilon$	foil surface emissivity	$n$	instantaneous number of $\text{ZrAl}$ moles per unit volume, $\text{m}^{-3}$
$\bar{C}_p$	average volumetric heat capacity, $\text{J}/\text{m}^3/\text{K}$	$n_o$	initial number of $\text{ZrAl}$ moles per unit volume, $\text{m}^{-3}$
$\phi$	degree of conversion	$Q_{in}$	enthalpy flux per unit volume due to the uptake of oxygen, $\text{W}/\text{m}^3$
$\sigma$	Stefan–Boltzmann constant, $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$	$Q_{ox}$	oxidation heat release rate per unit volume, $\text{W}/\text{m}^3$
$\nu$	rate of oxide layer growth, m/s	$Q_{rad}$	radiative heat loss per unit volume, $\text{W}/\text{m}^3$
$\zeta$	instantaneous thickness of the oxide layer, m	$R$	universal gas constant, $8.314 \text{ J}/\text{mole}/\text{K}$
$C_{p\text{O}_2}$	molar heat capacity of $\text{O}_2$ , $\text{J}/\text{mole}/\text{K}$	$T$	instantaneous temperature of the foil, K
$C_{p\text{ZrAl}_2}$	molar heat capacity of $\text{ZrAl}_2$ , $\text{J}/\text{mole}/\text{K}$	$T_o$	ambient temperature, K
$C_{p\text{ZrAl}}$	molar heat capacity of $\text{ZrAl}$ , $\text{J}/\text{mole}/\text{K}$		
$C_{p\text{ZrO}_2}$	molar heat capacity of $\text{ZrO}_2$ , $\text{J}/\text{mole}/\text{K}$		
$D$	diffusivity of oxygen in zirconia, $\text{m}^2/\text{s}$		

$\mathcal{O}(10^0 \text{ s})$ , and thus we focus exclusively on the oxidation phase. To describe the evolution of temperature during oxidation, we rely on an integral energy balance that accounts for oxygen uptake, heat generated by the Zr oxidation, and heat loss due to radiation. The resulting energy balance equation is coupled to a kinetic model for oxide growth. As discussed in Section 3, different formulations for the oxide growth are considered, including a diffusion controlled model, an surface-reaction controlled model, and a combined growth model that is based on contrasting the diffusion and surface-reaction controlled growth rates and selecting the limiting kinetics. The behavior and suitability of the resulting models are then analyzed in Sections 4 and 5 in light of recent experimental observations of nanostructured Zr/Al multilayers ignited in air. Major conclusions are finally highlighted in Section 6.

## 2. Model formulation

A thermal model is developed to describe the temperature evolution during the oxidation of a 1:1 Zr/Al multilayer foil. Following recent experimental observations [38,39], the model assumes that the formation reaction is essentially complete prior to the start of

the oxidation process. Thus, the initial foil temperature at the start of oxidation can be approximated as the adiabatic temperature corresponding to the anaerobic formation reaction. As shown in Fig. 1, for a Zr/Al foil with a 1:1 ratio of the reactants, this temperature is approximately 1500 K.

The present development of the thermal model is based on the following simplifying assumptions:

1. The foil temperature is treated as spatially uniform, and the oxidation process can be considered as isothermal.
2. Convective and conductive heat losses are ignored, but radiative heat losses are retained.
3. Constant molar heat capacity estimates at the oxidation temperature are used throughout the computations.
4. Volumetric changes due to expansion or contraction during the oxidation process are neglected.

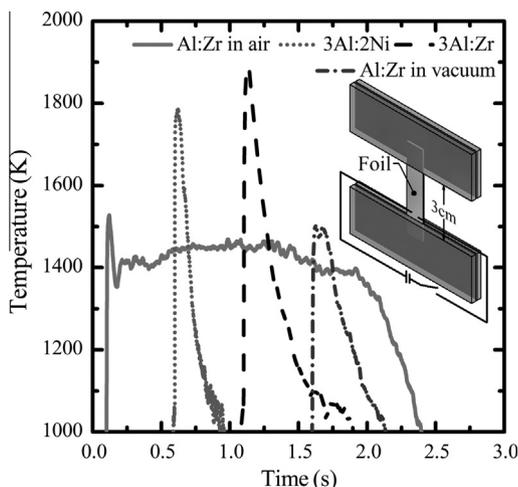
Note that neglect of conductive and convective losses is informed by the study of Joress et al. [37], who performed a careful analysis of the cooling rates at the end of the oxidation period. In particular, near the oxidation temperature, the cooling rate was observed to vary as  $T^{3.7}$ , i.e. with an exponent that is close to that appearing in the Stefan–Boltzmann law. Thus, at elevated temperatures radiative losses are evidently dominant. On the other hand, our first assumption can be justified a priori, especially in light of experimental observations that reveal temperature variations during the oxidation process. Consequently, our approximation of this phenomenon by a temperature plateau deserves additional scrutiny. This is conducted in Section 5.1 in light of computed predictions.

In the lumped parameter approximation, the evolution of the temperature field is governed by the volume averaged energy equation:

$$\bar{C}_p \frac{dT}{dt} = Q_{ox} - Q_{rad} + Q_{in} \quad (1)$$

where  $T$  is the instantaneous temperature of the foil and  $\bar{C}_p$  is its average volumetric heat capacity. As schematically illustrated in Fig. 2,  $Q_{ox}$ ,  $Q_{rad}$ ,  $Q_{in}$  respectively denote the oxidation heat release rate per unit volume, the radiative heat loss per unit volume, and the enthalpy flux per unit volume due to the uptake of oxygen.

Below, we derive suitable expressions for  $\bar{C}_p$ , the volumetric heat release term, and the surface fluxes which, together with



**Fig. 1.** Profiles of temperature versus time for Zr/Al foils with different chemistries. The multilayer with 50:50 composition maintains high temperature over longer times when reacted in air. Also shown is a schematic of the experimental assembly. Adapted from [37].

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