Development and Calibration of Reaction Models for Multilayered Nanocomposites

by

Manav Vohra

Department of Mechanical Engineering and Materials Science
Duke University

Date: ______________________
Approved:

___________________________
Omar M. Knio, Supervisor

___________________________
Stefano Curtarolo

___________________________
Nico Hotz

___________________________
Guglielmo Scovazzi

Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechanical Engineering and Materials Science in the Graduate School of Duke University

2015
ABSTRACT

Development and Calibration of Reaction Models for Multilayered Nanocomposites

by

Manav Vohra

Department of Mechanical Engineering and Materials Science
Duke University

Date: ______________________

Approved:

________________________
Omar M. Knio, Supervisor

________________________
Stefano Curtarolo

________________________
Nico Hotz

________________________
Guglielmo Scovazzi

An abstract of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechanical Engineering and Materials Science in the Graduate School of Duke University 2015
Abstract

This dissertation focuses on the development and calibration of reaction models for multilayered nanocomposites. The nanocomposites comprise sputter deposited alternating layers of distinct metallic elements. Specifically, we focus on the equimolar Ni-Al and Zr-Al multilayered systems. Computational models are developed to capture the transient reaction phenomena as well as understand the dependence of reaction properties on the microstructure, composition and geometry of the multilayers. Together with the available experimental data, simulations are used to calibrate the models and enhance the accuracy of their predictions.

Recent modeling efforts for the Ni-Al system have investigated the nature of self-propagating reactions in the multilayers. Model fidelity was enhanced by incorporating melting effects due to aluminum [Besnoin et al. (2002)]. Salloum and Knio formulated a reduced model to mitigate computational costs associated with multi-dimensional reaction simulations [Salloum and Knio (2010a)]. However, existing formulations relied on a single Arrhenius correlation for diffusivity, estimated for the self-propagating reactions, and cannot be used to quantify mixing rates at lower temperatures within reasonable accuracy [Fritz (2011)]. We thus develop a thermal model for a multilayer stack comprising a reactive Ni-Al bilayer (nanocalorimeter) and exploit temperature evolution measurements to calibrate the diffusion parameters associated with solid state mixing (≈ 720 K - 860 K) in the bilayer.

The equimolar Zr-Al multilayered system when reacted aerobically is shown to
exhibit slow aerobic oxidation of zirconium (in the intermetallic), sustained for about 2-10 seconds after completion of the formation reaction. In a collaborative effort, we aim to exploit the sustained heat release for bio-agent defeat application. A simplified computational model is developed to capture the extended reaction regime characterized by oxidation of Zr-Al multilayers. Simulations provide insight into the growth phenomenon for the zirconia layer during the oxidation process. It is observed that the growth of zirconia is predominantly governed by surface-reaction. However, once the layer thickens, the growth is controlled by the diffusion of oxygen in zirconia.

A computational model is developed for formation reactions in Zr-Al multilayers. We estimate Arrhenius diffusivity correlations for a low temperature mixing regime characterized by homogeneous ignition in the multilayers, and a high temperature mixing regime characterized by self-propagating reactions in the multilayers. Experimental measurements for temperature and reaction velocity are used for this purpose. Diffusivity estimates for the two regimes are first inferred using regression analysis and full posterior distributions are then estimated for the diffusion parameters using Bayesian statistical approaches. A tight bound on posteriors is observed in the ignition regime whereas estimates for the self-propagating regime exhibit large levels of uncertainty. We further discuss a framework for optimal design of experiments to assess and optimize the utility of a set of experimental measurements for application to reaction models.
To my parents, Sunita and Ajay Vohra
## Contents

Abstract iv  
List of Tables x  
List of Figures xi  
List of Abbreviations and Symbols xvi  
Acknowledgments xx  

1 Introduction 1  
1.1 Reactive Multilayers ............................... 1  
1.2 Significance and Innovation ........................ 5  
1.3 Reaction models: Background ....................... 6  
1.4 Objectives ........................................... 9  
1.5 Organization ......................................... 10  

2 Nanocalorimetric Analysis of Interdiffusion in a Ni-Al bilayer 12  
2.1 Thermal Model ....................................... 15  
2.2 Inference of Diffusivity ............................. 19  
2.3 Results ............................................... 21  
2.4 Conclusions .......................................... 28  

3 Oxidation of Equimolar Zr-Al Multilayers 32  
3.1 Model Formulation ................................... 33  
3.2 Growth of Oxide Layers ............................. 39
5.1.1 Problem set-up .............................. 101
5.1.2 Adaptive pseudo-spectral projection .................. 102
5.1.3 Numerical approximation of expected utility ............ 105
5.1.4 Application .................................. 107
5.1.5 Future work ................................ 110

6 Summary ........................................ 111

Bibliography .................................... 115

Biography ...................................... 123
List of Tables

2.1 Density and heat capacity of the materials present in the nanocalorimeter stack. The values for Al$_2$O$_3$ and SiN$_x$ are adapted from [Munro (1997); Riley (2000)]. ........................................ 16
List of Figures

1.1 (a) DC magnetron sputtering chamber with a rotating octahedral carousel. (b) Sputter deposited nanolaminate foils. .......................... 2

1.2 2D schematic of a Zr-Al bilayer. $\lambda$ denotes the bilayer thickness. The thicknesses of the individual Al and Zr layers are $2(\delta - w)$ and $2\gamma(\delta - w)$, respectively. The initial premix width at the interface is $2w$. .... 3

1.3 Temperature contours of uniform self-propagating reaction fronts for $\lambda = 64$ nm, 79 nm and 87 nm. Size of the computational domain is 1000 microns along the direction of front propagation (X) and 20 microns in the direction normal to front propagation (Y). ............... 4

1.4 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 [Joress et al. (2012)]. .... 7

2.1 Schematic illustration of a multilayer configuration found in a typical nanocalorimeter. Also shown are the leads for 4-pt current and voltage drop measurement. .......................... 13

2.2 Schematic illustration of a representative Ni-Al bilayer where $\lambda$ is the bilayer thickness, $2\delta$ is thickness of the Aluminum layer and $x$ is the spatial coordinate. .......................... 18

2.3 Flow diagram for inference of Arrhenius diffusion parameters using the reduced model. .......................... 20

2.4 Joule heating applied to the nanocalorimeter configuration for the two cases. .......................... 21

2.5 Raw data and smooth curve fit of the chemical source term in K/sec. Left: $\lambda = 50$ nm; right: $\lambda = 60$ nm. Two exotherms are observed around the peak in both cases. .......................... 23
2.6 Inferred diffusivity, $D$, versus temperature, $T$. Curves are generated for the 50 nm and 60 nm bilayers, as indicated. Also shown is the extrapolated correlation of Fritz [Fritz (2011)].

2.7 Ratio of the chemical heat release rate to the maximum Joule heating rate versus temperature. Plotted are results obtained for $\lambda = 50$ nm.

2.8 Natural logarithm of $D$ plotted against $T^{-1}$. Curves are generated for the 50 nm and 60 nm bilayers, as indicated.

2.9 Temperature versus time for $\lambda = 50$ nm (left) and 60 nm (right). Plotted are curves depicting a comparison between raw experimental data and simulated results.

2.10 Chemical source term versus time for $\lambda = 50$ nm (left) and 60 nm (right). Plotted are curves depicting experimental and simulation results, as indicated.

2.11 Evolution of the temperature for $\lambda = 50$ nm. Plotted are experimental data obtained using the nanocalorimeter after the first initiation, as well as simulation results obtained by omitting the chemical source term.

3.1 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 [Joress et al. (2012)].

3.2 $Q_{in}$, $Q_{ox}$ and $Q_{rad}$ respectively denote the enthalpy flux due to oxygen intake, the heat generated by the oxidation reaction, and the radiative heat loss. Also shown is the growing zirconia layer on the foil.

3.3 Schematic representation of the structure of an oxidizing Zr-Al multilayer. $d_0$ and $d$ respectively denote the initial thickness of the multilayer, and the instantaneous thickness of the depleting intermetallic “core”. The total thickness of the oxidized layers (top and bottom) is $d_0 - d$.

3.4 (a) Temperature versus time using a diffusion-limited growth model. (b) Temperature versus time using a coupled growth model. Curves are generated using different values of $\epsilon$, as indicated.

3.5 Rate of conversion versus time for a 50:50 Zr-Al multilayer foil. Plotted are results obtained for $\epsilon = 0.1, 0.2$. 

xii
3.6 Rate of conversion versus time for a 50:50 Zr-Al multilayer foil. Plotted are results obtained for $\epsilon = 0.3, 0.4$. .......................... 49

3.7 Time evolution of the degree of conversion and of the instantaneous conversion factor. Plotted are curves generated using different values of $\epsilon$, as indicated. .......................... 50

3.8 Temperature versus time for three different foil thicknesses, each comprising Zr-Al with 1:1 ratio of the reactants. The simulations are performed using the combined model with $\epsilon = 0.1$. .......................... 51

3.9 Temperature versus time for an oxidizing Zr-Al with 1:1 ratio of the reactants. Top: Experimental measurements for a 16 microns thick foil, and the predicted temperature profile during oxidation. Bottom: Experimental measurements for a 40 microns thick foil, and the predicted temperature profile during oxidation. An emissivity value 0.1 was used in both cases. .......................... 52

3.10 Experimental temperature versus time plot for the Al:Zr foil (40 $\mu$m thick) during oxidation. .......................... 55

3.11 (a) Temperature profiles using diffusivity estimates by Pawel and Campbell [Pawel and Campbell (1981)], Kingery et al. [Kingery et al. (1959)] and Douglass [Douglass (1962)]. Also shown is the experimental data. Foil thickness 40 microns and initial temperature 1500 K is used in the computations. (b) Semi-log plot for Arrhenius diffusivity of Oxygen in Zirconia as estimated by Pawel and Campbell [Pawel and Campbell (1981)], Kingery et al. [Kingery et al. (1959)] and Douglass [Douglass (1962)]. .......................... 57

4.1 Ignition temperature versus bilayer for a 20 $\mu$m-thick Zr-Al foil. Error bars correspond to a standard deviation of $\pm$ 5 degrees in ignition points for individual foil fragments used in hot plate tests. .......................... 63

4.2 Shown above is a 50:50 Zr-Al nanolaminate foil held firmly between two glass slides with one end protruding. Also shown is an optical fiber assembly for measuring the front propagation velocity. .......................... 64

4.3 (a) Molar heat capacity versus temperature for Zr and Al [Barin et al. (1977)]. Also shown are averaged estimates for ZrAl on a per mol-atom basis. (b) Estimated thermal conductivity versus temperature for Zr [Fink and Leibowitz (1995)]. .......................... 69
4.4 Measured and simulated temperature profiles. Plotted are curves obtained for (a) $\lambda=68$ nm and (b) $\lambda=72$ nm, and different values of $D_0$ as indicated. The insets reveal the occurrence of a temperature plateau corresponding to the melting of Al. The parameters of the current pulse are also indicated.

4.5 Velocity vs bilayer thickness. (a) Simulated results obtained with $E_a = 55$ kJ/mol and different values of $D_0$, as indicated. (b) Simulated results obtained with $D_0 = 3.13 \times 10^{-9}$ m²/s, and different values of $E_a$, as indicated. The experimentally measured velocities, corresponding to $\lambda = 64$ nm, 79 nm, 81 nm and 87 nm, are also depicted.

4.6 Semi-log plot of Arrhenius atomic diffusivity, $D(T)$ versus ($\frac{1}{T}$). A sharp discontinuity is observed at the melting point of Al, 933 K. Optimized estimates for diffusion parameters, based on regression analysis are also shown for both high and low temperature regimes.

4.7 (a) Reaction times (symbols) computed at the Gauss-Legendre quadrature nodes for uniform ignition at $T = 600$ K. (b) Reaction velocities (symbols) computed at the Gauss-Legendre quadrature nodes for $\lambda = 64$ nm. The continuous surfaces depict the corresponding PC representations.

4.8 Probability density functions for the uniform ignition reaction time and self-propagation reaction velocity. (a) Distributions for $T = 600$ K, 700 K, 800 K and 900 K are plotted. (b) Distributions for $\lambda = 64$ nm, 79 nm, 81 nm and 87 nm are plotted. The PDFs are obtained for the PC representation using kernel density estimation.

4.9 First-order and total sensitivity as estimated using Sobol indices for, (a) ignition regime and (b) propagation regime.

4.10 Bayesian inference results based on data for uniform ignition. Posterior chain samples for (a) $D_0$, (b) $E_a$, and (c) $\sigma_T^2$ are illustrated. Frame (d) shows the joint posterior of $D_0$ and $E_a$.

4.11 Marginal distribution of the posterior for, (a) $D_0$ and (b) $E_a$. The uniform priors and MAP estimates are also plotted. Results are obtained based on uniform ignition measurements.

4.12 Measured and simulated reaction time versus temperature for the case of $\lambda = 68$ nm. The MAP estimates for $D_0$ and $E_a$ are used.
4.13 (a) Marginal distribution of the posterior for $D_0$. (b) Marginal distribution of the posterior for $E_a$. The prior distributions and the MAP estimates are also shown. (c) Joint posterior for $D_0$ and $E_a$. Results are obtained based on measured velocity data. 93

4.14 Scatter plot of the experimental reaction velocity data for different bilayers. Also shown are mean reaction velocity estimates, obtained by sampling the Markov Chain. The error bars correspond to $\pm 2\sigma$, where $\sigma$ is the standard deviation. 94

4.15 Reaction velocity versus bilayer thickness. Simulated results obtained for $w = 0.5$ nm and 0.8 nm are plotted. The insets highlight the occurrence of a plateau in the simulated velocity curves. The experimentally measured reaction velocities are also depicted for reference purposes. 96

5.1 Experimental set-up for homogeneous ignition of a multilayered foil [Fritz (2011)]. 101

5.2 Contours for reaction time using model simulations in (a) and (b); surrogate in (c) and (d). 104

5.3 PDFs for reaction time at foil surface temperature, $T = 600$ K, 700 K, 800 K and 900 K; obtained using kernel density estimation. 105

5.4 First-order and total sensitivity estimates for the physical and design parameters using Sobol indices. 106

5.5 (a) Foil surface temperature evolution during homogeneous ignition for $\lambda = 72$ nm. (b) Contours for expected utility, $U(d)$ evaluated using 1000 Monte Carlo samples and 400 design points at $T = 900$ K and $\lambda = 72$ nm. Point ‘P’ corresponds to maximum utility. 108

5.6 Contours for expected utility, $U(d)$ evaluated using Latin Hypercube Sampling at (a) $N_d = 100$ and (b) $N_d = 400$. 109
List of Abbreviations and Symbols

Chapter 2

\( V \)  Multilayer stack volume, \( m^3 \)
\( \mathcal{V} \)  Ni-Al bilayer volume, \( m^3 \)
\( P \)  Power dissipated in the stack due to Joule heating, W
\( R \)  Radiative heat loss rate, W
\( \dot{Q} \)  Rate of chemical energy release per unit volume, W/m\(^3\)
\( H \)  Instantaneous enthalpy of multilayer stack per unit volume, J/m\(^3\)
\( T \)  Instantaneous homogeneous temperature of multilayer stack, K
\( \rho^i \)  Density of the the \( i \)-th layer within the stack, kg/m\(^3\)
\( C_p^i \)  Heat capacity of the the \( i \)-th layer within the stack, J/kg/K
\( t^i \)  Thickness of the the \( i \)-th layer within the stack, m
\( V' \)  Applied voltage drop across the stack, V
\( I \)  Applied current, A
\( \sigma \)  Stefan-Boltzmann constant
\( \epsilon_t \)  Emissivity of the top surface of the stack
\( \epsilon_b \)  Emissivity of the bottom surface of the stack
\( A_t \)  Exposed area of the top surface of the stack, m\(^2\)
\( A_b \)  Exposed area of the bottom surface of the stack, m\(^2\)
\( T_a \)  Ambient temperature, K
\( \Delta \tilde{H} \)  Heat released in the bilayer, J/m\(^3\)
\( \tau \) Normalized time variable

\( \rho^{\text{Al}} \) Density of aluminum, kg/m\(^3\)

\( C_{p}^{\text{Al}} \) Heat capacity of aluminum, J/kg/K

\( M^{\text{Al}} \) Molar mass of aluminum, kg

\( \rho^{\text{Ni}} \) Density of nickel, kg/m\(^3\)

\( C_{p}^{\text{Ni}} \) Heat capacity of nickel, J/kg/K

\( M^{\text{Ni}} \) Molar mass of nickel, kg

\( D \) Atomic diffusivity of the Ni-Al system, m\(^2\)/s

\( \delta \) Al semi-layer thickness, m

\( D_{0} \) Pre-exponent of the diffusivity, m\(^2\)/s

\( E \) Activation energy, kJ/mol

\( R \) Universal gas constant, J/mol/K

\( \dot{T} \) Rate of temperature increase of the stack, K/s

\( \dot{P} \) Rate of stack temperature increase due to joule heating, K/s

\( \dot{E} \) Rate of stack temperature increase due to chemical mixing, K/s

\( \dot{R} \) Rate of stack temperature decrease due to radiation loss, K/s

Chapter 3

\( \Delta H_{f}(\text{O}_2) \) Heat of formation of O\(_2\), kJ/mole

\( \Delta H_{f}(\text{ZrAl}_2) \) Heat of formation of ZrAl\(_2\), kJ/mole

\( \Delta H_{f}(\text{ZrAl}) \) Heat of formation of ZrAl, kJ/mole

\( \Delta H_{f}(\text{ZrO}_2) \) Heat of formation of ZrO\(_2\), kJ/mole

\( \Delta H_{\text{ox}} \) Heat of Oxidation of ZrAl, kJ/mole

\( \epsilon \) Foil surface emissivity

\( \overline{C_{p}} \) Average volumetric heat capacity, J/m\(^3\)/K

\( \phi \) Degree of conversion

xvii
\( \sigma \) Stefan-Boltzmann constant, \( 5.67 \times 10^{-8} \) Wm\(^{-2}\)K\(^{-4}\)

\( v \) Rate of oxide layer growth, m/s

\( \zeta \) Instantaneous thickness of the oxide layer, m

\( C_{PO_2} \) Molar heat capacity of O\(_2\), J/mol/K

\( C_{ZrAl_2} \) Molar heat capacity of ZrAl\(_2\) J/mol/K

\( C_{ZrAl} \) Molar heat capacity of ZrAl, J/mol/K

\( C_{ZrO_2} \) Molar heat capacity of ZrO\(_2\), J/mol/K

\( D \) Diffusivity of oxygen in zirconia, m\(^2\)/s

\( d \) Instantaneous thickness of the depleting inter-metallic core (Fig. 3.3), m

\( D_o \) Diffusivity pre-exponent, m\(^2\)/s

\( d_o \) Total foil thickness, m

\( E_a \) Activation Energy, kJ/mole

\( m \) Instantaneous number of ZrAl\(_2\) and ZrO\(_2\) moles per unit volume, m\(^{-3}\)

\( n \) Instantaneous number of ZrAl moles per unit volume, m\(^{-3}\)

\( n_o \) Initial number of ZrAl moles per unit volume, m\(^{-3}\)

\( Q_m \) Enthalpy flux per unit volume due to the uptake of oxygen, W/m\(^3\)

\( Q_{ox} \) Oxidation heat release rate per unit volume, W/m\(^3\)

\( Q_{rad} \) Radiative heat loss per unit volume, W/m\(^3\)

\( R \) Universal gas constant, 8.314 J/mol/K

\( T \) Instantaneous temperature of the foil, K

\( T_o \) Ambient temperature, K
Chapter 4

\[ \dot{H} \] Rate of change of volume-averaged foil enthalpy, W/m³

\[ \dot{P} \] Power input due to Joule heating per unit of foil volume, W/m³

\[ \dot{Q} \] Chemical heating rate per unit of foil volume, W/m³

\[ \dot{L} \] Rate of heat loss by convection per unit of foil volume, W/m³

\[ V' \] Applied voltage across the foil, V

\[ I \] Applied current during homogeneous reaction in the foil, A

\[ V_{foil} \] Foil volume, m³

\[ d \] Foil thickness, m

\[ T_0 \] Ambient temperature, K

\[ h \] Heat transfer coefficient, W/m²/K

\[ L_c \] Characteristic length, m

\[ D \] Atomic diffusivity, m²/s

\[ C \] Concentration (degree of mixing)

\[ D_0 \] Pre-exponent of diffusivity, m²/s

\[ E_a \] Activation energy, kJ/mol

\[ \bar{\rho} \] Mean density of the equimolar Zr-Al system, kg/m³

\[ \bar{\rho}C_p \] Mean thermal capacity of the equimolar Zr-Al system, J/m³/K

\[ H \] Instantaneous enthalpy, J/m³

\[ \Delta T_f \] Adiabatic temperature increase over ambient, K

\[ \bar{k} \] Mean thermal conductivity of the equimolar Zr-Al system, W/m/K
Acknowledgments

First and foremost, I would like to express my profound gratitude to my supervisor, Prof. Omar M. Knio for his guidance and support during the course of my graduate studies at Johns Hopkins and Duke. I had a short term research experience during my bachelors in India and consider myself extremely fortunate to have been a part of his research group, initially at Hopkins and now at Duke. I feel extremely privileged to have been involved in numerous insightful and enjoyable research discussions with him which helped me contribute significantly towards the development of reaction models for reactive multilayered systems. I am truly grateful for his affable nature as he would not mind my unplanned visits to his office at any time and always helped me in the best possible way. In addition to honing the required computational and analytical skills, I am indebted for his inputs on effective means of scientific communication through technical presentations at conferences, research posters, and journal publications.

