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A generalized reduced model of uniform and self-propagating reactions in reactive nanolaminates

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ABSTRACT

A multiscale inference analysis is conducted in order to infer intermixing rates prevailing during different reaction regimes in Ni/Al nanolaminates. The analysis combines the results of molecular dynamics (MD) simulations, used in conjunction with a mixing measure theory to characterize intermixing rates under adiabatic conditions. When incorporated into reduced reaction models, however, information extracted from MD computations leads to front propagation velocities that conflict with experimental observations, and the discrepancies indicate that our MD simulations over-estimate the atomic intermixing rates. Thus, using only insights gained from MD computations, a generalized diffusivity law is developed that exhibits a sharp rise near the melting temperature of Al. By calibrating the intermixing rates at high temperatures from experimental observations of self-propagating fronts, and inferring the intermixing rates at low and intermediate temperatures from ignition and nanocalorimetry experiments, the dependence of the diffusivity on temperature is inferred in a suitably wide temperature range. Using this generalized diffusivity law, one obtains a generalized reduced model that, for the first time, enables us to reproduce measurements of low-temperature ignition, homogeneous reactions at intermediate temperatures, as well as the dependence of the velocity of self-propagating reaction fronts on microstructural parameters.

1. Introduction

Recent studies of multilayered materials have been motivated from both a fundamental science perspective and by potential applications. The former have particularly aimed at taking advantage of the fact that these materials offer a unique setting for analyzing phase transformations under rapid heating and large compositional gradients [1–12]. The latter have spanned various areas including joining, brazing, sealing, and ignition of secondary reactions [13–28].

Most commonly manufactured are binary systems [1,29–35,25], in which the layers alternate between elements or alloys that mix exothermically. A variety of fabrication techniques can be used to generate materials with layering in the nanoscale or microscale range, including physical vapor deposition [1,25,35,36], and mechanical formation [37–40].

Sustained reactions can be initiated in reactive multilayers via a localized stimulus (e.g. electric or laser discharge), resulting in self-propagating fronts that propagate away from the ignition source. When the individual layers are thin (i.e. in the range of tens of nanometers), large front velocities are frequently observed. For instance, for the Ni/Al system, self-propagating reaction fronts with speeds exceeding 10 m/s are frequently observed [41,35,25].

Numerous computational studies have aimed at characterizing the velocity of self-propagating reaction fronts in multilayered materials, and their dependence on microstructure and composition. In [42,43], a simplified continuum analytical model was implemented that assumes constant thermophysical properties and that the heat released by the reaction is deposited near the reaction temperature. Subsequent computational studies have aimed at systematically relaxing the simplifications of the analytical model, and have incorporated more elaborate models to account for property variation, phase change effects, heat losses, as well as the dependence of heat release on composition [44–54].

Continuum approaches generally rely on a simplified, phenomenological description of the intermixing process, namely using a scalar composition field, and for the dependence of the heat released on composition. The evolution of the composition (or conserved scalar) is typically described in terms of a Fickian (or quasi-Fickian) process, governed by a temperature-dependent diffusivity. The latter is assumed to follow an Arrhenius law, and the pre-exponent and activation energy parameters that appear in the

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corresponding expression, are usually calibrated as best fits based on experimental measurements of the velocity of self-propagating fronts [42,43]. With this approach, computational models have proven to be effective at capturing the dependence of the front velocity on composition and microstructural parameters.

However, recent experiments on low-temperature ignition and the subsequent evolution of homogeneous reactions in multilayered materials have revealed that the prevailing rates of intermixing are not consistent with those predicted by the global Arrhenius fit of the atomic diffusivity. These investigations include the measurements of Fritz [55], who examined the ignition of multilayer foils using electric currents and hot plates, as well as nanocalorimetry experiments [56,57] that have focused on characterizing the evolution of an essentially homogeneous reaction within a single bilayer. Consequently, it appears that the calibration of the atomic diffusivity based on velocity observations would not lead to a diffusivity law that is valid throughout the temperature range characterizing the reaction.

The present work is motivated by a desire to address the above limitation. Specifically, the questions we aim to address are: Would it be possible to combine the information gained from low-temperature ignition experiments and from nanocalorimetry measurements in order to refine the phenomenological description of intermixing rates in continuum models? Provided this is possible, would models using the resulting diffusivity law be able to simultaneously capture the evolution of homogeneous reactions at low and intermediate temperatures, as well as the velocity of self-propagating fronts?