It has been a pleasure to collaborate with Prof. Timothy P. Weihs and his graduate student, Kyle Overdeep at the department of Materials Science and Engineering at Johns Hopkins. I am immensely grateful to Prof. Weihs for his guidance and mentorship during the course of my doctoral work. His inputs during our bi-weekly project meetings have always been instrumental in making progress and identifying future goals in my research. My work has largely depended on the experimental data that Kyle has provided me and I am truly grateful for his utmost dedication in this
regard. His insights on experimental procedures have helped me identify suitable assumptions and understand the limitations of my models. I am also grateful to the Defense Threat Reduction Agency (DTRA) of the United States for supporting my doctoral research as a part of a collaborative effort to develop an effective strategy for bio-agent defeat using reactive multilayered particles.

I pursued an advanced course in uncertainty quantification (UQ) during the spring semester in 2013 at Duke. The course helped me develop an understanding and appreciation for the scope of implementation of UQ in my work. I am immensely grateful to the course instructor, Dr. O. P. Le Maître, for his insightful discussions inside as well as outside the classroom. Justin Winokur, a colleague and a dear friend, contributed significantly towards the implementation of UQ in my research by allowing me to use his Matlab tools for constructing model surrogates. He further helped me improve my understanding of various aspects of UQ through discussions and computational demonstrations. I will always cherish having him as a co-author in one of my journal articles.

I would further like to express my sincere gratitude towards Dr. Stefano Curtarolo, Dr. Nico Hotz and Dr. Guglielmo Scovazzi for serving on my preliminary examination committee as well as my dissertation committee.

Last but not the least, I am grateful for the love and blessings of my family. During times of struggle, I did not despair and continued to persevere owing to their support. My experiences during the course of graduate studies and doctoral research will always be a guideline for me in the future.
1.1 Reactive Multilayers

Reactive multilayers in the present context refer to nano-structured composite materials comprising alternating arrangements of chemically distinct metallic elements. Advanced fabrication techniques for such multilayered systems include physical vapor deposition whereby the individual layers are sputter deposited on a substrate [Blobaum et al. (2003); Gavens et al. (2000); Reiss et al. (1999); Wang et al. (2004); Rogachev et al. (2004); Gachon et al. (2005); Adams et al. (2006a,b)]. Typically, individual layers have thicknesses in the order of tens of nanometers. Thousands of geometrically flat layers, sputter deposited on brass substrates are referred to as ‘nanolaminates’. Fig. 1.1 depicts nanolaminate foils as well as a schematic of a DC magnetron sputtering chamber used to fabricate them. The nanolaminates are tens of microns thick.

A fundamental repeating unit in a reactive multilayered system is referred to as the ‘bilayer’, illustrated in Fig. 1.2 for the Zr-Al system. The bilayer comprises a combination of individual layers of the two metals separated by a so-called premixed
Figure 1.1: (a) DC magnetron sputtering chamber with a rotating octahedral carousel. (b) Sputter deposited nanolaminate foils.
region, formed during the sputtering process.

\[ \lambda \approx 2(1+\gamma)\delta \]

Figure 1.2: 2D schematic of a Zr-Al bilayer. $\lambda$ denotes the bilayer thickness. The thicknesses of the individual Al and Zr layers are $2(\delta - w)$ and $2\gamma(\delta - w)$, respectively. The initial premix width at the interface is $2w$.

Rapid intermixing in the bilayers due to steep concentration gradients and small atomic diffusion distance across the layers (along Y in Fig. 1.2) leads to a large amount of localized heat release. When initiated by means of a high energy source such as a thermal spark, an electric spark or a laser beam, the reaction is observed to self-propagate along the direction of layering (along X in Fig. 1.2). Fig. 1.3 illustrates uniform self-propagating reaction fronts using 2D temperature contours for three different bilayer thicknesses; $\lambda = 50$ nm, 70 nm and 90 nm. Characteristic to the nature of self-propagating reactions in such systems, the front velocity decreases as the bilayer thickness increases.

Reaction front velocities show a wide range from 1-100 m/s [Salloum and Knio (2010a)] based on foil microstructure, composition and geometry. The multilayered system can thus be engineered for desired reaction properties which makes them suitable for fundamental as well as applied research for various applications as discussed
Figure 1.3: Temperature contours of uniform self-propagating reaction fronts for $\lambda = 50$ nm, 70 nm and 90 nm. Size of the computational domain is 1000 microns along the direction of front propagation (X) and 20 microns in the direction normal to front propagation (Y).

Large amount of heat released due to intermixing in the bilayers makes reactive multilayers suitable for various joining applications such as welding, brazing, and soldering [Duckham et al. (2004); Van Heerden et al. (2008); Wang et al. (2008)]. With the advent of improved fabrication technologies enabling deposition and control of the micro-structure of these materials at atomistic levels, a much larger spectrum of applications of reactive multilayered systems is being identified and explored. Some of these applications include high performance coatings, capacitors and thermal batteries for energy storage, magnetic transducers and smart materials for sensors.

The duration of heat release in conventional multilayered systems is limited to the order of a few milliseconds. As a result, their use is restricted to applications that do
not require a sustained release of heat. However, recent experimental investigations by Joress et al. at Johns Hopkins, revealed that the duration of heat release can be increased by roughly three orders of magnitude [Joress et al. (2012)]. Precisely, when a nanolaminate foil with an equimolar composition of Zr and Al was reacted in air, a temperature plateau sustained for about 2-3 seconds was observed as discussed further below and in much detail in chapter 3. These findings have motivated the application of reactive multilayers as energetic materials for bio-agent defeat.

1.2 Significance and Innovation

Research groups at Johns Hopkins and Duke have collaborated to develop an effective strategy for bio-agent defeat using reactive multilayered particles. It essentially involves thermal as well as chemical deactivation of spore forming biological warfare agents such as Bacillus Anthracis. Existing methodologies involve the use of high explosives (HEs) that pose a safety concern to the war personnel using them. Additionally, effective decontamination is not achieved by using HEs due to dispersion of spores as a result of high pressure blast wave during explosion. We seek a much safer alternative to the HEs and are investigating potential application of reactive multilayered particles that are much safer to handle, use and transport. Moreover, significant pressure variations leading to potential spore dispersion are naturally avoided as well. In order to obtain the desired reaction properties, we are developing computational models to understand their dependence on composition, geometry and microstructure of the multilayers using nanolaminate foils.

To achieve effective decontamination of the spores, we are focusing on utilizing the heat released during reactions in the particles to neutralize the spores thermally as well as release a biocidal agent such as Iodine to neutralize the spore chemically. For this purpose, we are exploring several combinations of reactive particles and Iodine containing compounds such as I$_2$O$_5$ and HIO$_3$.
It is thus clear that the application of heat released in the multilayers is two fold. One is the deactivation of spores by thermal means and the other involves the release of a biocidal agent for chemical deactivation. The duration of heat release during reaction in the particles is therefore critical to the performance of the agent-defeat composition. Intermetallic formation in conventional multilayered systems comprising Ni and Al results in heat release for a few milliseconds. As discussed earlier in this section, a series of experiments conducted by Joress et al. [Joress et al. (2012)] with different foil chemistries revealed that an equimolar composition of Zr and Al would help sustain the heat release for about 2-3 seconds. Fig. 1.4 illustrates the temperature-time plots for nanolaminate foils with different chemistries reacted anaerobically as well as aerobically. Clearly, a temperature plateau is observed in the case of Zr:Al (equimolar) nanolaminate foil reacted aerobically. Intermetallic formation in the multilayers is followed by a slow oxidation process whereby zirconium in the system is oxidized to form zirconia. One of the objectives of my research is to develop a computational model to understand the mechanism of oxide layer growth during the oxidation of equimolar Zr-Al multilayers, discussed further below and in much detail in chapter 3.

1.3 Reaction models: Background

Advancements in fabrication techniques enabling control of the microstructure of the reactive multilayers at the atomistic levels as well as simultaneous discovery of novel applications has motivated a continuous development of reaction models for over three decades. Model predictions help understand characteristic reaction properties and identify optimal microstructure, composition, and geometry suited for a particular application. In this section, we focus on significant developments in reaction models over the past two decades and identify key challenges that my doctoral research aims to address for advancing the state of the art.
Figure 1.4: 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 [Joress et al. (2012)].

Reaction evolution during intermetallic formation in the multilayers was described using a conserved variable, $c$ (also referred to as the local concentration), in early reaction models [Jayaraman et al. (1999)]. Specifically for the Ni-Al system, $c$ was defined such that: $c = 1$ for pure Al, $c = -1$ for pure Ni and $c = 0$ for pure NiAl and its evolution was described using the following parabolic differential equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c)$$  \hspace{1cm} (1.1)
where $D$ is the atomic diffusivity. For simulating self-propagating reactions, the above equation was coupled with an energy conservation equation based on a balance between the evolution of enthalpy, thermal flux due to heat conduction and heat evolution due to chemical mixing in the bilayers. The detailed formulation was based on the following fundamental assumptions: (A) Intermixing in the reactive bilayers is a Fickian process that can be described using a diffusivity, $D$, that shows an Arrhenius variation with temperature. The diffusivity is thus assumed to be independent of concentration. (B) Thermophysical properties such as thermal conductivity and heat capacity are assumed to be independent of temperature and composition. (C) Rapid intermixing characterized by a diffusion-limited growth of the intermetallic is considered. (D) As thermal diffusivity is several orders of magnitude larger than atomic diffusivity, temperatures variations across the layers are ignored.

Besnoin et al. [Besnoin et al. (2002)] extended the formulation of Jayaraman et al. to account for the effects of melting in reactants and products for the Ni-Al system. Furthermore, the study focused on the effects of melting on the properties of self-propagating reactions in Ni-Al nanolaminate foils.

Salloum and Knio [Salloum and Knio (2010a,b,c)] published a series of papers focusing on a reduced formulation to mitigate computational costs associated with simulation of transient multi-dimensional reactions in Ni-Al multilayered systems. Precisely, the governing equation for $c$, given by Eq. 1.1 was transformed into a canonical form using a lumped parameter, $\tau$, referred to as the normalized “age” of the mixed layer as discussed later in chapter 2 and chapter 4. Reduced model simulations were shown to predict the front propagation characteristics as inferred using the detailed formulation, with an order of magnitude increase in computational speed [Salloum and Knio (2010a)].

Effect of variable thermal conductivity on the nature of self-propagating reaction fronts in non-uniform Ni-Al multilayers was investigated by Alawieh et al. [Alawieh
Simulations were performed using the reduced continuum reaction model developed by Salloum and Knio as discussed earlier. A generalized approach was adopted whereby the thermal conductivity was considered to be dependent on the direction of propagation, local concentration, composition, microstructure, and temperature.

1.4 Objectives

The focus of my doctoral research is to develop and calibrate reaction models to capture the evolution of transient reactions in metallic multilayers. Calibration of model parameters using simulations as well as the available experimental data is pursued to enhance the fidelity of model predictions. In particular, we are interested in calibrating the intermixing rates during anaerobic formation in the equimolar, Ni-Al and Zr-Al multilayered systems by estimating the Arrhenius diffusion parameters (pre-exponent and activation energy). For the Zr-Al system, we further explore an extended reaction regime characterized by a slow aerobic oxidation of the multilayers. My research aims to improve the fidelity of existing formulations for the Ni-Al system as well as develop and calibrate new formulations to capture the evolution of anaerobic formation as well as aerobic oxidation in the Zr-Al multilayered system. Model predictions would help understand the dependence of reaction properties on the microstructure, composition and geometry of the multilayered particles. Furthermore, it would help improve the design of particles for enhancing the efficacy associated with agent neutralization. Specific research objectives are enlisted as follows:

- Utilize the available temperature evolution data during anaerobic formation reactions in a nanocalorimeter comprising a Ni-Al bilayer to assess interdiffusion in the system for an intermediate temperature range (≈ 720 K - 860 K).

- Develop and validate a simplified computational model for capturing the ob-
served temperature plateau as well as understand the kinetics of oxide layer growth during aerobic reactions in a nanolaminate foil comprising an equimolar composition of Zr and Al.

- Develop a reaction model and calibrate intermixing rates in an equimolar Zr-Al system using available experimental data and model predictions. Refine initial diffusivity estimates by regression in a robust Bayesian setting.

- Establish a framework for optimal design of experiments for application to reaction models.

1.5 Organization

My doctoral thesis is organized as follows. In chapter 2, we develop a thermal model for a multilayer stack in a typical nanocalorimeter, comprising a reactive Ni-Al bilayer. Model predictions and experimental measurements for the evolution of surface temperature of the stack are used to quantify mixing rates in an intermediate reaction regime, ranging from temperature, $T = 720 \text{ K} - 860 \text{ K}$. We thus focus on solid state mixing in the Ni-Al bilayers and do not account for the effects of melting of aluminum on intermixing rates in the system. Moreover, since our estimates rely on heat release rates due to chemical mixing in the bilayers, a lower bound of about 720 K is observed as significant mixing does not take place below these temperature levels.

Chapter 3 focuses on the development of a simplified model for oxidation of a nanolaminate foil comprising equimolar Zr-Al multilayers. Temperature evolution of the foil during oxidation is simulated using a volume averaged enthalpy equation coupled with growth models for two competing mechanisms, surface reaction-control and diffusion control.
Anaerobic reaction model is developed for an equimolar Zr-Al multilayered system in chapter 4. Model predictions and available experimental measurements for temperature and reaction velocity are used to calibrate mixing rates during intermetallic formation in the multilayers. Specifically, we consider a low temperature homogeneous ignition regime for temperatures below the melting of Al, and a high temperature self-propagating regime of the reaction for temperatures above the melting of Al. Diffusion parameters for both branches of diffusivity are estimated using regression analysis and further refined using Bayesian inference.

In chapter 5, we develop a framework for optimal design of experiments for improved calibration of reaction models. The framework is applied to the homogeneous reaction model developed in chapter 4. Optimal experimental conditions for homogeneous ignition of an equimolar Zr-Al nanolaminate foil are inferred.

Finally, in chapter 6, we summarize all the contributions towards development and calibration of reaction models for the Ni-Al and Zr-Al multilayered systems.
Nanocalorimetric Analysis of Interdiffusion in a Ni-Al bilayer

Nanocalorimetry is a chip-based measurement technique of thermal and thermodynamic phenomena taking place within nanoscale material samples. When used in conjunction with fast scanning instruments, nanocalorimetry offers the possibility of resolving phenomena at times scales that are several order of magnitude smaller than is possible with conventional nanocalorimetry. This chapter specifically focuses on exploring, computationally, the potential of using temperature measurements obtained using a differential scanning nanocalorimeter [Lopeandia et al. (2006); Kummamuru et al. (2009)] in order to quantify the heat release in a reactive Ni-Al bilayer, and consequently infer instantaneous mixing rates and their temperature dependence.

The experimental data used as input to the present study have been obtained using the nanocalorimeter design shown in Figure 2.1. As illustrated in the sketch, the nanocalorimeter comprises a stack of nanoscale layers, that are deposited onto a silicon nitride substrate. On the top side of the substrate, the stack features a 3nm-thick Ti layer and a 50nm-thick Pt layer; on the bottom side, the stack features
a Ni-Al bilayer having with a 1:1 ratio of the elements, that is embedded within two, 10nm-thick, alumina layers. The Pt layer was deposited by e-beam evaporation; the measured values of heat capacity and density were found to be consistent with bulk values.

**Figure 2.1**: Schematic illustration of a multilayer configuration found in a typical nanocalorimeter. Also shown are the leads for 4-pt current and voltage drop measurement.

The device operates by driving a current through the stack, with pulse duration of the order of tens of milliseconds. The current and voltage across the stack are also recorded during the pulse using a four-point probe. Typical currents are less than 100 mA. With a stack cross-section of 0.5mm x 6mm, the current density is approximately 30000 A/m². Consequently, electromigration is not expected to be significant in the present set-up. The applied joule heating for two separate devices, one comprising a 50 nm thick Ni-Al bilayer and the other comprising a 60 nm thick Ni-Al bilayer, is illustrated in Fig. 2.4. As expected, the temperature increases sharply once the reaction in the bilayer is initiated and plateaus upon completion of the reaction.

The temperature on the Pt surface is determined from the temperature versus resistance calibration obtained using a one-color, optical pyrometer operating at
1550 nm. The error in the temperature measurement was found to be 2.5°C [Swaminathan et al. (2011)].

Thus, available experimental inputs include the time histories of the current and voltage across the stack, and the temperature at the Pt surface. Details on the construction of the nanocalorimeter and on measurement techniques will be provided elsewhere [Swaminathan et al. (2013)].

With an increase in temperature due to Joule heating, intermixing between Ni and Al occurs at increasingly higher rates. This highly exothermic process leads to additional heating within the stack, at least until the reaction between Ni and Al is fully complete. Note that on time scales on the order of the current pulse i.e. $\mathcal{O}(10^{-3})$s, the thermal penetration width is of the order of hundreds of microns and hence is by several orders of magnitude larger than the thickness of the stack, whereas it is substantially smaller than the stack length which is of the order of millimeters. This implies that temperature is essentially uniform across the thickness of the stack, and that it is also uniform over substantially most of the stack length. Thus, the reaction in the Ni-Al bilayer occurs in an essentially spatially homogeneous fashion.

This reaction regime offers an interesting approach to characterizing mixing and reaction in multilayer materials, which complements prior attempts that have primarily relied on conventional differential scanning calorimetry Michaelsen et al. (1997); Mann et al. (1997) or on observations of self-propagating reaction fronts [Reiss et al. (1999); Ma et al. (1990); Dyer et al. (1994); Weihs et al. (1997); Weihs (1998); Rogachev (2008); Gavens et al. (2000); Jayaraman et al. (1998a,b, 1999, 2001); Besnoin et al. (2002); Knepper et al. (2009)]. Advantageous features afforded by the present approach include fast, time resolved measurements, and the homogeneous nature of the reaction which leads to simplified models and circumvents the need for accurate representation of conductive heat fluxes [Alawieh et al. (2011)].

In this chapter, we develop a simplified model of the evolution of the temperature
within nanocalorimeter stacks similar to that depicted in Fig. 2.1. An outline of the development of the simplified model is given in section 2.1. The thermal model is then exploited in section 2.2 in order to develop a procedure for inferring the atomic diffusivity based on the measured voltage and current across the stack, and on the measured temperature. As discussed in [Swaminathan et al. (2013)], the latter is determined using a temperature versus resistance correlation, obtained using a pyrometer. This analysis is then applied in section 2.3 to estimate the diffusivity and characterize its dependence on the temperature. The results are then used to estimate the parameters of the Arrhenius diffusivity law assumed by the Ni-Al reaction model. Major conclusions are given in section 2.4.

2.1 Thermal Model

A simplified thermal model for the evolution of temperature within the nanocalorimeter is developed for a regime dominated by solid state intermixing in the Ni-Al bilayer. Reaction time scales associated with this regime are typically of the order of a few milliseconds. In this limit, the temperature within the nanocalorimeter can be treated as spatially homogeneous, and its evolution is governed by the volume-averaged energy conservation equation:

$$V \frac{\partial H}{\partial t} = \mathcal{V} \dot{Q} + P - R$$  \hspace{1cm} (2.1)

where $V$ is the stack volume, $\mathcal{V}$ is the bilayer volume, $P$ is the power dissipated within the stack due to Joule heating, $R$ is the radiative heat loss, and $\dot{Q}$ is the rate of chemical energy release per unit volume.

Note that, consistent with the small-time limit, the conductive heat flux has been ignored. In addition, thermal losses due to convection have been ignored as well, since we focus on devices triggered under vacuum. Furthermore, the present
analysis also ignores the potential effect of melting of Al, Ni, or compounds thereof. Thus, the left-hand-side of (2.1) can be rewritten as:

\[
\frac{\partial H}{\partial t} = \rho C_p \frac{dT}{dt}
\]

(2.2)

where

\[
\rho C_p = \frac{\sum_{i=1}^{N} \rho^i C_{p}^i t^i}{\sum_{i=1}^{N} t^i},
\]

(2.3)

\(\rho^i, C_{p}^i,\) and \(t^i\) respectively denote the density, heat capacity, and thickness of the \(i\)-th layer within the stack, and \(N\) is the total number of individual layers. Table 2.1 provides the values of density and heat capacity used in the computations. The emissivity values used for Pt and Al\(_2\)O\(_3\) are 0.23 and 0.75, respectively.

Table 2.1: Density and heat capacity of the materials present in the nanocalorimeter stack. The values for Al\(_2\)O\(_3\) and SiN\(_x\) are adapted from [Munro (1997); Riley (2000)].

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m(^3))</th>
<th>Specific Heat (J/kg/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>2700</td>
<td>904</td>
</tr>
<tr>
<td>Nickel</td>
<td>8908</td>
<td>445</td>
</tr>
<tr>
<td>Platinum</td>
<td>21090</td>
<td>133</td>
</tr>
<tr>
<td>Titanium</td>
<td>4507</td>
<td>520</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>3950</td>
<td>1030</td>
</tr>
<tr>
<td>SiN(_x)</td>
<td>3440</td>
<td>877</td>
</tr>
</tbody>
</table>

To complete the formulation, expressions must be provided for the source terms appearing on the right-hand side of the energy equation. The Joule heating term may be simply estimated from:

\[
P = V'I
\]

(2.4)

where \(V'\) is the applied voltage drop across the stack, and \(I\) is the corresponding current. In the analysis below, both \(V'\) and \(I\) are time-dependent experimental inputs. Meanwhile, the radiative heat loss term is estimated from

\[
R = \sigma (\epsilon_t A_t + \epsilon_b A_b) (T_4^4 - T_a^4)
\]

(2.5)
where \( \sigma \) is the Stefan-Boltzmann constant \([\text{Stefan (1879); Boltzmann (1884)}]\), \( \epsilon \) is the emissivity, \( A \) is the surface area of the stack, the subscripts \( t \) and \( b \) refer to the top and bottom surfaces, respectively, and \( T_a \) is the ambient temperature. In deriving (2.5), we have assumed grey body radiation, and ignored radiative losses losses from the sides of the stack because the corresponding areas are substantially smaller than the horizontal surface area.

The heat of reaction is estimated using the reduced reaction formalism recently introduced in \([\text{Salloum and Knio (2010a,b,c)}]\). In this model, the reaction source term is expressed in terms of stretched, normalized time variable, \( \tau \), that describes the age of the mixed Ni-Al layer. Specifically, for Ni-Al bilayers with a 1:1 ratio of the reactants, \( \dot{Q} \) is expressed as \([\text{Salloum and Knio (2010a)}]\):

\[
\dot{Q} = \Delta \tilde{H} g(\tau) \frac{d\tau}{dt}
\]

where

\[
\Delta \tilde{H} = \frac{\rho^{Al} C^{Al}_p + \gamma \rho^{Ni} C^{Ni}_p}{(1 + \gamma)} \Delta T_f
\]

(2.7)

is the heat of reaction, \( \Delta T_f \approx 1661 \text{ K} \) is the adiabatic flame temperature,

\[
\gamma = \frac{M^{Ni} \rho^{Al}}{M^{Al} \rho^{Ni}}
\]

(2.8)

\( \rho^{Al}, C^{Al}_p, \) and \( M^{Al} \) respectively denote the density, heat capacity, and molecular mass of Al, \( \rho^{Ni}, C^{Ni}_p, \) and \( M^{Ni} \) denote the density, heat capacity and molecular mass of Ni, respectively, whereas \( g \) is a canonical solution of the heat equation which is given by \([\text{Salloum and Knio (2010a)}]\):

\[
g(\tau) = 4 \sum_{n=1}^{\infty} \exp \left[ -\frac{(2n - 1)^2 \pi^2}{2} \tau \right]
\]

(2.9)
The evolution of the stretched time variable is governed by:

\[
\frac{d\tau}{dt} \equiv \frac{D(T)}{\delta^2}
\]  

where \( D \) is the temperature-dependent atomic diffusivity. As in [Salloum and Knio (2010a)], \( \tau \) is normalized using \( \delta \), the half-thickness of an Al layer, see Fig. 2.2. Typically, an Arrhenius dependence of \( D \) on temperature is assumed,

\[
D = D_0 \exp\left(-\frac{E}{RT}\right)
\]  

and the pre-exponential factor, \( D_0 \), and activation energy, \( E \), are obtained from fits to experimental data. As mentioned earlier, observations of the velocity of self-propagating reaction fronts have primarily been used for this purpose [Mann et al. (1997)].

\[
\begin{array}{c}
\lambda \\
\chi \\
\end{array}
\]

\[
\begin{array}{c}
\text{Al} \\
2\delta \\
\text{Ni} \\
\end{array}
\]

**Figure 2.2:** Schematic illustration of a representative Ni-Al bilayer where \( \lambda \) is the bilayer thickness, \( 2\delta \) is thickness of the Aluminum layer and \( \chi \) is the spatial coordinate.

Below, an alternative strategy is explored based on measurements of the temperature in the nanocalorimeter stack. Before outlining this strategy, however, we note that if the atomic diffusivity and the resistive power input into the calorimeter are known, then the evolution of the temperature within the nanocalorimeter can be
obtained by integrating the coupled system:

\[
\frac{dT}{dt} = -\frac{\Delta \tilde{H}}{\rho C_p V} g(\tau) \frac{d\tau}{dt} + \frac{V' I}{\rho C_p V} - \frac{\sigma}{\rho C_p V} (\epsilon_r A_r + \epsilon_b A_b) (T^4 - T_0^4) \quad (2.12)
\]

\[
\frac{d\tau}{dt} = \frac{D(T)}{\delta^2} \quad (2.13)
\]

In the computations, we integrate (2.13) using an explicit second-order Adams-Bashforth scheme, and (2.12) using an operator-split scheme where a fourth-order Runge-Kutta scheme is applied in a first fractional step in order to account for Joule heating and radiative heat loss terms, and exact integration is used in a second fractional step to account for the reaction source term.

### 2.2 Inference of Diffusivity

In this section, a simplified procedure is developed that combines the simplified thermal model developed in the previous section with experimental measurements of temperature and power dissipation in order to infer the reaction source term and consequently the atomic diffusivity in the Ni-Al bilayer.

In order to outline the analysis, we start by rewriting (2.12) symbolically as:

\[
\hat{T} = \hat{P} + \hat{E} - \hat{R} \quad (2.14)
\]

where \(\hat{T}\) is the heating rate of the stack, \(\hat{P}\), \(\hat{E}\) and \(\hat{R}\) refer to the Joule heating rate, the chemical source term, and the radiation loss, respectively.

We first start by isolating heat release term, \(\hat{E}\), since it directly involves the atomic diffusion rate [Salloum and Knio (2010a)]. To this end, we first note that the Joule heating rate, \(\hat{P}\), is readily available from the experimental measurements, which includes the voltage drop across the stack and the current flowing through it; \(\hat{P}\) follows immediately from their product. In addition, experimental data also includes the measured temperature. Based on this instantaneous measurement, the radiative
heat loss rate, \( \dot{R} \) can be readily estimated as well. In addition, the temperature measurements can also be exploited to estimate the total heating rate, \( \dot{T} \), namely by fitting a smooth curve to the experimental data and differentiating this curve. Based on the estimates of the total heating rate, radiative loss, and Joule heating rate, the chemical source term can be estimated using (2.14), namely as \( \dot{E} = \dot{T} - \dot{P} + \dot{R} \). Of course, several limitations arise concerning the validity of this estimate, as further discussed in the following section.

Ignoring these limitations for the time being, let us assume that a suitable signal has been obtained of \( \dot{E} \) versus time. One can immediately exploit this signal in conjunction with (2.6) in order to isolate a differential equation for \( d\tau/dt \) that involves only \( \tau \) and \( t \). Integrating this differential equation yields signals of \( \tau \) and \( d\tau/dt \) versus time. Substituting the latter into (2.10) yields the desired estimates of \( D \) as a function of time, or alternatively as a function of temperature. Based on this derived functional relationship, the parameters \( D_0 \) and \( E \) are estimated through a least-squares minimization procedure. A flow diagram for the inference of diffusion parameters is illustrated in Fig. 2.3.
2.3 Results

Experimental data were obtained for two nanocalorimeter configurations, both having the same design as sketched in Fig. 2.1. The first configuration incorporates a Ni-Al bilayer that is 50 nm thick, whereas the second configuration comprises a 60 nm thick bilayer. Apart from the bilayer thickness, there is also a difference in the thickness of the SiNx layer. In the case of the 50 nm bilayer, the SiNx layer is 100 nm thick, whereas for the 60 nm bilayer, it is 60 nm thick. As a result, the thermal mass of the device in the case of the 60 nm bilayer is smaller than that in the 50 nm bilayer case. This is reflected by the fact that in the initial stages of heating, the rates of temperature rise are similar for both cases, though the power dissipation is higher in the 50 nm bilayer case; see Figs. 2.4 and 2.9 below.

![Figure 2.4](image)

**Figure 2.4**: Joule heating applied to the nanocalorimeter configuration for the two cases.

Both devices are triggered under vacuum, using a short 20 ms long capacitive discharge. The typical time constant of the circuit is 3 s, much larger than the discharge time. Figure 2.4 depicts the transient resistive power dissipated into the stack due to Joule heating associated with the corresponding current pulse. The curves shows a rapid rise over about a 10ms interval, following which the power
dissipation remains essentially constant. The current is interrupted following the plateau depicted in the curves. Using a representative thermal diffusivity, $\alpha$, of about $10^{-5}$ m$^2$/s, the thermal penetration depth corresponding to the electrical pulse duration is estimated as $\delta_t \simeq \sqrt{\alpha t_p} = 0.45$ mm. This justifies the approximations used in section 2.1, namely that the temperature is essentially uniform within the stack over short times of order $t_p$.

Figure 2.5 shows the evolution of the heat release term, estimated from the temperature, voltage, and current measurement following the procedure outlined in the previous section. Note that $\dot{E}$ is expected to be a positive quantity, as the mixing of Ni and Al occurs exothermically. At early and late stages, however, the estimates reveal small-amplitude negative values. These occur because at early stages, the heat release rate is small, because the temperature is low and accordingly the mixing rates are very small. Thus, in this regime, Joule heating is essentially balanced by temperature rise and small amount of radiative heat loss. Estimates of the heat release term are consequently susceptible to noise in the measurements at very small mixing rates that are prevalent at early stages and later stages when the reaction nears completion. The fact, that at later stages the heat release term is also small, has been experimentally verified, namely through subsequent heating steps which did not reveal any measurable release of chemical energy. Thus, at the late stages, the estimates are also susceptible to measurement noise. In order to minimize the impact of this noise on diffusivity estimates, a smooth interpolant to the experimentally-based estimates is constructed, subject to the constraint that the heat release term remains non-negative. The smooth interpolant averages the heat release rate over different phases that occur during the interdiffusion in the Ni-Al bilayer. In particular, the two neighboring peaks occurring in the experimental curve (inset of Fig. 2.5) are merged in the smoothing procedure. The smooth curves, which are also plotted in Fig. 2.5 are then used for the purpose of inferring the atomic diffusivity.
The inferred values of $D$ are plotted against temperature in Fig. 2.6. Plotted are curves for the 50-nm and 60-nm bilayers. The curves are in good agreement with each other, which indicates that the description of mixing using a Fickian approximation is consistent with the data, at least in the regime considered. As expected, $D$ increases rapidly with $T$, in the range depicted. At higher values (not shown), the inferred diffusivity drops sharply, because the heat release term becomes unobservable. This may be due to potential phase change as $T$ approaches the melting point of Al and/or the consumption of the reactants. Evidently, under these conditions the measurement of temperature is not suitable to infer either the heat release or the associated mixing rate. This constitutes another limitation of the present characterization approach.

In order to quantify these trends, we plot in Fig. 2.7 the ratio, $Z \equiv \dot{E}/\dot{P}_{max}$, of the chemical heat release term to the peak Joule heating term associated with the electric
Figure 2.6: Inferred diffusivity, $D$, versus temperature, $T$. Curves are generated for the 50 nm and 60 nm bilayers, as indicated. Also shown is the extrapolated correlation of Fritz [Fritz (2011)].

discharge. This ratio rises rapidly from low temperatures, peaks around 860 K, and then drops rapidly at high temperatures. Clearly, the estimated heat release is least susceptible to measurement noise when $Z$ is large. In particular, values $Z > 2$ would conservatively ensure that the chemical heat release is a dominant contributor to the observed temperature rise, and consequently that the estimates are least affected by measurement noise or cancellation errors. Based on the results in Fig. 2.7, $Z > 2$ for temperatures ranging from 720 K to 860 K. A rapid decrease in the heat release is observed beyond 860 K as the reaction nears completion. Consequently, this temperature regime is considered to be optimal for estimating the diffusion parameters for the interdiffusion in the Ni-Al bilayer. A similar observation is made for the 60 nm bilayers; the corresponding results are consequently omitted.

We further analyze the dependence of $D$ on temperature by plotting the natural logarithm of the diffusivity against $T^{-1}$. Figure 2.8 shows curves of $\ln(D)$ generated for both bilayers, with the temperature restricted to the range of 720-860 K. A
Figure 2.7: Ratio of the chemical heat release rate to the maximum Joule heating rate versus temperature. Plotted are results obtained for $\lambda = 50$ nm.

straight line fit to the data is also depicted in the plot. Over the temperature range considered, the data may be closely approximated by a straight line, which indicates that an Arrhenius correlation is suitable. The corresponding values of the pre-exponent and activation energy are $D_0 = 2.79 \times 10^{-10} \text{ m}^2/\text{s}$ and $E = 57.37 \text{ kJ/mole}$.

Of course, it would have been ideal to conduct direct comparison of the presently-inferred values with other estimates obtained by independent measurement techniques. Unfortunately, for the present range of temperatures, direct measurements are not readily available. In general, estimates of Ni-Al interdiffusion rates at temperatures that are high enough for reactions to initiate but smaller than the melting temperature of Al remain quite scarce. Recently, however, Fritz [Fritz (2011)] attempted to estimate diffusion rates based on an experimental analysis of the ignition temperature and ignition thresholds of nanostructured Ni-Al bilayers. The experimental correlation resulting from Fritz’s analysis is also plotted in Fig. 2.6. Though
quantitative differences between Fritz’s correlation and the present estimates are evident, the consistency between the estimates and the overall trends is encouraging.

In order to verify the present diffusivity estimates, we substitute the Arrhenius correlation derived from Fig. 2.8 into the governing equations (2.12-2.13), and perform the integration. Since data is not available for $T < 720$ K, the correlation obtained by Fritz [Fritz (2011)] is used for this temperature range. For the same reason, the presently-inferred Arrhenius correlation is simply extrapolated to higher temperatures. The experimental measurement of the Joule heating term is used as input to the calculations, but all other variables are computed in the model based on known dimensions and thermophysical properties. Figure 2.9 shows the evolution of the computed temperature during and following the application of the electrical stimulus. Plotted are curves for the 50 nm and 60 nm bilayers; the corresponding experimental temperature measurements are also shown for comparison. For both cases, a very close agreement is observed between simulation results and measured data. This supports the validity of the diffusivity estimates at least in the intermediate temperature range where the chemical heat release term is large.

To further verify the present predictions, Fig. 2.10 compares the experimentally
inferred and computationally determined heat release rates for both the 50 nm and 60 nm bilayers. As observed for temperature, the experimental and computational curves for the heat release term are in close agreement, at intermediate times when the magnitude of the heat release is large. Within the corresponding range of temperatures, this agreement further supports the inferred diffusivity estimates.

Finally, we examine the assumption made in the analysis that complete mixing occurs when the nanocalorimeter is triggered with a sufficiently strong electric stimulus. To this end, we once again rely on the experimental measurements, which subjected the same nanocalorimeter to multiple, nominally-identical electric stimuli and monitored the subsequent rise and decay of the temperature. The experimental observations showed that the temperature response of the nanocalorimeter was essentially identical following the first stimulus, which indicates that under the present conditions, no significant exothermic energy release occurs following the first experimental test. To further verify this claim, we have performed simulations of an
“inert” nanocalorimeter, namely by integrating (2.12) with the first term omitted. Figure 2.11 compares the results of these simulations with the experimental temperature curves obtained for the second test. An excellent agreement between the experimental and computational curves can be observed. This further supports the assumption that mixing is complete during the first test, and lends confidence in our thermal radiation loss model.

2.4 Conclusions

A computational model was developed to describe the evolution of the temperature field in a nanocalorimeter that comprises inert layers on which a Ni-Al bilayer is deposited. The model incorporates a reduced continuum description of mixing and heat release in the Ni-Al bilayer, and of the energy equation in the inert layers. Due to the small thicknesses of individual layers, that are several orders of magnitude smaller than the corresponding length, a simplified, transient, homogeneous repre-
sentation of the temperature field was adopted. The resulting lumped model is valid over short enough timescales, which are nonetheless sufficiently large to capture the formation reaction. Attention is focused on nanocalorimeters triggered electrically under vacuum, so that the global energy balance accounts for the effects of Joule heating, chemical heat release, and radiative heat losses.

By using experimental observations of the evolution of the temperature, the computational model is used to estimate the transient heat release rate. Assuming an Arrhenius model for the mixing between Ni and Al, the estimated heat release rate is then used to determine the pre-exponent and activation energy in the corresponding correlation for the atomic diffusivity. The model is applied to analyze experimental observations of the response of two nanocalorimeter configurations, the first 50 nm Ni-Al bilayer, whereas the second comprises a 60 nm Ni-Al bilayer. In both cases,
the nanocalorimeter is triggered using a short electrical discharge, and the experimental observations included the evolution of the current and voltage drop across the device, as well as the temperature. Each nanocalorimeter was triggered multiple times, particularly to verify that the heat of reaction is released during the first test. Thus, experimental data included the response of both “live” and “spent” devices.

Application of the computational model to analyze experimental observations of both nanocalorimeter configurations indicates that:

1. The predicted values of the diffusivity obtained from the 50 nm and 60 nm configurations are consistent with each other. Thus, the simplified description of interdiffusion appears to be consistent with the experimental observations, at least in the regime considered.

2. Limitations to the present analysis arise (a) at lower temperatures, due to the low magnitude of the heat release term, and (b) at higher temperatures, due to phase-change effects and/or the rapid drop in heat release as reactants are consumed. In both cases, the heat release rate is susceptible to measurement noise and is consequently unobservable. For the present setting, the diffusivity was reliably extracted for an intermediate temperature range extending from about 700 K to 860 K.

3. A very good agreement was observed between the temperature field simulated using inferred diffusivity and the experimental observations, and between the simulated and experimentally inferred heat release rates. Excellent agreement was also observed between the simulated and observed thermal response of the spent device.

Overall, the present experiences indicate that nanocalorimetric measurements appear to be providing a promising means of characterizing atomic diffusion rates for
solid state mixing in a Ni-Al bilayer. This effort is a significant step towards implementation of a composite diffusivity based on more than one Arrhenius correlations to improve the accuracy of reaction models.
In this chapter, we shift our focus to the equimolar Zr-Al multilayered system, shown to be a suitable chemistry for extending the duration of heat release in multilayered systems [Joress et al. (2012)]. Typically, the heat released during intermetallic formation reactions is sustained for a very short duration (milliseconds or smaller), owing to short consumption timescales and/or large velocities of the self-propagating fronts [Rogachev et al. (1993, 1994, 1995); Weihs (1998); Rogachev (2008)]. As a result, such multilayered systems would not be suitable for applications that require a much longer duration of heat release. Recently, Joress et al. explored the possibility of achieving extended duration of heat release in metallic multilayered systems in [Joress et al. (2012)]. For this purpose, sputter-deposited [Weihs (1998)] 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 [Joress et al. (2012)]. For Zr-Al multilayers with 50:50 composition, the experiments in [Joress et al. (2012)] revealed the occurrence of an
extended temperature plateau following the completion of the anaerobic ZrAl for-
mation reaction (see Figure 3.1). 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$_2$, 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 chapter 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 3.1, our approach exploits the observed dispar-
ity between the timescales of the formation $\mathcal{O}(10^{-3} \text{s})$ and oxidation reactions $\mathcal{O}(10^9$
$s)$, and thus we focus exclusively on the oxidation phase. To describe the evolu-
tion 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 3.2, different formulations for the oxide growth
are considered, including a diffusion controlled model, a 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 be-
behavior and suitability of the resulting models are then analyzed in sections 3.3 and
3.4 in light of recent experimental observations of nanostructured Zr-Al multilayers
ignited in air. Major conclusions are finally highlighted in section 3.5.

3.1 Model Formulation

A thermal model is developed to describe the temperature evolution during the oxi-
dation of a 1:1 Zr-Al multilayer foil. Following the recent experimental observations
of [Barron et al. (2013); Fisher et al. (2013)], 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. 3.1, for a Zr-Al foil with a 1:1 ratio of the reactants, this temperature is approximately 1500 K.

![Figure 3.1: 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 [Joress et al. (2012)].](image)

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. [Joress et al. (2012)], 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 cannot 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 3.4.1 in light of computed predictions.

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

$$\overline{C_p} \frac{dT}{dt} = Q_{ox} - Q_{rad} + Q_{in}$$

(3.1)

where $T$ is the instantaneous temperature of the foil and $\overline{C_p}$ is its average volumetric heat capacity. As schematically illustrated in Fig. 3.2, $Q_{ox}$, $Q_{rad}$, $Q_{in}$ 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 $\overline{C_p}$, the volumetric heat release term,
Figure 3.2: $Q_{\text{in}}$, $Q_{\text{ox}}$ and $Q_{\text{rad}}$ respectively denote the enthalpy flux due to oxygen intake, the heat generated by the oxidation reaction, and the radiative heat loss. Also shown is the growing zirconia layer on the foil.

and the surface fluxes which, together with the initial foil temperature are needed to complete the formulation of the simplified model.

The radiative heat loss per unit volume is estimated using the Stefan-Boltzmann law [Stefan (1879); Boltzmann (1884)]. Assuming that the losses from the foil top and bottom surfaces are dominant results in:

$$Q_{\text{rad}} = \frac{2\sigma \epsilon}{d_o} (T^4 - T_o^4) \quad (3.2)$$

where $\sigma$ is the Stefan-Boltzmann constant, $\epsilon$ the foil emissivity, $d_o$ the foil thickness, and $T_o$ is the ambient temperature.

In order to estimate the oxidation heat released due to the oxidizing intermetallic, we consider the following oxidation reaction:

$$\text{ZrAl} + \frac{1}{2} \text{O}_2 \rightarrow \frac{1}{2} \text{ZrO}_2 + \frac{1}{2} \text{ZrAl}_2, \quad (3.3)$$
and define the degree of conversion, $\phi$, of the intermetallic according:

$$
\phi = \frac{n_o - n}{n_o}
$$

(3.4)

where $n$ is the instantaneous number of moles of ZrAl per unit volume of the oxidizing foil, and $n_o$ is its initial value. Hence, the number of moles of ZrAl reacted per unit volume are $n_o \phi$. Note that $\phi = 0$ at the start of the oxidation process, and that $\phi = 1$ when reaction (3.3) is complete.

The heat of reaction can be evaluated using the heats of formation of the individual reactants and products. As discussed by Wang et al. [Wang et al. (2001)], we have on a per unit mole of compound basis, $\Delta H_f(ZrAl_2) = -157.8$ kJ/mole, $\Delta H_f(ZrAl) = -130$ kJ/mole, $\Delta H_f(ZrO_2) = -1080$ kJ/mole and $\Delta H_f(O_2) = 0$ kJ/mole. Consequently, the heat of reaction can be evaluated from:

$$
\Delta H_{ox} = \frac{1}{2} \Delta H_f(ZrO_2) + \frac{1}{2} \Delta H_f(ZrAl_2) - \Delta H_f(ZrAl) - \frac{1}{2} \Delta H_f(O_2)
$$

Substituting for the heats of formation of the individual species yields $\Delta H_{ox} = -488.9$ kJ/mole of ZrAl. Finally, using the definition above, the oxidation heat release rate can be estimated from:

$$
Q_{ox} = -n_o \Delta H_{ox} \frac{d\phi}{dt},
$$

(3.5)

with $d\phi/dt$ subsequently referred to as the rate of conversion.

Based on stoichiometric coefficients in (3.3), the instantaneous number of moles per unit volume of ZrO$_2$ and ZrAl$_2$ is given by $m \equiv \frac{n_o \phi}{2}$. Clearly, this would require the consumption of $m$ moles of O$_2$ per unit volume of oxidizing intermetallic. Consequently, the enthalpy flux of oxygen per unit volume may be expressed as:

$$
Q_{in} = \frac{n_o C_{pO_2} T_o}{2} \frac{d\phi}{dt}
$$

(3.6)

where $C_{pO_2}$ is the heat capacity of O$_2$ per unit mole.
The volumetric heat capacity, \( \overline{C}_p \) (J/m\(^3\)/K) varies as the oxidation reaction (3.3) in the foil proceeds. Here, we provide an expression for an averaged value of this quantity based on the constituents of the foil at any given instant:

\[
\overline{C}_p = nC_{pZrAl} + mC_{pZrO_2} + mC_{pZrAl_2} \tag{3.7}
\]

Note that \( n \) and \( m \) depend on \( \phi \) and denote the instantaneous number of moles per unit volume of the reactant (ZrAl) and products (ZrAl\(_2\), ZrO\(_2\)) respectively. The specific heat capacity of zirconia is obtained as 77.2 J/mole/K at 1500 K from [Arimondi et al. (1997)]. Averaged specific heat values of ZrAl and ZrAl\(_2\) at 1500 K were determined using individual specific heats of Al and Zr as 75 J/mole/K and 110 J/mole/K, respectively.

Finally, by substituting the expressions of bulk heat capacity and source term into the energy balance equation (3.1), we obtain:

\[
\overline{C}_p \frac{dT}{dt} = -n_\circ \Delta H_{ox} \frac{d\phi}{dt} - \frac{2\sigma \epsilon}{d_\circ} (T^4 - T_\circ^4) + \frac{n_\circ C_{pZrO_2} T_\circ}{2} \frac{d\phi}{dt} \tag{3.8}
\]

Equation (3.8) governs the evolution of the temperature in a thin multilayer foil, oxidizing according to (3.3). Clearly, in order to be able to determine the evolution of temperature, suitable expressions for \( d\phi/dt \) must first be specified. This will be addressed in the following section.

Before doing so, however, we note that if the three source terms are in balance, the rate of change of temperature vanishes, and knowledge of the foil temperature at which such balance occurs can be readily used to estimate the rate of conversion. In this situation, we have:

\[
\frac{d\phi}{dt} = \frac{2\sigma \epsilon (T^4 - T_\circ^4)}{n_\circ C_{pZrO_2} T_\circ} - \frac{n_\circ \Delta H_{ox}}{2} \tag{3.9}
\]

Equation (3.9) can be used for determining the characteristic growth rate associated
with the growth of the oxide layer in a surface-reaction controlled growth regime, as discussed below.

3.2 Growth of Oxide Layers

As mentioned in the introduction, we examine the suitability of two Zr oxide growth models, namely a diffusion controlled growth model and a surface-reaction controlled growth model. These models are briefly outlined in the following sections.

3.2.1 Kinetic model: diffusion limited growth

In the previous section, the degree of conversion ($\phi$) of the oxidizing intermetallic was defined as the ratio of the number of moles of the reactant consumed during oxidation to its initial moles. For the purpose of developing a diffusion limited growth model of the oxide, the degree of conversion is first related to the thickness of the oxide layers (see Fig. 3.3), namely according to:

$$\phi = \frac{d_o - d}{d_o} \quad (3.10)$$

where $d_o$ is the total foil and $d$ is the instantaneous thickness of the depleting intermetallic core. As previously mentioned and as illustrated in Fig. 3.3, we consider that oxide layers grow on the top and bottom surfaces of the foil.

For the case of spherical metal particles undergoing oxidation, Fromhold [Fromhold (1988)] introduced a diffusion limited growth law that expresses the growth of the oxide layer in terms of a phenomenological diffusion constant. In the case of an oxidizing flat foil, Fromhold’s law can be expressed as:

$$\frac{d\zeta}{dt} = \frac{D}{\zeta} \quad (3.11)$$

where,

$$\zeta = \frac{d_o - d}{2} \quad (3.12)$$
Figure 3.3: Schematic representation of the structure of an oxidizing Zr-Al multilayer. $d_0$ and $d$ respectively denote the initial thickness of the multilayer, and the instantaneous thickness of the depleting intermetallic “core”. The total thickness of the oxidized layers (top and bottom) is $d_0 - d$.

is the instantaneous thickness of the oxide layer, and $D$ is the diffusivity of oxygen through zirconia. $D$ is assumed to exhibit an Arrhenius dependence on temperature, namely

$$D = D_o \exp(-E_a/RT)$$  \hspace{1cm} (3.13)

where $D_o$ is the pre-exponent and $E_a$ is the activation energy. Estimates for $D_o$ and $E_a$ as provided by Pawel and Campbell [Pawel and Campbell (1981)], and used by Arimondi et al. [Arimondi et al. (1997)] to analyze the oxidation of Zr particles are used in this work. In section 3.4.3, we perform a qualitative assessment of the sensitivity of computed predictions to assumed correlations for $D$, namely by contrasting predictions obtained using the pre-exponent and activation energy above, with results obtained using correlations from [Kingery et al. (1959)] and [Douglass (1962)].
Using Eq. (3.10), a relationship between the evolution of $\phi$ and $\zeta$ can be readily derived. We obtain:

$$\frac{d\phi}{dt} = 2 \frac{d\zeta}{d_o dt}$$  
(3.14)

Combining with Eq. (3.11) leads to:

$$\frac{d\phi}{dt} = 2 \frac{D}{d_o^2 \frac{d\zeta}{d_o}}$$  
(3.15)

Finally, substituting the definition of $\zeta$ from Eq. (3.12), we get

$$\frac{d\phi}{dt} = 4 \frac{D}{d_o^2 \phi}$$  
(3.16)

the governing equation for the “rate of conversion,” $d\phi/dt$ for diffusion limited growth. Note that the above relationship shows an inverse dependence of growth rate on the oxide layer thickness, characteristic to the diffusion limited growth regime.

3.2.2 Surface-reaction controlled growth

In our initial computations aimed at describing the oxidation process by determining the bulk averaged heat capacity of the foil, the degree and rate of conversion as well as the temperature-time plot, it was realized that the kinetic model as developed in section 3.2.1 for a diffusion limited growth of the oxide alone is not sufficient. It was shown experimentally that the temperature of the foil remained nearly constant during oxidation (Figure 3.1). Since the diffusion limited growth model could not reproduce the experimental findings especially in the initial stages of oxidation, a surface-reaction controlled growth regime is investigated for the oxidizing foil. This refers to a regime in which reaction kinetics at the surface control the rate of formation of zirconia, not the diffusion of oxygen.
The rate of oxide layer growth for a surface-reaction controlled growth is defined as follows:

$$\frac{d\zeta}{dt} = v(T)$$  \hspace{1cm} (3.17)

Characteristic to the surface-reaction controlled growth, the quantity $v(T)$ is constant for a given temperature. Using the definitions for the instantaneous oxide layer thickness or the consumption factor ($\zeta$), degree of conversion ($\phi$), and the growth rate given by the above equation, the rate of conversion is obtained as follows:

$$\frac{d\phi}{dt} = \frac{2v}{d_o}$$  \hspace{1cm} (3.18)

Substituting the above expression for $\frac{d\phi}{dt}$ in Eq. 3.9, we obtain the following expression for the growth rate, $v(T)$:

$$v(T) = \frac{d_o}{2} \left( \frac{2\alpha \xi (T^4 - T_o^4)}{d_o} - n_o \Delta H_{ox} \right)$$  \hspace{1cm} (3.19)

3.2.3 Combined model

The combined model is based on comparing the individual rates for diffusion controlled growth and surface-reaction controlled growth, given respectively in Eq. 3.16 and Eq. 3.18. The combined model then selects the smaller of these two estimates, leading to the following expression for the rate of conversion:

$$\frac{d\phi}{dt} = \min \left( \frac{2v}{d_o}, \frac{4}{d_o^2} \phi \right)$$  \hspace{1cm} (3.20)

Implementation of all three models is discussed in further detail in the following section.

Note that when the two rates are equal, a “cross-over” takes place from one
growth regime to the other, and the corresponding degree of conversion ($\tilde{\phi}$) is:

$$\tilde{\phi} = \frac{2D}{d_o \upsilon}$$

(3.21)

Substituting the above expression for $\tilde{\phi}$ in Eq. 3.18, a closed form expression is obtained for cross-over time, $\tilde{t}$:

$$\tilde{t} = \frac{D}{\upsilon^2}$$

(3.22)

For a known value of diffusivity, $D$, and the growth rate during the surface-reaction controlled regime, $\upsilon$, the time interval during which the foil surface temperature maintains a steady value, can be evaluated using Eq. 3.22. The resulting estimate, however, indirectly depends on the adiabatic temperature of the foil at the onset of oxidation, as well as the foil surface emissivity.

3.3 Results

Computational models were constructed based on the formulations developed in sections 3.1 and 3.2. In all cases, the models combine the energy balance equation with a kinetic model for oxide growth. Thus, different formulations are considered according to the oxide growth model used. The governing equation system consists of Eqs. (3.8) and (3.16) for diffusion controlled growth, Eqs. (3.8) and (3.18) for surface-reaction controlled growth, and Eqs. (3.8) and (3.20) for the combined regime. Numerical resolution essentially consists in integrating the coupled evolution equations for the foil temperature, $T$, and for the rate of conversion, $\phi$. A fourth-order Runge Kutta scheme [Press et al. (1986)] is used for this purpose. In the simulations discussed below, a time step $\Delta t = 10 \mu s$ is used. Based on straightforward parameter refinement study, we found that this value falls in a range where the predictions are essentially independent of the time step. We focus our attention on Zr-Al multilayer
with a 50:50 composition; the molar density of ZrAl, \( n_\alpha \), is thus estimated to be approximately 37000 moles/m\(^3\).

In order to compute the evolution of the foil temperature, one needs to specify the foil temperature at the onset of the oxidation process. Experimental observations are used for this purpose. Specifically, we rely on two recent experiments conducted with 50:50 Zr-Al multilayers. The first experiment considered a 40 \( \mu \text{m} \) thick multilayer, whereas the second used a 16 \( \mu \text{m} \) thick multilayer. In both cases, the experimental observations (shown further below) exhibited sustained temperature plateaus similar to those illustrated in Fig. 3.1. Specifically, with the 40 \( \mu \text{m} \) foil the experiments revealed a temperature plateau at about 1500 K that extends for approximately 2 s, whereas for the 16 \( \mu \text{m} \) foil a temperature plateau at about 1400 K was observed that is approximately 1s in duration. For the purpose of analyzing the suitability of the presently considered oxide growth formulations, we focus primarily on the 40 microns case and consider the initial foil temperature as 1500 K in our simulations. The model is then validated by demonstrating the suitability of the predictions using the measurements for the thinner foil.

We begin by examining the suitability of a pure diffusion-controlled oxide growth model, particularly by examining whether the resulting model is able to recover the experimental observations. Figure 3.4(a) shows predicted temperature profiles generated using emissivity values ranging from 0.37 to 0.40. This range has been determined so as to enhance the potential agreement between the predictions of the diffusion-controlled model and the measurements. However, as can be seen from Fig. 3.4(a), it is evident that the temperature profiles obtained using the diffusion-controlled model do not yield, even in an approximate sense, a temperature plateau similar to that observed experimentally. Specifically, the profiles shown exhibit a rapid rise followed by a sharp drop, with the temperature falling below its initial value within a time span well below the duration of the experimentally observed
plateau. We have attempted to consider lower emissivity values in order to extend the time period over which the foil remains at or above its initial temperature. However, the resulting predictions revealed very elevated temperature peaks that are not consistent with the occurrence of a temperature plateau. Consequently, it appears that a diffusion controlled growth model is unsuitable for capturing the experimental measurements. In fact, this finding is not very surprising since the power law behavior associated with diffusion-controlled growth is generally inconsistent with an extended period during which heat generation and heat losses are nearly in balance.

Since the diffusion controlled growth could not capture the experimentally observed behavior of the foil temperature during oxidation, we analyzed whether the temperature plateau could be recovered using a surface-reaction controlled growth model. As discussed in section 3.2.2, at fixed temperature this model reflects a so-called “linear growth” of the thickness of the oxide layer, at a rate that is constant for a fixed temperature. In order to accommodate lack of detailed knowledge about the growth velocity and its dependence on temperature, as well as uncertainty in the rate of radiative heat losses, we have considered different values of the emissivity, $\epsilon$, in broad interval ranging from 0.1 to 0.4. Once a value of $\epsilon$ is selected, the characteristic velocity is determined using Eq. (3.19), based on the requirement that the rates of heat generation and heat loss balance at the start of the oxidation process, leading to a vanishing slope of the temperature profile. This completes the specification of all inputs needed to initialize the computations. Since this procedure also holds for the combined model, we shall for brevity restrict our attention to the results obtained with the combined model. This enables us to analyze both the occurrence of the temperature plateau as well as its duration.

Figure 3.4(b) shows temperature profiles obtained using the combined model. Plotted are results obtained using four values of the emissivity, $\epsilon = 0.1, 0.2, 0.3$ and 0.4. Qualitatively, in all cases the temperature profile exhibit a plateau at the initial
Figure 3.4: (a) Temperature versus time using a diffusion-limited growth model. (b) Temperature versus time using a coupled growth model. Curves are generated using different values of $\epsilon$, as indicated.
temperature value. Once the oxide layer has sufficiently thickened, transition from surface-reaction controlled to diffusion controlled growth occurs, leading to a drop in the foil temperature. This limits the duration of the temperature plateau which, as shown in Fig. 3.4(b), increases dramatically as the emissivity decreases.

In order to further analyze the trend above, we plot in Figs. 3.5 and 3.6, the evolution of the rate of conversion associated for the same cases as in Fig. 3.4(b). Plotted are curves depicting the rate of conversion corresponding to surface-reaction limited and diffusion limited growth regimes; as previously mentioned, the combined model selects the smaller of the two. As expected, the results indicate that in the initial stages of the oxidation process, the rate of conversion associated with surface-reaction controlled growth assumes a smaller value, and is consequently selected by the combined model. However, as the oxide layer thickens, a cross-over occurs and the rate of conversion associated with diffusion-controlled growth becomes limiting. Consistent with the trends observed in Fig. 3.4(b), the time instant at which this phenomenon takes place increases as $\epsilon$ decreases. Also note that the magnitude of rate of conversion at the cross-over point increases as $\epsilon$ increases.

To further characterize the cross-over between surface-reaction controlled and diffusion controlled oxide growth, Fig. 3.7 depicts the evolution of the degree of conversion, $\phi$, and consumption factor, $\zeta$, for the same four cases specified above. Consistent with the results in Figs. 3.4(b), 3.5 and 3.6, at early stages, a linear growth is observed in the degree of conversion and in the thickness of the oxide layer. In addition, the slope of the curve during surface-reaction controlled oxide growth increases with emissivity whereas the duration of this regime decreases with emissivity. Once cross-over occurs, a sharp decline in the rate of conversion occurs, and both curves appear to level off immediately following cross over. Thus, for the present setup, most of the oxide growth occurs during the surface-reaction controlled regime, and the overall thickness of the oxide layers is seen to increase as $\epsilon$ decreases.
Figure 3.5: Rate of conversion versus time for a 50:50 Zr-Al multilayer foil. Plotted are results obtained for $\epsilon = 0.1, 0.2$. 
Figure 3.6: Rate of conversion versus time for a 50:50 Zr-Al multilayer foil. Plotted are results obtained for $\epsilon = 0.3, 0.4$. 

\[ \epsilon = 0.3 \]

\[ \epsilon = 0.4 \]
Figure 3.7: Time evolution of the degree of conversion and of the instantaneous conversion factor. Plotted are curves generated using different values of $\epsilon$, as indicated.

Also note that, in the framework of the present simplified oxidation model, for fixed $\epsilon$ the transition from surface-reaction limited to diffusion limited oxide growth is independent of the assumed foil thickness (provided of course that the foil is thick enough that it is not consumed during the surface-reaction limited regime). This is consistent with the expression for the cross-over time in Eq. 3.22, that is independent of foil thickness. We briefly illustrate this claim by plotting in Fig. 3.8, temperature profiles for three foils that are 30, 40 and 50 $\mu$m thick, all using the same value of $\epsilon$. The results clearly show that the width of the temperature plateau is identical in all three cases. However, as expected, following cross-over the temperature decay rate increases as the thickness decreases.

The suitability of the combined model was first examined by contrasting the predicted duration of the temperature plateau to experimental observation. Figure 3.9 shows experimental measurements of the temperature of Zr-Al foils ignited in air. Plotted are results obtained with a 40 $\mu$m and a 16 $\mu$m thick foil. In each
Figure 3.8: Temperature versus time for three different foil thicknesses, each comprising Zr-Al with 1:1 ratio of the reactants. The simulations are performed using the combined model with $\epsilon = 0.1$.

case, the plots also depict computed temperature profiles obtained using the present combined oxidation model with an emissivity $\epsilon = 0.1$. The results indicate that in both cases the predicted width of the temperature plateau agrees favorably with the experimental observations.

An additional test of the model predictions was conducted by comparing the computed thickness of the zirconia layers to measurements reported in [Joress et al. (2012)]. Specifically, the EDS analysis [Joress et al. (2012)] conducted on a 40 $\mu$m, 50:50 Zr-Al foil (that was ignited in air and that exhibited a temperature plateau approximately 2s long) revealed oxide layers that are about 2$\mu$m thick. This measurement also compares favorably well with the results in Fig. 3.7, which indicate that with $\epsilon = 0.1$, the value of $\zeta$ at the end of the computations is approximately 2.5 $\mu$m. Thus, reasonable quantitative agreement is observed between measured and
**Figure 3.9:** Temperature versus time for an oxidizing Zr-Al with 1:1 ratio of the reactants. Top: Experimental measurements for a 16 microns thick foil, and the predicted temperature profile during oxidation. Bottom: Experimental measurements for a 40 microns thick foil, and the predicted temperature profile during oxidation. An emissivity value 0.1 was used in both cases.
computed oxide layer thickness. Also note that in the present simplified model we have ignored the oxidation of Al, and consequently its contribution to oxidation heat. This could explain why the predicted growth of the zirconium oxide layer is slightly larger than observed experimentally.

3.4 Discussion

As discussed in section 3.3, our present estimates for characteristic growth velocity of the oxide layer during surface-reaction controlled regime assumed a constant temperature profile. In order to verify the suitability of this assumption in the present setting, an order of magnitude analysis is conducted in section 3.4.1 below, based on computed predictions and experimentally observed temperature profile.

In addition, our phenomenological description of the kinetics of oxide growth considered two limiting phenomena, surface-reaction kinetics and diffusion through the oxide layer. In doing so, potential rate limiting effects associated with diffusion of oxygen from the ambient atmosphere towards the foil surface were ignored. In section 3.4.2, a boundary layer analysis is conducted in order to assess the validity of this approximation.

Finally, model predictions presented above have relied upon the diffusivity estimates for oxygen in zirconia as provided by Pawel et al. in [Pawel and Campbell (1981)]. In section 3.4.3, we perform a qualitative analysis of the sensitivity of the model predictions to the selected correlation, namely by considering other diffusivity correlations available in the literature.

3.4.1 Constant temperature assumption

As seen in Fig. 3.9, the experimentally observed temperature profile corresponding to the oxidation phase of the 50:50 Zr-Al foils is not constant. To assess whether the constant temperature approximation is justified, we perform a scaling analysis of the
source terms estimated based on this approximation, and contrast the corresponding estimates to the experimentally observed transient term. Specifically, we compute the ratio of the temperature rise that would be induced by the predicted heat release term alone and of the characteristic temperature change observed in the experimental profile.

We start by estimating the temperature rise due to oxidation based on the computed rate of conversion, $\frac{d\phi}{dt}$ (7.92 \times 10^{-2} \text{s}^{-1}), as follows:

$$\left( \frac{dT}{dt} \right)_{\text{oxn}} = -n_o \Delta H_{\text{ox}} \frac{d\phi}{dt} \frac{1}{C_p} \quad (3.23)$$

Substituting the values for $n_o$ (37000 moles/m$^3$), $\Delta H_{\text{ox}}$ (-488.9 kJ/mole) and $C_p$ ($\approx 2775.06$ kJ/m$^3$/K) in the above expression yields $\left( \frac{dT}{dt} \right)_{\text{oxn}} = 506.27$ K/s.

Let us now consider the experimental temperature profile shown in the Fig. 3.10. Based on the observed variations during the plateau range, one can estimate a characteristic value $\left( \frac{\Delta T}{\Delta t} \right)_\text{exp} \approx 55.15$ K/s. Consequently, the ratio:

$$\frac{\left( \frac{\Delta T}{\Delta t} \right)_\text{exp}}{\left( \frac{dT}{dt} \right)_{\text{oxn}}}$$

is about 0.11. In other words, the estimated heat release term would lead to a temperature rise that is by an order of magnitude larger than the experimentally observed unsteady term. This justifies neglecting the transient term during the observed plateau phase.

3.4.2 Gas phase diffusion of oxygen

To assess the potential role of oxygen transport in the gas surrounding the foil, a boundary layer analysis is conducted that conservatively assumes that natural convection conditions prevail and exploits the analogy between heat and mass transfer to estimate the mass transfer coefficient.
For the present foil length and width, \( l = 0.03 \) m, \( w = 12.2 \) mm, and the present surface (\( T = 1500 \) K) and far-field (\( T = 298 \) K) temperatures, the mean oxygen concentration is estimated as \( \overline{C_{O_2}} = 9.38 \) moles/m\(^3\). Using a diffusivity value \( D_{O_2} = 2.7 \times 10^{-5} \) m\(^2\)/s, we estimate the Grashof and Schmidt numbers, respectively \( Gr = 2182.8 \) and \( Sc = 0.615 \). Finally, using the heat and mass transfer analogy into the correlation for Nusselt number for a flat vertical plate in laminar flow [Incropera et al. (2011)]:

\[
Nu = 0.68 + \frac{0.670 Ra^{1/4}}{[1 + (0.492/Pr)^{9/16}]^{4/9}}
\]

yields the following estimates of the Sherwood number and the mass transfer coefficient, respectively \( Sh = 3.75 \), and \( k_m \approx 0.02 \) m/s. The limiting oxygen flux due to diffusion in the gas phase can now be estimated from:

\[
J_{lim} = k_m \overline{C_{O_2}}. \tag{3.24}
\]

Substituting the estimated values of \( k_m \) and \( \overline{C_{O_2}} \) yields \( J_{lim} \approx 0.2 \) moles/m\(^2\)/s.
To check whether diffusion through the boundary layer can become limiting, we compute the oxygen flux at the foil surface as predicted by the simplified model. Using the predicted growth of the zirconia layer, and the stoichiometry of the reaction, the oxygen flux is estimated as $J_{O_2} \approx 0.073 \text{ moles/m}^2/\text{s}$. Comparing the estimates for $J_{O_2}$ and $J_{\text{lim}}$ as obtained earlier, one observes that $\frac{J_{\text{lim}}}{J_{O_2}} \approx 3$, i.e. the limiting flux of oxygen is about three times larger than the flux of oxygen consumed by the foil in the computational model. Consequently, gas phase mass diffusion of $O_2$ is not expected to play an important role for the present setup.

3.4.3 Sensitivity of correlation of oxygen diffusion through ZrO$_2$

Numerous efforts have focused on estimating diffusion rates of oxygen in zirconia and other zirconium alloys, and the dependence of these rates on temperature. These efforts have led to correlations of the diffusivity that may exhibit significant quantitative differences.

We briefly examine the sensitivity of the computed predictions to the corresponding estimates by considering the correlations determined by Kingery et al. [Kingery et al. (1959)] and Douglass [Douglass (1962)]. In the case of Kingery et al. [Kingery et al. (1959)], the diffusivity estimates correspond to diffusion of oxygen in cubic fluorite (Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$) whereas in Douglass (1962) they correspond to diffusion of oxygen in sintered ZrO$_{1.954}$ pellets. They are valid in the approximate temperature range 973 – 1373 K. Diffusivity estimates by Pawel and Campbell [Pawel and Campbell (1981)] are valid for a wider range of temperatures (1000 - 4000 K), which motivated their use in the present work.

As shown in Fig. 3.11 (a), temperature profiles simulated using correlations from [Pawel and Campbell (1981)] and [Douglass (1962)] show similar trends. The width of the plateau appears to be extended further using estimates from [Kingery et al. (1959)]. The model predictions can thus be sensitive to diffusion parameters; con-
Figure 3.11: (a) Temperature profiles using diffusivity estimates by Pawel and Campbell [Pawel and Campbell (1981)], Kingery et al. [Kingery et al. (1959)] and Douglass [Douglass (1962)]. Also shown is the experimental data. Foil thickness 40 microns and initial temperature 1500 K is used in the computations. (b) Semi-log plot for Arrhenius diffusivity of Oxygen in Zirconia as estimated by Pawel and Campbell [Pawel and Campbell (1981)], Kingery et al. [Kingery et al. (1959)] and Douglass [Douglass (1962)].
sequently, inferred quantities may need to be re-calibrated as diffusion models and radiation estimates are refined.

3.5 Conclusions

A simplified model is developed for the oxidation of a Zr-Al multilayered foil with 50:50 composition. The model is based on coupling the integral energy balance for the oxidizing foil, with a combined oxide growth model. The latter determines the rate limiting mechanism of oxide growth by contrasting the kinetics of diffusion-controlled and surface-reaction controlled regimes.

The model was implemented to predict the evolution of foil temperature and thickness of the oxide layers in a regime in which experimental measurements are available. In particular, the computations showed that:

1. Diffusion controlled growth kinetics alone cannot reproduce the temperature plateau as observed experimentally during foil oxidation.

2. Computations performed using the combined growth model reveal a temperature plateau whose width is limited by cross-over from surface-reaction controlled to diffusion controlled growth.

3. The duration of the temperature plateau is sensitive to the assumed value of emissivity, and increases sharply as $\epsilon$ is reduced.

4. With calibrated emissivity value, good agreement is observed between the predicted and measured duration of the temperature plateau. A reasonable agreement is also observed between computed thickness of the oxide layer and available experimental measurements.

While the present experiences have shed insight into the evolution of oxide growth in Zr:Al multilayers following the consumption of the anaerobic reaction, the devel-
opment of the present oxidation model would benefit from additional experimental measurements. Of specific interest would be conditions that would assist us in better estimating heat losses during oxidation, as well as the dependence of oxidation kinetics on temperature, and if relevant on the ambient oxygen concentration. Experiments conducted for different partial pressures of oxygen would be suitable for this purpose.
Reduced Model of Formation Reactions in Zr-Al Nanolaminates

Despite the availability of a body of experimental evidence concerning anaerobic formation reactions in the Zr-Al system (see, e.g. [Fisher et al. (2013)] and references therein), a computational model that can describe the evolution of anaerobic formation reactions in the Zr-Al system is not available. In this chapter, we focus on the development of such a model.

While numerous models for the simulation of transient reactions in reactive multilayered systems have been developed and refined over the past three decades [Mann et al. (1997); Gavens et al. (2000); Besnoin et al. (2002); Jayaraman et al. (2001); Salloum and Knio (2010a,b,c); Makino (2003, 2007); Alawieh et al. (2011); Vohra et al. (2011)], the adaptation of existing models to characterize anaerobic reactions in Zr-Al system are limited by a lack of suitable characterization of atomic intermixing rates, and the dependence of these rates on the local temperature. To overcome this hurdle, we rely on recent experimental observations for two reaction regimes. The first concerns essentially homogeneous reactions initiated by means of a current pulse, and the second concerns measurements of the velocity of self-propagating reac-
tion fronts. Following the methodology outlined in [Alawieh et al. (2013)], we exploit experimental temperature measurements during uniform ignition of the foil to estimate the atomic diffusivity in a low temperature range. The uniform ignition ranges approximately from the ignition temperature (below which the temperature of the sample is primarily affected by the external stimulus) to approximately the melting point of Al (above which the temperature rise is too fast for accurate information to be drawn). To calibrate intermixing rates at higher temperatures, extending beyond the melting of Al, we rely on experimental measurements of reaction velocity using foils with varying bilayer thicknesses [Fritz (2011)]. The comparison of model predictions and experimental data enables us to determine diffusivity estimates in a suitably wide temperature range.

This chapter is organized as follows. In section 4.1, we provide a brief description of the experimental measurements used to support our inference of key parameters needed in the construction of the model for anaerobic Zr-Al reactions in nanolaminates. The formulation of the computational model is then outlined in section 4.2. Section 4.3 then discusses two approaches for inferring the intermixing rates based on the experimental measurements. The first is based on a simple regression methodology that aims at minimizing the square error between model predictions and experimental observations, whereas the second is based on a more elaborate Bayesian inference formalism that enables us to take into account measurement uncertainties and to quantify the discrepancy between the measurements and the corresponding model predictions. Computed results are discussed and analyzed in section 4.4, and major conclusions are highlighted in section 4.5.

4.1 Data Sources

As mentioned earlier, our experimental data sources consist of: (i) hot plate ignition experiments, (ii) homogeneous ignition experiments, and (iii) measurements of the
velocity of self-propagating reaction fronts.

The hot plate ignition experiments consisted in dropping small fragments of reactive Zr-Al foils on a hot plate, and measuring the plate temperature using a thermocouple pressed against its surface. Precisely 15 different foil fragments were used to account for the variability in the respective ignition points depending upon their size and orientation on the plate surface. The overall ignition point corresponds to the minimum temperature at which all the fragments were ignited. The ignition point is achieved within an accuracy of ± 5 degrees by systematically increasing or decreasing the plate surface temperature using an iterative process. Tests were conducted for bilayer thicknesses ranging from about 50 nm to 90 nm and the data recorded for the case of a 20 µm thick nanolaminate foil is illustrated in Fig. 4.1. Following the analysis developed by Fritz et al. [Fritz et al. (2013)], the ignition temperatures are exploited to estimate the activation energy of atomic diffusion in the low temperature regime. For the equimolar Zr-Al system, it is estimated to be approximately 53 kJ/mol, accurate within ± 1.3 kJ/mol. This initial estimate of the activation energy is used in a regression analysis aimed at determining the Arrhenius correlation for atomic diffusivity at low temperatures.

To infer the pre-exponent, we rely on ignition experiments in which the Zr-Al multilayered foils are ignited using a current pulse of finite duration. The process involves holding a Zr-Al foil between two copper electrodes connected to a current-pulse generator. The experimental set-up is the same as that described in [Fritz (2011)]. As a result of uniform ohmic heating of the foil, the reaction evolves in an essentially homogeneous fashion. The pulse duration is optimized to the minimum value that enables ignition in the reactive multilayers. A one-color optical pyrometer, focused at the center of the foil is used to measure the foil surface temperature. The pyrometer calibration error is ± 100 K. The experimental observables thus consist in the recorded time evolution of the electrical power input into the foil, and the foil
surface temperature. Variations in foil surface emissivity are not expected to have a significant impact on the measurements, due to the low temperatures during ignition and our focus on a temperature range bounded above by the melting temperature of Al. As further discussed in section 4.4 below, homogeneous ignition profiles obtained for Zr-Al multilayered foils with $\lambda = 68$ nm and $\lambda = 72$ nm are made available.

Our experimental database also includes reaction velocity measurements for Zr-Al multilayered foils with four different bilayer thicknesses, namely $\lambda = 64$ nm, 79 nm, 81 nm and 87 nm. To achieve this, a given foil is secured firmly between glass slides such that one end of the foil is protruding. The glass slides prevent further oxidation of the foil in the presence of ambient oxygen. An assembly of five optical fibers with
known spacing is held above the foil and a self-propagating reaction is initiated by applying an electric spark at the protruding end. The experimental set-up is shown below in Fig. 4.2.

![Experimental Set-up]

**Figure 4.2**: Shown above is a 50:50 Zr-Al nanolaminate foil held firmly between two glass slides with one end protruding. Also shown is an optical fiber assembly for measuring the front propagation velocity.

As the reaction front propagates along the length of the foil, velocity is estimated using the time taken by the front to pass each fiber in the arrangement. As discussed in [Alawieh et al. (2013)], the velocity-bilayer data pairs are used to infer atomic diffusion parameters in the high temperature range.

### 4.2 Model Formulation

In this section, we provide brief outlines of the models used for the simulation of uniform ignition, and transient reaction fronts in equimolar Zr-Al nanolaminates. As illustrated in Fig. 1.2, the multilayered system is assumed to have a uniform
microstructure, with an alternating arrangement of flat layers of Zr and Al. For a 1:1 molar ratio, the thickness ratio of individual Al and Zr layer is given by

$$\gamma \equiv \frac{\rho^{Al} M^{Zr}}{\rho^{Zr} M^{Al}}$$

where $\rho$ denotes the density, $M$ is the atomic mass, and the superscripts refer to individual elements. For compositionally pure layers, $\gamma = 1.4$. The elemental layers are assumed to be separated by a premixed region of thickness, $2w \approx 1.6$ nm, that forms during the deposition process.

The evolution of the reactions in the Zr-Al system are described in terms of continuum models that are based on the assumptions that the atomic intermixing can be described in terms of Arrhenius rate expressions, and that volumetric changes during the reaction can be ignored. For uniform ignition experiments, the reaction is assumed to proceed uniformly throughout the foil. This enables us to adopt a simplified formulation consisting of ordinary differential equations that govern the evolution of the enthalpy and the degree of mixing. For self-propagating fronts, a space-time formulation is adopted that also accounts for thermal transport in the layered medium. The formulations of the ignition model and transient front propagation model are discussed in sections 4.2.1 and 4.2.2, respectively.

### 4.2.1 Homogeneous reaction model

The development of the homogeneous reaction model is specifically tailored to uniform ignition experiments in which spatial variations within the reacting multilayers are negligible. The approach based on a lumped parameter formulation of the energy equation is used, namely [Fritz (2011)]:

$$\dot{H} = \dot{P} + \dot{Q} - \dot{L}$$

where $\dot{H}$ denotes rate of change of volume-averaged foil enthalpy, whereas $\dot{P}$, $\dot{Q}$ and $\dot{L}$ respectively denote the power input due to Joule heating by the current pulse, the
rate of heat release due to chemical reaction, and the rate of heat loss by means of natural convection to the surroundings, all on a volumetric basis. Note that heat loss by radiation has been neglected in the ignition model [Fritz et al. (2013)] in light of the limited range of the temperature measurements, and that heat losses to the surroundings are considered to be dominated by natural convection [Alawieh et al. (2013)]. Conductive heat loss to the copper blocks (see experimental set-up in [Fritz (2011)]) is not expected to affect the measurements significantly as the pyrometer is focused at the center of the foil and since the length of the foil remains significantly larger than the thermal penetration depth during the short duration of the experiment.

The power input due to Joule heating per unit volume is given by:

\[ \dot{P} = \frac{V'I}{V_{foil}} \]  

(4.2)

where, \( V' \) and \( I \) are the applied voltage and current across the foil, respectively, and \( V_{foil} \) denotes the foil volume.

The rate of heat loss to the surroundings per unit of foil volume due to natural convection is expressed as:

\[ \dot{L} = \frac{h}{d}(T_{foil} - T_0) \]  

(4.3)

where \( d \) is foil thickness, \( T_0 \) is the ambient temperature,

\[ h = 1.32 \left( \frac{\Delta T}{L_c} \right)^{0.25} \]  

(4.4)

is the associated heat transfer coefficient [Goldstein et al. (1973); Lloyd and Moran (1974)], and \( L_c \) is a characteristic length defined as the ratio of the foil surface area and the perimeter of the cross-section.

The heat release rate is related to the rate of atomic intermixing. The latter is described in terms of a conserved scalar, \( C \) [Salloum and Knio (2010a,b,c)], assumed
to be governed by a Fickian diffusion process, namely according to:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D(T)\nabla C)$$

(4.5)

where $D(T)$ is the atomic diffusivity. The scalar $C$, also referred to as concentration, quantifies the degree of atomic mixing; it assumes a value of 1 for pure Al, -1 for pure Zr, and 0 for the fully mixed intermetallic. The atomic diffusivity is assumed to follow an Arrhenius dependence on temperature:

$$D = D_0 \exp \left( -\frac{E_a}{RT} \right)$$

(4.6)

where $D_0$ is the pre-exponent and $E_a$ is the activation energy.

Following the reduced formalism developed in [Salloum and Knio (2010a)], the PDE in Eq. (4.5) is transformed into an ODE by introducing the stretched time variable

$$\tau \equiv \int_0^t \frac{D(T)}{\delta^2} dt'.$$

(4.7)

This enables us to transform Eq. (4.5) into a canonical form:

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \xi^2}$$

(4.8)

where $\xi \equiv \frac{y}{\delta}$ is a normalized spatial variable. The solution of Eq. (4.8) is computed in a pre-processing step and made available to the computations [Salloum and Knio (2010a,b,c)].

The volume-averaged heat release rate, $\dot{Q}$, is related to the evolution of intermixing through [Salloum and Knio (2010a,b,c); Sraj et al. (2013)]:

$$\dot{Q} = -\rho C_p \Delta T_f \frac{\partial C^2}{\partial t}$$

(4.9)
where $\overline{\rho C_p}$ is the mean thermal capacity of the system (J/m$^3$/K) and $\overline{\rho} \equiv (\rho_{Al} + \gamma \rho_{Zr})/(1 + \gamma)$ is the average density. The temperature-dependent molar heat capacities of Zr and Al, depicted in Fig. 4.3, are used to estimate $\overline{C_p}$. Note that the mean-square concentration, $\overline{C^2}(\tau)$, can also be derived from the canonical solution, as outlined in [Salloum and Knio (2010b)]. Also note that $\Delta T_f \equiv \Delta H_{rxn}/\overline{\rho C_p}$ estimates the temperature rise under adiabatic conditions, and is estimated from the heat of mixing, $\Delta H_{rxn} \approx 90$ kJ per mole-atom [Kematick and Franzen (1984)]. For the Zr-Al system, $\Delta T_f$ is estimated to be 1758 K.

Substituting individual expressions for $\dot{P}$, $\dot{Q}$ and $\dot{L}$ in Eq. 4.1 results in:

$$\frac{dH}{dt} = \frac{V' \dot{I}}{V_{foil}} H[t_p - t] - \frac{\overline{\rho C_p} \Delta T_f}{\overline{cC^2}} \frac{\partial \overline{C^2}}{\partial t} - \frac{h}{\overline{c}} (T_{foil} - T_0)$$

(4.10)

Note that $H[t_p - t]$ is the Heaviside unit step function and $t_p$ is the duration of current pulse.

The instantaneous temperature is recovered from the instantaneous enthalpy estimates obtained from the numerical integration of Eq. (4.10) using the following relationship that accounts for the heats of fusion, adapted from [Besnoin et al. (2002)]:

$$T = \begin{cases} 
H/\overline{\rho C_p} & \text{if } H_0 < H < H_1 \\
T_{m}^{Al} & \text{if } H_1 < H < H_2 \\
T_{m}^{Al} + (H - H_2)/\overline{\rho C_p} & \text{if } H_2 < H < H_3 \\
T_{m}^{ZrAl} & \text{if } H_3 < H < H_4 \\
T_{m}^{ZrAl} + (H - H_4)/\overline{\rho C_p} & \text{if } H_4 < H < H_5 \\
T_{m}^{Zr} & \text{if } H_5 < H < H_6 
\end{cases}$$

(4.11)
Figure 4.3: (a) Molar heat capacity versus temperature for Zr and Al [Barin et al. (1977)]. Also shown are averaged estimates for ZrAl on a per mol-atom basis. (b) Estimated thermal conductivity versus temperature for Zr [Fink and Leibowitz (1995)].
For the Zr-Al system, the individual enthalpies, $H_0 \rightarrow H_6$, are defined by:

\[
H_0 = \rho C_p T_0, \quad (4.12a)
\]

\[
H_1 = \rho C_p T_{m}^{Al}, \quad (4.12b)
\]

\[
H_2 = H_1 + \beta \Delta H_f^{Al}, \quad (4.12c)
\]

\[
H_3 = H_2 + \rho C_p (T_{m}^{Zr,Al} - T_{m}^{Al}), \quad (4.12d)
\]

\[
H_4 = H_3 + (1 - \beta) \Delta H_f^{Zr,Al}, \quad (4.12e)
\]

\[
H_5 = H_4 + \rho C_p (T_{m}^{Zr} - T_{m}^{Zr,Al}), \quad (4.12f)
\]

\[
H_6 = H_5 + \beta \gamma \Delta H_f^{Zr}, \quad (4.12g)
\]

where $\beta = \overline{C}/(1 + \gamma)$ is the fraction of unmixed, pure Al; $H_f^{Al} = \frac{\rho^{Al}}{M^{Al}} H_f^{Al}$, $H_f^{Zr} = \frac{\rho^{Zr}}{M^{Zr}} H_f^{Zr}$, and $H_f^{Zr,Al} = \frac{\rho_f}{M_{\gamma}^{Zr,Al}} H_f^{Zr,Al}$. $H_f^{Al}$, $H_f^{Zr}$ and $H_f^{Zr,Al}$ denote individual heats of fusion in J/m$^3$ for Al, Zr and ZrAl respectively. We use $H_f^{Al} = 10.7$ kJ/mol [McDonald (1967)], $H_f^{Zr} = 19.25$ kJ/mole [Rösner-Kuhn et al. (2001)] and $H_f^{Zr,Al} = 10.75$ kJ/(mol-atom) [Banerjee (1996)], together with the following values for the melting temperatures of Al, Zr, and ZrAl, $T_{m}^{Al} = 933$ K, $T_{m}^{Zr} = 2125$ K, and $T_{m}^{Zr,Al} = 1758$ K. Note that in the range of temperature measurements in ignition experiments, the temperature falls below the melting temperature of Al, so that the enthalpy falls below $H_1$. Consequently, the simulations in this regime are not affected by phase change effects.

### 4.2.2 Distributed reaction model

The modeling of self-propagating reaction fronts relies on a similar methodology, namely based on coupling the energy conservation equation with the evolution equation for the conserved scalar. In the present formulation, however, thermal transport must be accounted for, and so the conservation of energy over a region (or computational cell), $\Omega$, is expressed in integral form as [Salloum and Knio (2010a,b,c); Sraj...
where $q$ is the heat flux, and the region-averaged chemical heat release term, $\frac{\partial Q}{\partial t}$, is estimated using Eq. 4.9. The conduction heat flux is assumed to be given by Fourier’s law:

$$ q = -k \nabla T $$

where $k$ is mean thermal conductivity, obtained using the temperature-dependent thermal conductivities for Zr [Fink and Leibowitz (1995)]:

$$ k_{Zr} = (8.85) + (7.08 \times 10^{-3})T + (2.53 \times 10^{-6})T^2 + (2.99 \times 10^3)T^{-1} $$

and Al [Powell et al. (1966)]:

$$ k_{Al} = \begin{cases} 237.05, & T < 933 \text{ K} \\ 97, & \text{otherwise} \end{cases} $$

Specifically, it is estimated using:

$$ \bar{k} = \frac{k_{Al} + \gamma k_{Zr}}{1 + \gamma} $$

and the resulting estimates are plotted in Fig. 4.3. The temperature-enthalpy relationship, Eq. (4.13), is inverted to extract the temperature from the enthalpy.

#### 4.2.3 Numerical simulation

For the case of a homogeneous reaction, the enthalpy and concentration fields degenerate into scalars, and the state is consequently described by the two-dimensional state vector, $(H, \tau)$. The evolution of this state vector is obtained by numerically integrating Eqs. 4.7 and 4.1 using a finite difference methodology. The integration
scheme developed in [Salloum and Knio (2010b)] is used for this purpose. A small integration time step, $\Delta t = 100$ ns is used to ensure a stable and accurate solution.

Simulation of the non-homogeneous reaction model is based on a finite difference methodology. The computational domain consists of a two-dimensional rectangular region, described using a uniform grid with mesh size $\Delta x = \Delta y = 1 \, \mu m$. Adiabatic boundary conditions are imposed, and the coupled system consisting of Eqs. (4.13) and (4.7) is integrated over each of the computational cells. A second-order central-difference is used to approximate the conduction heat flux. The numerical scheme developed in [Salloum and Knio (2010c)] is used in the simulation, with an integration time step, $\Delta t = 50$ ns.

4.3 Inference of Diffusivity

As discussed earlier, our model formulation for Zr-Al nanolaminates lacks key parameters describing the dependence of intermixing rates on temperature. To address this hurdle, we follow the methodology recently developed in [Alawieh et al. (2013)] for the Ni-Al system. Briefly, the analysis in [Alawieh et al. (2013)] revealed that a single Arrhenius correlation for the atomic diffusivity cannot provide suitable estimates of intermixing rates in a sufficiently wide temperature range. This problem was overcome by estimating Arrhenius branches for temperatures falling below and above the melting temperature of Al. Specifically, parameters for the first branch were calibrated using homogeneous ignition measurements, whereas parameters for the second branch were estimated based on reaction front velocity measurements.

We shall adopt the methodology developed in [Alawieh et al. (2013)] to the Zr-Al system. In the implementation, we explore two approaches for extracting the desired coefficients from measured data. The first is based on a regression analysis, whereas the second relies on a more elaborate Bayesian inference formalism. Both approaches are outlined below.
4.3.1 Regression analysis

The regression approach is based on an optimization procedure that aims at minimizing the root mean square (RMS) error between the numerical predictions and the data. For the low temperature branch, the procedure essentially consists in fixing the value of the activation energy based on the hot plate ignition experiments, and calibrating the pre-exponent, $D_0$, using the measured temperature profiles obtained from the uniform ignition experiments.

For the high temperature branch, our implementation aims at minimizing the RMS error between reaction velocity measurements for different bilayer thicknesses and the corresponding model predictions. The procedure iteratively updates both the pre-exponent, $D_0$ and the activation energy, $E_a$, and yields an optimal pair such that the RMS error falls below a set tolerance limit. In this case, the approach is the same as that outlined in [Alawieh et al. (2013)].

4.3.2 Bayesian inference

In contrast to the regression approach, which generally identifies optimal parameter values, the Bayesian inference approach exploits the measured data in determining the full posterior distribution of the parameters being calibrated. This offers the advantage of readily yielding quantitative estimates of the information gained from the data, the impact of measurement uncertainties, and consequently, the level of confidence in calibrated parameters.

In the present implementation, the inference specifically aims at determining the posterior distributions of the diffusion parameters, $D_0$ and $E_a$. Assuming reasonable prior distributions for these parameters, the posterior is determined through the application of Bayes’ rule [Berger (1985); Epstein (1985)]:

$$ P(X|T_i) \propto \mathcal{L}(T_i|X)P(X) $$

(4.18)
where $X \equiv (D_0, E_a, \sigma^2)$ is the extended parameter vector, $\sigma^2$ is the hyper-parameter (defined below), $\mathcal{P}(X|T_i)$ is the posterior of $X$ given the observations $T_i$, and $\mathcal{L}(T_i|X)$ is the likelihood of observing the data given a parameter $X$.

For the uniform ignition experiments, the data $T_i$ consist of the temperature measurements at times $t_i$ from the start of the current pulse. In this case, we assume a likelihood of the form:

$$\mathcal{L}(T_i|X) = \prod_{i=1}^{N} \frac{1}{\sqrt{2\pi\sigma^2_T}} \exp \left( -\frac{(t_i - M_i)^2}{2\sigma^2_T} \right)$$  \hspace{1cm} (4.19)

where $N$ is the number of data pairs. The quantity $\frac{dT}{dt}$ represents mean slope of the temperature versus time profile. Note that the discrepancy between the model and experimental data, $(t_i - M_i)$, is assumed to be normally distributed with zero mean and variance, $\sigma^2_T$. Here, $M_i$ is the time at which the simulated temperature coincides with the experimentally recorded temperature, $T_i$. Note that the variance is not known a priori and is consequently treated as hyper-parameter to be determined.

When calibrating the diffusion parameters in the high-temperature Arrhenius branch, the likelihood function is assumed to be given by:

$$\mathcal{L}(v_i|X) = \prod_{i=1}^{N} \frac{1}{\sqrt{2\pi\sigma^2_v}} \exp \left( -\frac{(v_i - M_i)^2}{2\sigma^2_v} \right)$$  \hspace{1cm} (4.20)

where $v_i$ denotes the measured front velocity, $M_i$ denotes the computed front velocity, $\sigma^2_v$ is the hyper-parameter, and $N$ is the total number of velocity measurements.

The prior $\mathcal{P}(X)$ is assumed to be given by the product of individual probabilities, $\mathcal{P}(D_0)$, $\mathcal{P}(E_a)$ and $\mathcal{P}(\sigma^2)$. This is a reasonable assumption since no prior information is given concerning either the physical parameters or the hyper-parameter. The prior distributions of $D_0$ and $E_a$ are assumed to be uniform over a finite width interval. We use our knowledge from the regression approach to select appropriate bounds.
For the hyper-parameter, an uninformative distribution is assumed based on Jeffrey’s prior [Sivia (1996)]:

\[
P(\sigma^2) = \begin{cases} 
\frac{1}{\sigma^2} & \text{if } \sigma^2 > 0 \\
0 & \text{otherwise} 
\end{cases} 
\quad (4.21)
\]

To construct the posterior distribution, we rely on a Markov Chain Monte Carlo (MCMC) method, and conduct the simulations using the adaptive Metropolis algorithm [Haario et al. (2001)]. This requires that a sufficiently large number of samples be generated to suitably characterize the likelihood, and consequently the posterior. To mitigate the costs of repeated model evaluations (at different values of the physical parameters) [Marzouk et al. (2007); Marzouk and Najm (2009)], a surrogate is first constructed, which is then sampled in lieu of the actual model in estimating the likelihood. As discussed further below, we rely on a polynomial chaos (PC) methodology [Ghanem and Spanos (1991); Xiu and Karniadakis (2002); Wiener (1938); Debusschere et al. (2004); Najm (2009); Xiu (2009); Le Maître and Knio (2010)] for the purpose of constructing suitable surrogates for the experimental observables.

**Polynomial Chaos surrogate**

The Polynomial Chaos (PC) surrogate methodology is based on parameterizing the \(N\) uncertain inputs using canonical random variables, \(\xi_i, i = 1, \ldots, N\), and expressing the quantities of interest in terms of a truncated series expansion. For a generic quantity of interest (QoI), \(Q\), the surrogate is expanded according to [Ghanem and Spanos (1991); Xiu and Karniadakis (2002); Wiener (1938); Debusschere et al. (2004); Najm (2009); Xiu (2009); Le Maître and Knio (2010)]:

\[
Q(\xi) = \sum_{k=0}^{P} Q_k \Psi_k(\xi) 
\quad (4.22)
\]
where $\xi$ is the vector of uncertain parameters, $P + 1$ is the total number of terms retained in the expansion, and the $\Psi_k$'s form an orthogonal polynomial basis in the space of functionals that are square integrable with respect to the probability measure characterizing the canonical random variables. Note that in the present implementation, the germ, $\xi = (\xi_1, \xi_2)$; where $\xi_1$ and $\xi_2$ are independent random variables uniformly distributed in the interval $[-1, 1]$, and respectively used to parameterize the pre-exponent, $D_0$, and activation energy, $E_a$. Accordingly, the $\Psi_k$'s are multidimensional Legendre polynomials acting on the germ, $\xi$ [Xiu and Karniadakis (2002); Le Maître and Knio (2010)]. As is customary in polynomial approximations, the PC basis is truncated by retaining polynomials with total order less than or equal to $p$, leading to a basis of size $P + 1 = \frac{(N + p)!}{N!p!}$ [Le Maître and Knio (2010)].

To determine the coefficients of the expansion, a non-intrusive spectral projection (NISP) approach is adopted [Le Maître and Knio (2010)]. NISP essentially consists in exploiting the orthogonality of the basis functions by expressing the modes $Q_k$ as integrals, and approximating the integrals using appropriate quadratures. In the implementations below, we rely on a fully tensored quadrature formula [Le Maître and Knio (2010)] with sufficiently high order to determine the coefficients accurately.

Finally, note that the availability of the PC representation enables us to readily assess the contribution of the individual parameters to the overall variability of the corresponding quantity. Suitable metrics are provided by the so-called Sobol sensitivity (global) indices [Crestaux et al. (2009); Homma and Saltelli (1996); Le Maître and Knio (2010); Sobol’ (2001); Sudret (2008); Alexanderian et al. (2012)]. In the analysis below, we rely on the first-order indices and total sensitivity indices associated with the first and second components of the germ. The first-order sensitivity indices, $S_1$ and $S_2$, essentially quantify the direct contribution of $\xi_1$ ($D_0$) and $\xi_2$ ($E_a$) to the variance of the QoI, $Q$, whereas the total sensitivity indices, $T_1$ and $T_2$ combine the direct contribution with that arising from mixed terms.
Note that for the present two-dimensional germ, simplified expressions for the Sobol indices can be obtained. Specifically, defining \( K_1 \) to be the subset of the index set \( \mathcal{L} \equiv \{1, \ldots, P\} \), consisting of indices for which the corresponding polynomial is order 0 in \( \xi_2 \), and \( K_2 \) to be the subset of \( \mathcal{L} \), consisting of indices for which the corresponding polynomial is order 0 in \( \xi_1 \). Then the \( S_i \)'s and \( T_i \)'s can be readily obtained from:

\[
S_{1,2} = \frac{ \sum_{k \in K_{1,2}} Q_k^2 \Psi_k^2 }{ \sum_{k \in \mathcal{L}} Q_k^2 \Psi_k^2 } \quad i = 1, 2
\]

and

\[
T_{1,2} = \frac{ \sum_{k \in \mathcal{L} \setminus K_{2,1}} Q_k^2 \Psi_k^2 }{ \sum_{k \in \mathcal{L}} Q_k^2 \Psi_k^2 } \quad i = 1, 2
\]

respectively. As further discussed below, the Sobol indices can provide valuable insight into the impact of individual components to the variability in the selected QoI's, even prior to introducing (or collecting) the data or performing the inverse (calibration) analysis.

4.4 Results

We now focus on inferring the parameters of the atomic diffusivity correlations based on the temperatures measured during uniform ignition tests, and the reaction front velocity measured during self-propagation. We start by presenting results obtained using the regression analysis and then discuss results obtained using the Bayesian inference. We conclude with a brief discussion of some features of the propagation velocity versus bilayer curve, generated using calibrated diffusivity parameters.
4.4.1 Regression analysis

We focus first on the low-temperature branch, and rely on the measured temperature versus time profiles to calibrate the pre-exponent in the atomic diffusivity law. As discussed earlier, the activation energy is held fixed, \( E_a = 53 \text{ kJ/mol} \), which coincides with the estimate obtained from the hot plate ignition experiments. The analysis is conducted for Zr-Al nanolaminates with \( \lambda = 68 \text{ nm} \) and \( \lambda = 72 \text{ nm} \), for which experimental temperature profiles are available.

Figure 4.4 shows computed temperature profiles for different values of the pre-exponent. Included are plots obtained for both values of \( \lambda \). The experimental temperature profiles are also shown for comparison. In each plot, the computed temperature profiles correspond to a value of \( D_0 \) that minimizes the RMS difference between the model predictions and the experimental results (dashed lines), and to values above and below this optimum. The results indicate that for \( D_0 \approx 1 \times 10^{-10} \text{ m}^2/\text{s} \), a very good agreement between model predictions and experimental results can be observed, and that there is close agreement between the optimal values of \( D_0 \) for both bilayers. This is further examined below using the Bayesian inference computations. Also note that, owing to the limitations of the one-color pyrometer used to measure the temperature, no experimental data are available below a temperature of 473 K. However, this measurement limitation does not impact the analysis because in the range \( T \lesssim 500 \text{ K} \), the temperature rise is primarily governed by the applied current pulse. This is consistent with the observation that at low temperatures, the temperature rise is approximately linear.

To calibrate the intermixing parameters at higher temperatures, we exploit reaction velocity measurements for \( \lambda = 64 \text{ nm}, 79 \text{ nm}, 81 \text{ nm} \) and \( 87 \text{ nm} \). To this end, we adopt the two-parameter optimization algorithm developed by Alawieh et al. [Alawieh et al. (2013)]. The optimization algorithm determines the optimal pair of \( D_0 \)
Figure 4.4: Measured and simulated temperature profiles. Plotted are curves obtained for (a) $\lambda=68$ nm and (b) $\lambda=72$ nm, and different values of $D_0$ as indicated. The insets reveal the occurrence of a temperature plateau corresponding to the melting of Al. The parameters of the current pulse are also indicated.
and $E_a$ for $T \geq T_{m,Al}$. Intermixing rates at lower temperatures are simulated based on the optimized values provided above. The two-parameter optimization yields the following estimates for the high temperature branch, $D_0 = 3.13 \times 10^{-9}$ m$^2$/s and $E_a = 55$ kJ/mol.

To examine our predictions, we plot in Fig. 4.5, the computed and measured velocities for all four values $\lambda$. Shown are predictions obtained using the optimal $D_0$ and $E_a$ pair, as well as values lying on both sides of the optima. The results indicate that there is good agreement between computed and measured velocities at the optimal point. It is also seen that the velocity predictions increase sharply as $D_0$ increases, and decrease rapidly as $D_0$ is decreased. The reverse trends can be observed as $E_a$ is varied from the optimum.

Combining the results of two calibration analyses yields a composite curve for the atomic diffusivity as shown in Fig. 4.6. Note that the values of the activation energy for both branches are comparable whereas the pre-exponent in the high-temperature branch is significantly larger. Thus, significant enhancement in intermixing rates around the melting of Al is primarily attributed to the pre-exponent of diffusivity. Though one would expect smaller activation energy for diffusion in the liquid state compared to the solid state, because $D_0$ and $E_a$ are inferred simultaneously from the velocity data, the fact that a significant variation in the activation energy across the melting of Al is not observed is simply an outcome of the analysis. A similar result was observed in the analysis of intermixing rates in Ni-Al multilayers [Alawieh et al. (2013)], which showed small differences between the activation energies of the low and high-temperature branches, but slightly more pronounced than presently observed for the Zr-Al system.
Figure 4.5: Velocity vs bilayer thickness. (a) Simulated results obtained with $E_a = 55$ kJ/mol and different values of $D_0$, as indicated. (b) Simulated results obtained with $D_0 = 3.13 \times 10^{-9}$ m$^2$/s, and different values of $E_a$, as indicated. The experimentally measured velocities, corresponding to $\lambda = 64$ nm, 79 nm, 81 nm and 87 nm, are also depicted.
4.4.2 Bayesian inference

We start by constructing PC surrogates that can be used to support and accelerate the Bayesian inference of diffusivity parameters. Specifically, we are interested in constructing functional representations of the dependence on the pre-exponent and activation of (a) the temperature–time profile in homogeneous ignition experiments, and (b) the velocity–bilayer curve for self-propagating fronts. In both cases, we assume uniform priors for $D_0$ and $E_a$, and use previous knowledge from the regression analysis to define suitable ranges. For the low-temperature branch, we use $D_0 \in [0.62 \times 10^{-10}, 1.20 \times 10^{-10}]$ m$^2$/s, and $E_a \in [47.83, 52.87]$ kJ/mol. For the high-temperature branch, the uniform priors are defined according to $D_0 \in$
[1.88 × 10⁻⁹, 4.38 × 10⁻⁹] m²/s and $E_a \in [49.5, 60.5]$ kJ/mol. These distributions are parameterized in terms of independent, canonical random variables $\xi_1$ and $\xi_2$ that are uniformly distributed over $[-1, 1]$. We use a sixth-order fully-tensored Gauss-Legendre quadrature rule to evaluate the PC coefficients. Thus, the 1-D rule has 7 quadrature points, leading to a total of 49 realizations for the two dimensions.

Figure 4.7(a) depicts the time-temperature response surface as function of the uncertain inputs, for the case of homogeneous ignition of a Zr-Al foil with $\lambda = 68$ nm. Specifically, we construct surrogate models of the quantity $t(T; \xi_1, \xi_2)$, which is defined as the time needed for the foil to reach a temperature $T$, given realizations of $D_0$ and $E_a$ corresponding to $\xi_1$ and $\xi_2$. We illustrate in Figure 4.7(a), a two-dimensional surface corresponding to a selected value of temperature, $T = 600$ K. Also shown are the predictions generated at the nodes of the Gauss-Legendre quadrature used to determine the PC coefficients. Surrogate models are also obtained for the reaction front velocity, $V$, as function of the bilayer thickness, given realizations of the Arrhenius parameters of the high temperature branch. In all cases, the parameters of the low-temperature branch are held fixed; these correspond to the maximum a posteriori probability (MAP) estimates obtained from the Bayesian inference analysis using the ignition data (see discussion below). Thus, in this case we obtain functional representations of the form $V(\lambda; \xi_1, \xi_2)$, with $\xi_1$ and $\xi_2$ parameterizing the Arrhenius parameters of the high temperature branch. Again, a sixth-order Gauss-Legendre quadrature rule is used to build the the velocity surrogate. Response surface based on the resulting PC expansion is shown in Fig. 4.7(b), for the 64 nm bilayer. Note that as expected, for a fixed value of the bilayer, the reaction velocity increases as the pre-exponent increases and the activation energy decreases. Also note that, consistent with earlier studies on reactive multilayered systems [Besnoin et al. (2002); Knepper et al. (2009); Jayaraman et al. (2001); Mann et al. (1997)], the reaction velocity generally increases as the bilayer decreases.
Figure 4.7: (a) Reaction times (symbols) computed at the Gauss-Legendre quadrature nodes for uniform ignition at $T = 600$ K. (b) Reaction velocities (symbols) computed at the Gauss-Legendre quadrature nodes for $\lambda = 64$ nm. The continuous surfaces depict the corresponding PC representations.
It is observed that the distribution of the individual model predictions is in close agreement with the response surfaces, indicating that the surrogate is a faithful representation of the model. To quantify this, we evaluate the relative $l^2$ norm of the error, $E$, between the model realization and the surrogate at the quadrature nodes:

$$E = \left[ \sum_j \left( R(\xi_j) - \sum_k r_k \Psi_k(\xi_j) \right)^2 w_j \right]^{\frac{1}{2}}$$

where $R(\xi_j)$ are model realizations at the quadrature nodes, $\xi_j$, and $w_j$ are corresponding weights. For all temperatures, the results yield a value of $E$, $O(10^{-4})$, which supports the observations made earlier. The surrogate model for reaction velocity is also observed to be in very good agreement with the individual realizations at the quadrature nodes, and the estimate of the relative error, $E$ is $O(10^{-3})$, for all values of $\lambda$.

Figure 4.8 shows probability density functions (PDFs) of the reaction time for different values of $T$ and reaction velocities for different bilayer thicknesses, $\lambda$. The PDFs are generated by a large number of Monte Carlo samples of the surrogates, and applying a kernel density estimation to the resulting ensemble. The curves indicate that as the temperature increases, the location of the peak shifts to the right, while its spread increases. This first trend is expected because more time from ignition is needed to reach higher temperature values, while the widening of the PDF reflects an increased variability at higher temperatures.

Figure 4.9 illustrates the first-order and the total sensitivity indices of the temperature and the reaction velocity to the uncertain inputs, respectively in uniform ignition and self-propagation experiments. The results indicate that in both cases, the quantities of interest exhibit higher sensitivity to the activation energy than
Figure 4.8: Probability density functions for the uniform ignition reaction time and self propagation reaction velocity. (a) Distributions for $T = 600$ K, 700 K, 800 K and 900 K are plotted. (b) Distributions for $\lambda = 64$ nm, 79 nm, 81 nm and 87 nm are plotted. The PDFs are obtained for the PC representation using kernel density estimation.
the pre-exponent. For the case of reaction times, one observes a noticeable difference between first-order and total sensitivity indices, highlighting the importance of mixed terms in the corresponding PC expansion. In addition, unlike the first-order index, the total sensitivity index exhibits a significant variation with time, reflecting an increase in the total sensitivity of the pre-exponent and a decrease in the total sensitivity of the activation energy. Thus, the impact of the pre-exponent on the temperature variability is higher for higher temperatures. On the other hand, for the self-propagation velocity, the first-order and total sensitivity indices are comparable, and reflect essentially the same values for all bilayers. The latter observation is consistent with the analysis in [Alawieh et al. (2011)], which revealed that the mean concentration versus temperature curves for different bilayers essentially collapse on each other. Thus, for self-propagation, varying the bilayer essentially leads to a scaling of the solution. Consequently, in light of the analysis in [Alawieh et al. (2011)], the present observation that the sensitivities to $D_0$ and $E_a$ in the self-propagation regime match for different bilayers, is in fact expected.

Figures 4.10(a–c) respectively show sample chains for $D_0$, $E_a$ and the hyperparameter, $\sigma_T^2$. The chains extend for over $10^5$ steps of the adaptive MCMC algorithm. In all cases, good mixing properties can be observed following the initial burn-in period, indicating that the statistics of the posterior are well captured; this is also confirmed through the decay of the autocorrelation of the signals (not shown). Figure 4.10(d) shows the joint posterior distribution of the pre-exponent and activation energy. The results reveal the existence of a distinct peak, surrounded by a thin, region of high probability. Thus, the measured temperature profile appears to be quite informative, leading to a highly localized posterior.

Consistent with the observations for the joint posterior, the marginal distributions of $D_0$ and $E_a$, plotted in Fig. 4.11, reflect the occurrence of sharp peaks. Estimates corresponding to the MAP, $D_0 = 7.436 \times 10^{-11}$ m$^2$/s and $E_a = 50.59$ kJ/mol, are in
Figure 4.9: First-order and total sensitivity as estimated using Sobol indices for, (a) ignition regime and (b) propagation regime.
Figure 4.10: Bayesian inference results based on data for uniform ignition. Posterior chain samples for (a) $D_0$, (b) $E_a$, and (c) $\sigma_T^2$ are illustrated. Frame (d) shows the joint posterior of $D_0$ and $E_a$.

good agreement with the results of the regression analysis. (Note that the values obtained from the regression analysis fall within the high probability region, and are close to but do not coincide with the MAP estimates.)

To verify the predictions, simulations are conducted using the MAP values of the parameters for a multilayered foil with $\lambda = 68$ nm, and the resulting temperature profiles are contrasted with the corresponding measurements. As can be observed in Fig. 4.12, there is an excellent agreement between the simulations and experimental
Figure 4.11: Marginal distribution of the posterior for, (a) $D_0$ and (b) $E_a$. The uniform priors and MAP estimates are also plotted. Results are obtained based on uniform ignition measurements.
data. Also note that the amplitude of the fluctuations seen in the experimental profiles compare favorably with the most likely value of $\sigma_T$. This provides further confidence in the validity of the predictions.

![Graph showing reaction time vs. temperature for $\lambda = 68$ nm. The MAP estimates for $D_0$ and $E_a$ are used.](image)

**Figure 4.12**: Measured and simulated reaction time versus temperature for the case of $\lambda = 68$ nm. The MAP estimates for $D_0$ and $E_a$ are used.

Results of the Bayesian inference of the Arrhenius parameters of the high temperature branch are reported in Figs. 4.13 and 4.14. Fig. 4.13 shows the marginal distributions of $D_0$ and $E_a$, as well as their joint posterior. Note that the extension of the tails of the posterior distributions, beyond the prior range in both cases is an artifact of the kernel density estimation. In contrast to the results discussed earlier, in the present case, the data does not lead to a tight localization of the posterior distribution, as observed for the low-temperature branch. Specifically, the marginal distributions appear to be bimodal, with broad distributions around the local maxima. Consistent with these observations, the joint posterior distribution reflects
multiple regions of high probability, indicating non-identifiability of an optimal pair of diffusion parameters in this regime, due to the limitation in the amount of experimental data and the variability in the available measurements. Nonetheless, MAP values can still be clearly determined, $D_0 \approx 3.2 \times 10^{-9} \text{ m}^2/\text{s}$ and $E_a = 56 \text{ kJ/mol}$. These values are remarkably close to those determined in the regression analysis. While the agreement is reassuring, it underscores potential limitations of simplified optimization approaches, which generally do not readily yield information regarding the uncertainties in the corresponding predictions.

In light of the variability of the velocity measurements, we rely on a posterior predictive check in order to verify the computations and to quantify the uncertainty in the predictive model. To this end, the MCMC samples are used to simultaneously evaluate the mean and standard deviation of the velocity predictions for each of the bilayers at which velocity measurements are collected. Results are shown in Fig. 4.14; plotted for comparison are the individual reaction velocity measurements. Clearly, in the present case, limitations in the data do not lead to sharp predictions. Specifically, significant uncertainty in the predictions remains, with deviations that are consistent with the variability in the underlying data.

4.4.3 Propagation velocity

In this section, we briefly analyze details of the velocity–bilayer curve for a wider range of bilayer thicknesses than available experimentally, and contrast the results with recent experiences gained with the Ni-Al system [Alawieh et al. (2013)]. In particular, the latter indicated that the velocity bilayer curve for Ni-Al multilayer exhibits an anomalous velocity plateau, similar to what is observed experimentally with the Zr-Al system [Fisher et al. (2013)]. The study in [Alawieh et al. (2013)] also suggested a thermal mechanism for the occurrence of this anomaly, and observed that for the Ni/Al system the plateau occurs at bilayers such that $w/\delta \approx 5\%$, where
Figure 4.13: (a) Marginal distribution of the posterior for $D_0$. (b) Marginal distribution of the posterior for $E_a$. The prior distributions and the MAP estimates are also shown. (c) Joint posterior for $D_0$ and $E_a$. Results are obtained based on measured velocity data.
Figure 4.14: Scatter plot of the experimental reaction velocity data for different bilayers. Also shown are mean reaction velocity estimates, obtained by sampling the Markov Chain. The error bars correspond to $\pm 2\sigma$, where $\sigma$ is the standard deviation.

$w$ is the premix width. Thus, we also examine whether similar trends occur using the presently developed model for equimolar Zr-Al nanolaminates.

To address these questions, computations were performed for different values of $w$ and for bilayer thicknesses ranging from 10 nm to 100 nm, using MAP of the Arrhenius parameters in both temperature branches. Note that $w$ can be greatly affected by deposition conditions and can be manipulated by low temperature annealing. Consequently, the range of measured premixed widths can be quite wide [Fisher et al. (2013)]. We have not attempted a systematic analysis of the impact of $w$ over the range of possible values, but have rather restricted our attention to two representative values, $w = 0.5$ nm and $w = 0.8$ nm. These values lie within a typical range
of experimentally-measured premixed widths, and are sufficiently separated so as to lead to significant variations within the range of bilayers considered.

The velocity predictions are plotted against the bilayer in Fig. 4.15, and curves are generated for both values of $w$. Consistent with well known trends for nanostructured multilayered systems, the results indicate that following a peak at small $\delta$, the velocity curve generally decays as $\delta$ increases. However, in the present case, and similar to experiences in [Alawieh et al. (2013)], a velocity plateau is also observed. For $w = 0.5$ nm, the plateau can be observed at about $\delta = 10$ nm, whereas for $w = 0.8$ nm it occurs near $\delta = 16$ nm. Thus, the velocity anomaly in the present velocity-bilayer curves has features that are quite similar to those observed in [Alawieh et al. (2013)] for the Ni-Al system. Specifically, the location of the anomaly shifts to higher bilayers as the premix width increases, and occurs at $w/\delta \approx 5\%$. While the present observations support the analysis in [Alawieh et al. (2013); Fisher et al. (2013)], additional experimental observations are clearly needed in order to test the validity of the thermal mechanism hypothesis, and characterize how the occurrence and properties of the velocity anomaly depend on the composition of the multilayered system.

4.5 Conclusions

A reaction model is developed for the equimolar Zr-Al multilayered foils, also referred to as nanolaminates. Experimental data pertaining to temperature measurements during homogeneous reactions, and reaction velocity measurements during self-propagation, are exploited in order to characterize atomic intermixing rates. The intermixing rates are described in terms of Arrhenius diffusivity correlations, which are first estimated using a regression analysis. A more elaborate Bayesian inference methodology is needed to examine the regression predictions, and to assess the impact of uncertainty in measurements as well as potential discrepancies between the
Figure 4.15: Reaction velocity versus bilayer thickness. Simulated results obtained for \( w = 0.5 \) nm and 0.8 nm are plotted. The insets highlight the occurrence of a plateau in the simulated velocity curves. The experimentally measured reaction velocities are also depicted for reference purposes.

model predictions and experimental data. The reaction model incorporating optimal values of the atomic mixing parameters is finally used to briefly examine the behavior of the reaction front velocity for a wide range of bilayer thicknesses. Based on the results and analysis presented in this work, the following conclusions can be drawn:

1. Diffusivity estimates from a regression analysis exhibit two distinct branches, marked by a sharp jump in atomic intermixing rates around the melting point of aluminum. The jump is attributed to an order of magnitude increase in the diffusivity pre-exponent.

2. Bayesian inference analysis of the Arrhenius parameters in the low temperature branch yields MAP estimates that are consistent with the regression analysis. The posterior exhibits a tight distribution around the MAP values.
3. The MAP estimates of the Arrhenius parameters of the high-temperature branch are in close agreement with optimal values determined using regression. However, in this case, the Bayesian inference indicates large uncertainty levels arising due to the scatter in the velocity data and the availability of data in a narrow range of bilayers.

4. The reaction velocity trends for the equimolar Zr-Al system are observed to be similar to the Ni-Al system. In particular, following a peak at small bilayers, the velocity generally decreases as the bilayer thickness increases. A velocity anomaly is also observed, in the form of a distinct velocity plateau whose location depends on the premix width.

The reduced continuum formulation developed in this chapter would be useful in simulating transient anaerobic reactions in the equimolar Zr-Al multilayers. A generalized formulation of the model including our prior understanding of the oxidation [Vohra et al. (2014b)] would help capture both, anaerobic and aerobic reaction regimes in the equimolar Zr-Al system. Work is currently underway to further examine the validity of the present correlations for the atomic mixing rates, refine the predictions as additional data is collected, and demonstrate the performance of the reaction model in transient multidimensional settings.
Optimal Design of Experiments

Arrhenius diffusion parameters associated with intermixing in the equimolar Zr-Al system were estimated using regression analysis and further refined using Bayesian inference in chapter 4. Estimates for the low temperature homogeneous mixing regime were found to be reasonably accurate. However, Bayesian inference of diffusion parameters in the self-propagating regime of the reaction resulted in large uncertainty levels [Vohra et al. (2014a)]. Traditional approach to mitigating the problem would involve extending the existing experimental database for reaction velocity to a much wider range of bilayers. In this chapter, we discuss an alternate approach and introduce the concept of optimal design of experiments (ODE) as a potential tool for enhancing the expected utility associated with a given set of experimental data. A generalized framework for ODE is discussed as follows.

Define experimental goals: This involves laying down a set of objectives for the experiment. If the data is to be used for parameter inference, the objective function would reflect the degree of uncertainty in the inferred value and maximizing the objective function would essentially lead to a minimized variance in estimates of the parameter. In other words, we aim to maximize the expected information gain using
the available data as well as the objective function. On the other hand, if the focus is on accuracy of simulations, the objective function would be based on error estimates between model predictions and experimental observations. A robust definition of the objective function should also account for the underlying costs and feasibility of proposed experiments.

**Identify design parameters:** Experimental conditions or design parameters can contribute significantly to model predictions. For the reaction models developed in chapter 4, the foil heating rate as well as the pulse duration is expected to have a significant impact on model predictions during homogeneous ignition. Similarly, for the self-propagating regime of the reaction, initiated by means of a thermal spark, important design considerations could be spark width and temperature as well as initial temperature of the foil.

**Appropriate selection of observables:** To reduce the computational effort in performing Bayesian inference of model parameters, a standard approach is to employ a model surrogate in lieu of the actual model as discussed earlier in chapter 4. The surrogate is a functional relationship between the experimental observable, also referred to as the quantity of interest (QoI) and uncertain model parameters. In order to construct a surrogate over a reasonably wide range of input uncertainties, a QoI with smooth variation is preferred. For instance during homogeneous foil ignition, a steep increase in foil temperature, \( O(10^5 \text{ K/s}) \), is observed due to large heat release rates during chemical mixing in reactive multilayers. Therefore, in chapter 4, a surrogate for the reaction time at a fixed temperature as opposed to temperature at a fixed time proved to be much more effective. Selection of suitable observables in the model is therefore critical to parameter inference.

**Model calibration:** Accuracy of simulations largely depends on the accuracy of model parameters. We thus seek to achieve tighter bounds on the posterior distributions of the physical parameters in the model by applying the framework for optimal
design to reaction models. It has been demonstrated that data from an optimized set of experiments typically enhances the accuracy of parameter inference [Huan and Marzouk (2013)].

The above sequence of steps provides a basis for an effective strategy for experimental design in the presence of uncertainty that could potentially maximize the utilization of the data in simulations. It can further reduce the underlying costs associated with experimentation and model simulations. In the following section, we discuss the application of the experimental design framework to the homogeneous reaction model, developed earlier in chapter 4. A surrogate for the ignition model is constructed using adaptive pseudo-spectral projection to perform forward propagation of uncertainty in model parameters and sensitivity analysis. We further estimate optimal design conditions i.e. foil heating rate and current pulse duration for the ignition experiment based on an expected value of utility. In order to validate the approach, we compare inferred estimates for the optimal design conditions with those corresponding to a set of useful or informative data for temperature evolution during homogeneous foil ignition.

5.1 Design of ignition in Zr-Al multilayered foils

In this section, we discuss an on-going effort, focused on implementing the optimal design framework to the homogeneous reaction model, developed earlier in chapter 4. The underlying objective is to enhance the expected information gain for the diffusion parameters corresponding to mixing due to homogeneous ignition of a nanolaminate foil with an equimolar composition of Zr and Al. Experimental set-up is illustrated in Fig. 5.1. Bayesian inference of Arrhenius diffusion parameters using data from such an optimized experiment is expected to improve the calibration of mixing rates in the Zr-Al system [Huan and Marzouk (2013)]. As a test case, we consider a set of informative experimental data and predict optimal design conditions
using the definition of expected utility as discussed further below. Comparison of predictions based on the expected utility with actual experimental conditions pertaining to informative data is used to validate the present approach.

\[ \text{Figure 5.1: Experimental set-up for homogeneous ignition of a multilayered foil [Fritz (2011)].} \]

\[ \text{5.1.1 Problem set-up} \]

\textbf{Physical Parameters:}
\[ D_0 \in [0.6 \times 10^{-10}, 1.20 \times 10^{-10}] \text{ m}^2/\text{s} \rightarrow \xi_1[-1, 1] \]
\[ E_a \in [47, 53] \text{ kJ/mol} \rightarrow \xi_2[-1, 1] \]

\textbf{Design Parameters:}
\[ dT/dt \in [2.22 \times 10^4, 3.22 \times 10^4] \text{ K/s} \rightarrow \xi_3[-1, 1] \]
\[ t_p \in [8, 12] \text{ ms} \rightarrow \xi_4[-1, 1] \]

We select suitable intervals for the diffusion parameters, \( D_0 \) and \( E_a \), using previous knowledge from regression analysis and Bayesian inference for the homogeneous
ignition regime as discussed in chapter 4. Considered range for the design parameters, foil heating rate \((dT/dt)\) and pulse duration \((t_p)\), based on prior experience is also provided. We thus have four stochastic dimensions, parameterized as \(\xi_1\), \(\xi_2\), \(\xi_3\) and \(\xi_4\) in the interval \([-1, 1]\). The next step involves the construction of a polynomial chaos surrogate. As the stochastic dimensions have increased from two to four, a fully tensored quadrature (used in chapter 4) is no longer feasible owing to inherent computational costs. Adaptive pseudo-spectral projection (aPSP) based on Smolyak tensorization [Smolyak (1963)] approach is used to construct the surrogate [Conrad and Marzouk (2013); Winokur et al. (2013)]. The aPSP is a useful technique for constructing a surrogate with large number of stochastic dimensions for complex physical models.

5.1.2 Adaptive pseudo-spectral projection

Polynomial chaos expansions (PCEs) are widely used for constructing a surrogate for a model output to predict and analyze its dependence on uncertainty in model parameters. PCE coefficients can be evaluated using numerical quadratures. However, a fully tensored (Gaussian) quadrature could entail large computational costs that increase significantly with the number of uncertain model parameters, referred to as the curse of dimensionality. To overcome this hurdle, Smolyak tensorization technique for construction of sparse grids can be used [Smolyak (1963)]. A useful implementation of the Smolyak algorithm involves a surrogate representation using a sum of projections on a fully tensored quadrature. The resulting construction referred to as Smolyak pseudo-spectral projection is devoid of internal aliasing. Recent efforts have focused on enhancing the efficiency of Smolyak pseudo-spectral projection by constructing it adaptively [Conrad and Marzouk (2013); Winokur et al. (2013)]. The adaptive pseudo-spectral projection (aPSP) is particularly useful for representing a model output that shows anisotropic dependence on its parameters. The adap-
tive algorithm is free from internal aliasing and focuses its efforts on optimizing the multi-index set for quadrature levels in the different stochastic dimensions using a refinement indicator value [Conrad and Marzouk (2013); Winokur et al. (2013)]. The idea here is to capture dominating terms in the projection to achieve reasonable accuracy with minimized computational effort.

For the homogeneous reaction model, we construct the surrogate using aPSP. Precisely, the ‘reaction time’ for attaining a specified foil temperature during homogeneous ignition is expressed in terms of the physical parameters, $D_0$ and $E_a$, and design parameters, $dT/dt$ and $t_p$. Note that the reaction time is set to zero at the instant when the current pulse is applied.

Fig. 5.2 illustrates 2D contours for ‘reaction time’ at foil temperature, $T = 900$ K. The design parameters are fixed in (a) and (c) whereas physical parameters are fixed in (b) and (d). Contours plotted using model simulations are in excellent agreement with those plotted using the surrogate. We thus have a faithful representation of the reaction times in the polynomial chaos surrogate, constructed using aPSP.

The surrogate is used for forward propagation of uncertainty in model parameters. Probability density functions (PDFs) at different foil temperatures are illustrated in Fig. 5.3. As expected, the peaks shift to the right as foil temperature increases.

The surrogate is further used to perform a global sensitivity analysis using Sobol indices. Fig. 5.4 shows stacked bar-graphs for the first-order and total sensitivity at 900 K. It can be inferred that model predictions are more sensitive to the activation energy ($E_a$) and heating rate ($dT/dt$) of the foil, followed by the diffusivity pre-exponent ($D_0$) and pulse duration ($t_p$). It is noteworthy that the first-order and total
Figure 5.2: Contours for reaction time using model simulations in (a) and (b); surrogate in (c) and (d).

Sensitivities are reasonably close to each other indicating that coupling or mixed terms are not significant in the polynomial representation of the 'reaction time' during homogeneous ignition. Adaptive construction of the polynomial surrogate, typically preferred in cases where model parameters are not strongly coupled, is therefore suitable for the present set-up [Conrad and Marzouk (2013)].
5.1.3 Numerical approximation of expected utility

Expected utility can be used to quantify the usefulness associated with a given set of experimental data. It is evaluated as the expected information gain in uncertain physical parameters $\mathbf{X}$ using Kullback-Leibler (KL) divergence from posterior to the prior as given below [Huan and Marzouk (2013)]:

$$U(d) = \mathbb{E}_{y|d}[D_{KL}(p(\mathbf{X}|y, d)\|p(\mathbf{X}))]$$

(5.1)

where $d$ corresponds to the set of design conditions. Discrepancy between the experimental observations ($y$) and model predictions ($M$) can be expressed using a Gaussian random variable, $\epsilon$ as follows:

$$y = M + \epsilon$$

(5.2)
where $\epsilon \sim \mathcal{N}(0, \sigma^2)$. Standard deviation ($\sigma$) is considered as one-tenth of the model predictions, $M$. Following the steps discussed in [Huan and Marzouk (2013)], we can numerically estimate the expected utility in Eq. 5.1 using the following set of equations:

$$
U(d) \approx \frac{1}{N_{out}} \sum_{i=1}^{N_{out}} \{ln[p(y^{(i)}|X^{(i)}, d)] - ln[p(y^{(i)}|d)]\} 
$$

where $X^{(i)}$ is drawn from the prior distribution of physical parameters and corresponding $y^{(i)}$ is estimated using Eq. 5.2. $N_{out}$ denotes the number of outer Monte Carlo samples. Inner Monte Carlo estimator for $p(y^{(i)}|d)$ is given as follows:
\[ p(y^{(i)}|d) \approx \frac{1}{N_{\text{in}}} \sum_{j=1}^{N_{\text{in}}^{i,j}} p(y^{(i)}|X^{(i,j)},d) \]  \hspace{1cm} (5.4)

where \( N_{\text{in}} \) denotes the number of inner Monte Carlo samples. The combination of Eqs. 5.3 and 5.4 is thus used to numerically estimate the expected utility using a two stage Monte Carlo integration. In order to reduce the computational cost, we use the same set of samples for estimating both inner and outer sum i.e. \( N_{\text{out}} = N_{\text{in}} \). Such a treatment reduces computations for a fixed \( d \) from \( \mathcal{O}(N_{\text{out}}N_{\text{in}}) \) to \( \mathcal{O}(N_{\text{out}}) \).

5.1.4 Application

As we have initialized the problem and constructed the surrogate earlier in this section, we shift our focus to optimizing the design conditions for enhanced information gain using numerical approximation for the expected utility given by Eq. 5.3. For the homogeneous reaction model, the surrogate at 900 K is used in Eqs. 5.3 and 5.4 to estimate the expected utility, \( U(d) \). We select \( N_{\text{out}} = N_{\text{in}} = 1000 \) in our computations. \( U(d) \) is evaluated at \( N_{d} \) design points on a 2D grid of size \( \sqrt{N_{d}} \times \sqrt{N_{d}} \).

Fig. 5.5(b) illustrates contours for \( U(d) \) at 900 K, \( \lambda = 72 \) nm using 1000 Monte Carlo samples and \( N_{d} = 400 \). The maximum utility corresponds to a pulse duration, \( t_{p} = 8 \) ms and foil heating rate of about \( 2.25 \times 10^{4} \) K/s. Foil temperature at the end of pulse duration can thus be evaluated as about 480 K. These estimates are found to be consistent with the set of useful experimental data considered for \( \lambda = 72 \) nm, illustrated in Fig. 5.5(a).

Utility contours were also plotted for samples drawn from the prior using Latin Hypercube Sampling (LHS) at \( N_{d} = 100 \) and 400 design points, as shown in Fig. 5.6. Location of the optimal design point, \( P \) is consistent with the case of Monte Carlo sampling. This confirms that the inference of optimal design criteria is not affected by the choice of sampling approach.
Figure 5.5: (a) Foil surface temperature evolution during homogeneous ignition for $\lambda = 72 \text{ nm}$. (b) Contours for expected utility, $U(d)$ evaluated using 1000 Monte Carlo samples and 400 design points at $T = 900 \text{ K}$ and $\lambda = 72 \text{ nm}$. Point ‘P’ corresponds to maximum utility.
Heating Rate, $dT/dt$ (K/s)

Pulse Duration, $t_p$ (ms)

$N_{out} = N_{in} = 1000, N_d = 100, T = 900$ K

(a)

$N_{out} = N_{in} = 1000, N_d = 400, T = 900$ K

(b)

**Figure 5.6**: Contours for expected utility, $U(d)$ evaluated using Latin Hypercube Sampling at (a) $N_d = 100$ and (b) $N_d = 400$. 

109
5.1.5 Future work

• Perform Bayesian inference of diffusion parameters at optimal and non-optimal design points to further validate the existence of a strong correlation between optimal design criteria and tighter bounds on posterior distributions.

• Sequential experimental design to enable continued optimization of experimental conditions for a series of experiments, by using the posterior at one stage as the prior for the following stage. The approach is referred to as recursive or Greedy.

• Implementation of the experimental design framework to the distributed reaction model, developed in chapter 4 for simulating self-propagating reactions. Experimental data for a wide range of bilayers may not be sufficient for accurate model calibration since it typically leads to the scaling of the solution, as discussed in chapter 4. The implementation could help determine the optimal design criteria and thus improve the accuracy of parameter inference in this case.
This work aimed at developing and calibrating reaction models for multilayered, nano-structured composite materials. In particular, attention was focused on the equimolar Ni-Al and Zr-Al systems. Simulations and experimental measurements of temperature evolution and reaction front velocity during formation reactions in reactive multilayers were used to estimate regime specific Arrhenius diffusivity branches. Specifically, we developed a computational model to characterize mixing rates in a Ni-Al bilayer for an intermediate temperature regime ($\approx 720$ K - $860$ K) based on nanocalorimetry measurements. For the equimolar Zr-Al system, we developed a reduced reaction model and calibrated mixing rates below and above the melting of aluminum. Furthermore, we developed a simplified model to understand the phenomena of oxidation responsible for an extended duration of heat release in the equimolar Zr-Al system which makes it suitable for potential bio-agent defeat applications.

In chapter 2, we focused on calibrating solid state intermixing rates during formation reactions in a Ni-Al bilayer. A thermal model was developed to simulate the evolution of the surface temperature of a nanocalorimeter stack. The model accounts for Joule heating, chemical mixing in the bilayer, and radiation heat loss. Tempera-
ture measurements were used to estimate the Arrhenius diffusion parameters associated with intermixing in the Ni-Al bilayer. Melting effects due to aluminum were not considered and the estimates were restricted to a regime dominated by intermetallic formation in the bilayer. Precisely, we inferred consistent diffusivity estimates for two different bilayers, $\lambda = 50$ nm and $60$ nm in a temperature range, $720$ K - $860$ K. We showed that model predictions (based on inferred diffusivity estimates) for temperature as well as the rate of heat release due to chemical mixing agree quite favorably with the experimental measurements. Data from the nanocalorimetry experiments thus proved to be a useful resource for calibrating solid state mixing rates in a Ni-Al bilayer.

In chapter 3, we focused on developing a computational model for oxidation of the equimolar Zr-Al multilayers. The simplified computational model is based on an energy conservation during oxidation of a Zr-Al nanolaminate foil and accounts for the rate of heat release due to oxidation of the intermetallic, rate of thermal mass uptake of ambient oxygen and the rate of heat loss due to radiation. In order to determine the oxidation heat release rate, we focused our attention on identifying the governing mechanism for the zirconia (oxide) layer growth. For this purpose, we compared oxide layer growth rates for a diffusion controlled growth and a surface-reaction controlled growth. Kinetic models developed for the two growth mechanisms are coupled with energy conservation of the foil. We observed that the oxide layer growth is initially controlled by reaction kinetics at the interface of the intermetallic and the zirconia layer (surface-reaction control) followed by a transition to a growth regime controlled by the diffusion of oxygen through the zirconia layer (diffusion control). Model predictions, sensitive to the foil surface emissivity value, were validated for surface temperature evolution during oxidation and thickness of the oxide layer. Furthermore, it was demonstrated that for the considered set of conditions, the gas phase diffusion of oxygen to the foil surface does not play a limiting role in
the growth of the oxide layer.

In chapter 4, we developed a reaction model for formation in the Zr-Al multilayers. For the purpose of calibrating the atomic diffusivity in the multilayers, we considered two mixing regimes separated by the melting of Al. Surface temperature measurements during homogeneous reaction in the multilayers was utilized to calibrate the diffusivity in the low temperature regime. For the high temperature regime, we exploited reaction velocity measurements of the self-propagating reactions in the equimolar Zr-Al nanolaminate foils with varying bilayer thicknesses. Considering the presence of uncertainty in experimental measurements, limitations of the reaction model, and potential discrepancies between the model and experiments; we did not restrict our efforts to regression analysis involving least squares minimization of the error between model predictions and measurements. In fact, we obtained full posterior distributions of the diffusion parameters using Bayesian inference. A tight bound was observed on the posterior distributions for the homogeneous ignition regime, leading to reasonably accurate diffusivity estimates. On the other hand, for the self-propagating regime of the reaction, the posteriors indicate relatively large levels of uncertainty. Model predictions were found to be much more sensitive to the activation energy as compared to the pre-exponent of diffusivity in both regimes.

In chapter 5, we developed a framework for an optimal design of experiments focused on enhancing the utility of the experimental data for calibrating reaction models. The approach is based on maximizing the expected utility, quantified in terms of Kullback-Leibler (KL) divergence from the posterior to the prior. We applied this methodology to determine optimal experimental (design) conditions for homogeneous ignition in a nanolaminate foil comprising equimolar Zr-Al multilayers. In addition to the diffusion parameters, the experimental conditions i.e. foil heating rate and pulse duration were also considered to be uncertain. To mitigate computational costs associated with the evaluation of the expected utility as well
as Bayesian inference of the diffusion parameters, we constructed a surrogate for ‘reaction time’ (required to achieve a given foil temperature during ignition) using the adaptive Smolyak pseudo-spectral projection approach. The surrogate was used to perform a forward propagation of uncertainty in the model parameters as well as sensitivity analysis of the ignition model. Results of the sensitivity analysis indicated that model predictions are predominantly sensitive to the activation energy and the foil heating rate, followed by the pre-exponent of diffusivity and the pulse duration. We demonstrated applications of the optimal design framework by determining the optimal design conditions for homogeneous ignition of an equimolar Zr-Al nanolaminate foil. Results were found to be consistent with those corresponding to a set of informative experimental data for foil temperature during homogeneous ignition.
Bibliography


Berger, J. (1985), Statistical decision theory and Bayesian analysis, Springer.


119


Biography

Manav Vohra was born on November 18, 1985 in Kanpur, India. He pursued his bachelors in Mechanical Engineering at Indian School of Mines (August 2006 - May 2010) and was awarded the University Gold Medal for best academic performance in his class. He started graduate studies at The Johns Hopkins University in Baltimore, Maryland from August 2010 and completed his masters degree in Mechanical Engineering in May 2012. At Hopkins, he worked as a research assistant with a focus on developing reaction models for the Ni-Al multilayered systems under the supervision of Dr. Omar M. Knio. He was awarded a fellowship by the NSF to attend a Pan American conference in Costa Rica in recognition for his work on quantitative assessment of diffusion parameters for solid state reactions in a Ni-Al bilayer using nanocalorimetry which later got published in Journal of Applied Physics.

After completing his masters, Manav moved with his supervisor and continued his research endeavors for a PhD at Duke. Among other accolades, he was awarded the Abhijit Mahato fellowship following recommendation from the Director of Graduate Studies, MEMS in December 2013. During his doctoral work, he published three peer reviewed articles in prestigious journals. His research interests include numerical modeling, uncertainty quantification, optimization, and transport phenomena.