Our approach towards these objectives is based on combining all sources of available information. As discussed in Section 2.3, we focus our attention on the reduced model formalism introduced by Salloum and Knio [49–51] and recently extended by Alawieh et al. [52]. To guide the model development, molecular dynamics computations are performed in order to gain insight into the dependence of diffusivity on temperature. As discussed in Section 3, our approach for the microscale investigation is based on generalizing the mixing measure formalism introduced by Rizzi et al. [58] for isothermal systems to adiabatic conditions. Analysis of the MD computations is discussed in Section 4. Guided by the results of the MD analysis, the construction and implementation of a new composite diffusivity law based on information gained from macroscale experimental measurements are discussed in Section 5. Major results, ramifications, and conclusions from Sections 4 and 5 are finally discussed in Section 6.

2. Continuum and reduced macroscale formulations

2.1. Multilayer configuration

Unless otherwise noted, we consider nanolaminates consisting of geometrically flat, alternating layers of Ni/Al with a 1:1 atomic ratio. The layers are assumed to be initially separated by a thin premixed NiAl (product) region, but are otherwise compositionally pure. The thickness of each bilayer is $\lambda = 2(1+\gamma)\delta$ where $2(\delta - w)$ is the thickness of an Al layer, $2\gamma(\delta - w)$ is the thickness of a Ni layer,

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

is the ratio of the atomic densities of Al and Ni respectively, ρ^{Al} and ρ^{Ni} are the densities of Al and Ni respectively, and M^{Al} and M^{Ni} are the corresponding atomic weights. The thickness of the premixed region is $4w$. A representative schematic of a single Ni/Al bilayer is shown in Fig. 1.

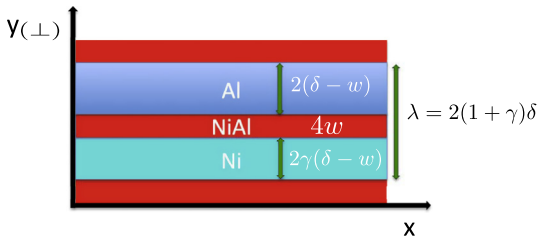

Fig. 1. 2D schematic of an unreacted (1:1) Ni/Al bilayer separated by a thin NiAl premix region. The total thickness of the bilayer is $\lambda = 2(1+\gamma)\delta$, where the Al, Ni, and premix layers have individual thicknesses of $2(\delta - w)$, $2\gamma(\delta - w)$, and $4w$, respectively.

2.2. Continuum approach

In the continuum approach of Besnoin et al. [48], the processes of atomic mixing and heat release in the multilayer are described in terms of a coupled system of partial differential equations expressing the evolution of conserved scalar and enthalpy fields:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D(T)\nabla C), \tag{1}$$

$$\bar{\rho}\frac{\partial h}{\partial t} = -\nabla \cdot \boldsymbol{q} + \frac{\partial Q}{\partial t}. \tag{2}$$

The dimensionless conserved scalar, C, hereafter referred to as "concentration", quantifies the degree of atomic mixing; it varies between $-1 \leqslant C \leqslant 1$, and is defined such that $C = 1$ is pure Al, $C = -1$ is pure Ni, and $C = 0$ is pure NiAl. As mentioned in the introduction, the atomic diffusivity, D, is assumed to obey a single Arrhenius law in the entire temperature range characterizing the reaction, namely according to:

$$D(T) = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where T is temperature, R is the universal gas constant, $D_0 = 2.18 \times 10^{-6}$ m^2/s is the pre-exponent, and $E_a = 137$ kJ/mol is the activation energy. As discussed in the introduction, the values of D_0 and E_a are obtained as best fits based on experimental measurements of the velocity of axially-propagating fronts [42].

In Eq. (2), h denotes the specific enthalpy, $\bar{\rho}$ is the mean density, and $\boldsymbol{q}$ is the conductive heat flux. Q is the heat released by the reaction and is assumed to exhibit a quadratic dependence on concentration [45,48]:

$$Q(C) = -\Delta H_{rxn} C^2 \tag{4}$$

where ΔH_{rxn} is the (negatively signed) change of enthalpy (reaction enthalpy). As discussed in [48], the temperature field, T, can be recovered from the enthalpy field, h, through a complex relationship that involves the heats of fusion of the reactants and products.

2.3. Reduced model formalism

Salloum and Knio [50] developed a reduced reaction formalism that aims at overcoming the stiffness of the coupled system of Eqs. (1), (2), thus resulting in a computational model that is substantially more efficient than that based on the continuum approach. The development is based on a boundary layer analysis, that enables one to replace the partial differential equation in Eq. (1) with an ordinary differential equation for a normalized "layer age,"

$$\tau \equiv \int_0^t \frac{D(T)}{\delta^2}\, dt', \tag{5}$$

and to replace the differential energy Eq. (2) with its volume-or region-averaged form. Consequently, the system of equations governing the evolution of the reaction is expressed as: