Exploring the reaction mechanism in self-propagating Al/Ni multilayers by adding inert material

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Abstract

We present a new class of reactive materials termed “inert-mediated reactive multilayers” (IMRMs) that use inert material to decouple the effects of chemistry and maximum temperature in a reactive multilayer. Important considerations in the selection of composition and thickness for reactive and inert material in an IMRM are detailed. We then present the results from a specific set of IMRM samples that we fabricated using 23-nm-bilayer 1:1 Al:Ni reactive sections and 2:3 Cu:Ni inert sections. In these samples we observe a systematic reduction of heats of reaction, maximum reaction temperatures, and reaction propagation velocities as the volume fraction of reactive material is reduced. At the same time, metrics sensitive to the reaction mechanism and products indicate that there is little if any cross-contamination between inert and reactive material in any of the samples. This indicates that the IMRM samples all undergo the same net reaction ($\text{Al/Ni} \rightarrow \text{AlNi}$) but at a range of different flame temperatures (roughly 1950 K to 1300 K). Using existing theoretical models for the relationship between flame temperature and propagation velocity, we analyze the experimental data to obtain the activation energy for the mixing process and find that this value varies significantly as the maximum reaction temperature changes. At high reaction temperatures we observe a very low activation energy (26 kJ/mol) which suggests diffusion of Ni in molten Al is the rate controlling mixing mechanism in agreement with the conclusions of other studies focused on un-mediated Al/Ni reactive multilayers. However, as the reaction temperature decreases the activation energy appears to shift to much larger values implying a change in the reaction mechanism. We postulate that this shift indicates that solid products are able to form earlier in the reaction at these temperatures, impeding atomic diffusion and intermixing.

Keywords: aluminum; nickel; reactive multilayers; self-propagating; propagation velocity

1. Introduction

Interfacial reactions can, in principle, occur anywhere two different miscible materials are in contact. They are especially relevant in nanoscale multilayers, since these structures exhibit unusually high ratios of interfacial area to volume. In the particular case that the interfacial reaction is highly exothermic, these are termed “reactive multilayers” [1] and a phenomenon known as a self-propagating reaction can be observed where the heat released by local mixing is sufficient to heat the adjacent material and produce a self-sustaining reaction front that moves through the sample with a characteristic velocity. Practically, reactive multilayers are of interest as heat sources for bonding [2,3], thermal batteries [4], and ignitors [5,6]. Scientifically, self-propagating reactions present a unique opportunity to investigate the processes that control atomic mixing and phase formation at the extremes of concentration gradient and heating rate. Such scientific investigations feed back into practical applications by enabling improved predictions of performance over a range of operating conditions and by identifying ways that performance can be tuned for specific applications.

One of the most-studied reactive multilayer systems is Al/Ni. Al and Ni are readily available, relatively inexpensive, and have a fairly large enthalpy of reaction (1381 J/g [7]). Al/Ni multilayers have been fabricated using a range of physical vapor deposition techniques as well as by mechanical processing, and have been investigated using differential scanning calorimetry (DSC) [8,9], time-resolved x-ray diffraction [10,11], and time-resolved transmission electron microscopy [12], as well as in many theoretical studies [13–18]. The references here are only a small sampling of the available literature - the system is generally very well characterized.

Despite this extensive body of work, several questions remain. Perhaps the most interesting is, “What physical processes control the reaction rate in self-propagating Al/Ni

multilayers?” A second, related question might be, “What role, if any, do intermetallic phases play in determining the reaction rate?” In order to answer these questions directly we would need to be able to resolve atomic-scale processes occurring at the reacting interface on extremely short timescales (< 100 ns). Existing instruments are capable of satisfying either the spatial or temporal resolution demands, but so far no instrument can meet both requirements simultaneously.

Instead, the best available experimental results regarding this question have been obtained by quenching self-propagating reactions. This relaxes the time-resolution constraint, allowing the use of conventional transmission electron microscopy to examine the interfaces of the partially reacted sample in high-resolution. Based on quenched microstructures it has generally been proposed that mixing into an Al-rich molten phase is the most likely rate-controlling process during self-propagating Al/Ni reactions [17–19]. However, this conclusion cannot be confirmed without experimental observation in the self-propagating state.

Another way to circumvent experimental limitations is to use molecular dynamics (MD) simulations. Simulations allow observation of the reacting interface in granular detail and at arbitrary temperatures. MD simulations of the Al/Ni reaction have been performed in a number of different thermodynamic ensembles, most notably the isobaric-adiabatic (NPH) and isobaric-isothermal (NPT). Studies using the NPH ensemble are most analogous to real experiments. In these [13–15], researchers observe a rapid temperature rise and the melting of Al relatively early in the reaction, similar to what is observed in time-resolved experiments [10–12]. Isothermal (NPT) simulations are less realistic but easier to analyze. Xu *et al.* conducted isothermal simulations of the Al/Ni interfacial reaction at multiple temperatures ranging from 2000 K (near the adiabatic flame temperature of 1:1 Al/Ni) down to 1300 K, and observed that different

mechanisms controlled the mixing rate depending on the simulation temperature [16]. Detailed explorations at even lower temperatures (1000 K) have also been performed [17,18]. These results are suggestive but again call for experimental validation, especially given that the MD potentials used [20–22] are known to be incapable of reproducing the Al-rich Al/Ni intermetallic phases.

Here, we seek an experimental assessment of the rate-controlling processes in self-propagating Al/Ni reactive multilayers that does not require quenching or atomic-scale resolution of the reacting interface. In general, one of the easiest ways to experimentally characterize a reaction mechanism is to observe how the reaction rate varies as a function of temperature. This variation can be summarized in the activation energy, a macroscopic parameter that is often strongly correlated with the underlying microscopic processes at work. The primary challenge in applying this principle to Al/Ni reactive multilayers is that in a traditional multilayer the reaction temperature cannot be altered in a controlled fashion. In this work, we introduce a new class of reactive materials intended to address this need. Dubbed “inert-mediated reactive multilayers” (IMRMs), these materials incorporate an inert material to suppress the heating rate and maximum temperature without altering the chemistry of the reaction. The adiabatic flame temperature of an IMRM can be tuned continuously over a wide range (in this work we demonstrate temperature reductions as large as ~ 650 K) simply by varying the ratio of reactive material to inert material in the system. By using flame speed as a macroscopic indicator of the underlying interfacial reaction kinetics, this new class of materials can provide needed experimental support for conclusions derived from molecular dynamics and quenching studies.

In the following, we begin by laying out the basic design principles for IMRMs in general and for Al/Ni in particular. We then present the results obtained, assess them in light of the

design requirements, and apply an analytical model for flame speed in reactive laminates to give scientific significance to the trends observed. We conclude by using these results to construct a picture of potential reaction mechanisms over the temperature range 1250 – 1950 K, supported by previous experimental and theoretical results.

2. Design of Inert-Mediated Reactive Multilayers

A schematic diagram of the IMRM design is shown in Fig. 1. It consists of alternating sections of reactive material and inert material with characteristic section thicknesses *SRM* and *SIM*. Multilayer sections possess a second level of periodicity characterized by the “bilayer spacing”. A bilayer is the characteristic repeat unit of a two-component multilayer and consists of one layer of each material. The bilayer spacing is the sum of these layer thicknesses. In designing the IMRMs for this work, the principle design considerations were (1) what materials to use in each section, (2) how those materials should be arranged within the section, and (3) how thick the sections should be.

2.1. Section Composition

The sections below outline the general considerations to be made when selecting materials for the reactive and inert sections, and how those decisions were made for the samples fabricated in this work.

2.1.1. Reactive Material

The main requirements for the reactive component of an IMRM are a composition that is of scientific interest and a small bilayer spacing that will yield a high propagation velocity. The latter requirement is motivated by the expectation that quickly propagating sections will be able to accommodate the largest temperature suppression before quenching. The Al/Ni system is extensively well characterized and presents outstanding scientific questions of interest.

Consulting a chart of flame speed versus bilayer spacing for 1:1 Al:Ni (e.g., [23]), a bilayer spacing of 23 nm yields a velocity very close to the maximum (~ 13 m/s). Consequently, the reactive component in this work was Al/Ni reactive multilayers with a 23 nm bilayer and a 1:1 molar ratio (approximately 3Al:2Ni by volume).

2.1.2. Inert Material

The ideal inert material undergoes no chemical reactions upon heating that would add or subtract from the energy output of the sample, and does not chemically mix with the material in the reactive sections so as to alter the products formed. It also has high volumetric heat capacity and high thermal conductivity to maximize the temperature reduction per volume and promote thermal uniformity across the sample. These requirements suggest a metallic inert material, which would have the added benefit of being easily incorporated into the physical vapor deposition processes that are typically used for multilayer fabrication. Finally, to conduct the activation energy analysis described in Sec. 5.1 it is helpful if all samples produced have the same net thermal diffusivity in the propagation direction. The easiest way to achieve this is by matching the in-plane thermal conductivity of the inert material to the in-plane thermal conductivity of the chosen reactive material. In general this is impossible to achieve using any single metallic element. Instead, an alloy or multilayer structure of multiple metals can be used where it is possible to tune the ratio of components as needed to adjust the thermal diffusivity.

We selected a multilayer structure of Cu and Ni as the inert material. Cu and Ni form a nearly ideal solution [24] so their enthalpy of mixing is negligible, and since Ni is already a component of the reactive material it presents no contamination concerns. Cu does have the potential to react with Al to form a variety of intermetallic compounds [25], but this risk is easily minimized by ensuring that Ni layers are always in contact at the interface between reactive and inert sections and minimizing the number of such interfaces. Cu has a very high thermal

conductivity ($4.0 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$) while that of Ni is quite low ($0.189 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$), so an appropriate mixture of the two can match the thermal diffusivity of a range of reactive material compositions. The in-plane thermal conductivity of 1:1 Al:Ni multilayers is approximately $0.456 \text{ cm}^2 \text{ s}^{-1}$, calculated using bulk, room-temperature values for pure Ni and Al. This can be matched using a mixture of 2Cu:3Ni by volume (an atomic ratio of 0.38Cu:0.62Ni). A multilayer was chosen as opposed to an alloy in order to more effectively control stress in the deposited structures. For example, after observing undesirably large residual stresses in IMRM 5 which had 28-nm-bilayer inert multilayers we were able to reduce residual stress significantly by increasing the bilayer spacing in the inert sections for the remaining samples.

2.2. Section Thicknesses

The section thicknesses are identified as *SRM* and *SIM* in Fig. 1. We identified two main concerns in deciding how large they should be:

1. Avoiding chemical contamination of the reactive material by the inert material.
2. Maintaining approximately uniform temperature through the thickness of the sample during reaction.

Chemical contamination is undesirable because it defeats the stated purpose of the IMRM approach: to change nothing about the reaction except the temperature at which it occurs. Contamination is best prevented by selecting inert materials that have relatively low reaction enthalpy with the reactive materials and then arranging the inert and reactive material so as to minimize their opportunity to interact. This is favored by thicker sections that minimize the number of interfaces between the inert and reactive materials in the structure.

Thermal uniformity is important in order to avoid reaction decoupling, a phenomenon observed in previous work that considered “dual-bilayer” Al/Ni multilayers [23]. Dual-bilayer

samples are reactive multilayers that feature two different bilayer spacings, one large and one small, arranged in sections with a characteristic thickness. That work found that if the thicknesses of the small bilayer (rapidly reacting) and large bilayer (slowly reacting) sections were small, the reaction in the two sections would couple and propagate with a velocity corresponding to the volume average bilayer spacing of the composite. However, if the section thicknesses became too large the reactions would decouple and each section would propagate at its natural speed. This argues for generally smaller sections.

In order to satisfy both requirements a balance between large and small section thickness is needed. We took the approach of first calculating a reasonable value for the maximum or “critical” section thickness based on thermal uniformity considerations, and then using the largest section thicknesses possible within that limit.

2.2.1. Derivation of Critical Section Thickness

The temperature will always vary somewhat between the reactive and the inert sections because only the reactive sections generate heat. The goal here is to derive a concise expression that estimates the temperature variation between reactive and inert layers given reasonable material properties. This expression can then be used to compute a “critical section thickness” based on the maximum allowable temperature variation. To simplify the analysis we assume that the section thicknesses are equal ($S_{RM}=S_{IM}=L$) and that the foil contains an infinite number of sections. This will enable a simple periodic solution. We assume that the heat capacities of inert and reactive material are equal and invariant with temperature, and finally we consider the problem in one dimension only (through the thickness of the IMRM). Fig. 2(a) shows the simplified picture of an IMRM based on these assumptions.

Heat flow in an adiabatic reacting system can be described by a thermal balance equation

$$T = \alpha \nabla^2 T + Q_{rxn} / \rho C_p \quad (1)$$

where T is the temperature in one or more spatial dimensions and time, α is the thermal diffusivity, ∇^2 is the Laplace operator, Q_{rxn} is the rate of heat release from the reaction, and ρC_p is the volumetric heat capacity. Writing Eq. (1) explicitly for the one-dimensional case,

$$T_{z,t} = \alpha_{\perp} \partial^2 T_{z,t} / \partial z^2 + Q_{rxn,z} / \rho C_p \quad (2)$$

where $\alpha_{\perp}$ is the out-of-plane thermal diffusivity (perpendicular to the layering) and we have explicitly written $Q_{rxn,z}$ as varying spatially because heat generation in an IMRM is heterogeneous.

The largest spatial variation in temperature will occur when the reaction rate in the reactive sections is at its highest since this represents the largest instantaneous power that must be dissipated into the inert material. We denote this power as a constant Q_{max} and apply it only in the reactive sections to produce the function $Q_{rxn,z}$ as depicted in Fig. 2(b). In a real sample this reaction rate is only achieved for a short time, but by applying it indefinitely we obtain a worst-case estimate of the temperature variation.

Since the heat release from reaction does not vary in time we know that after a sufficiently long time the spatially varying component of the solution to Eq. (2) will be in steady state. We thus propose a solution to Eq. (2) that is the superposition of two contributions, one varying only in time and the other varying only in position:

$$T_{z,t} = T_{tt} + T_{zz} \quad (3)$$

We are primarily interested in the spatial variation component T_{zz} , but it is easiest to first find T_{tt} . In order to account for the constant input power the time-varying component must just be the spatial average of temperature. The reaction is the only energetic contribution, and this comes from just half of the layers, so the reaction power averaged over the entire sample is $Q_{avg}=Q_{max}/2$ and the spatially averaged heating rate is $T_{avg}=Q_{avg}/\rho C_p$. This is easily integrated to obtain the time-varying component of Eq. (3):

$$T_{tt}=Q_{avg}\rho C_p t \quad (4)$$

Plugging this into Eq. (3) and that result into Eq. (2), we find

$$\partial^2 T_{zz} / \partial z^2 = -1/\alpha \perp \rho C_p Q_{rxnz} - Q_{avg} \quad (5)$$

The effect of subtracting Q_{avg} from Q_{rxnz} is to produce a square wave with period $2L$ and amplitude T_{avg} as shown in Fig. 2(c). A square wave with period $2L$ and unity amplitude can be represented as a Fourier series of the form

$$f_x = 4\pi n = 1, 3, 5, \dots \infty 1/n \sin n\pi x/L \quad (6)$$

Taking just the largest term in this sum ($n=1$), we can approximate $Q_{rxnz} - Q_{avg}$ as

$$Q_{rxnz} - Q_{avg} \approx Q_{avg} 4\pi \sin \pi z/L \quad (7)$$

Plugging this into Eq. (5) and integrating to solve for the spatial variation term T_{zz} , we obtain

$$T_{zz} = Q_{avg} \alpha \perp \rho C_p 4L 2\pi^3 \sin \pi z/L \quad (8)$$

This predicts a sinusoidal variation in temperature between sections of reactive and inert material as depicted schematically in Fig. 2(d). The peak-to-valley distance is the maximum temperature difference we seek, given by doubling the amplitude in Eq. (8):

$$\Delta T_{\max} = Q_{\max} \alpha \perp \rho C_p 4 L^2 \pi^3 \quad (9)$$

We see that increasing the layer thickness or the reaction rate in the reactive sections will increase the maximum temperature difference, while increasing the thermal diffusivity will reduce it. It is useful to replace the maximum reaction rate with the maximum heating rate for a purely reactive sample,

$$T_{\max RM} = Q_{\max} \rho C_p \quad (10)$$

This value is much easier to obtain than $Q_{\max}$ because it can be measured directly in experiments on unmediated reactive multilayers. Finally, given an allowable temperature deviation $\Delta T_{\max \text{crit}}$ we can solve for the critical section thickness

$$L_{\text{crit}} = \Delta T_{\max \text{crit}} T_{\max RM} \alpha \perp \pi^3 4 \quad (11)$$

Eq. (11) is applied to a specific materials system by substituting appropriate values for the maximum heating rate and thermal diffusivity. For the AlNi/CuNi IMRMs described in this work we performed our calculations using a value of 10^6 K/s for the maximum heating rate of pure Al/Ni and an out-of-plane thermal diffusivity of $0.081 \text{ cm}^2 \cdot \text{s}^{-1}$ calculated for 2Cu:3Ni multilayers. Specifying a 1 K difference between sections as the maximum allowable, we obtained a value of $L_{\text{crit}} = 7.9 \text{ } \mu\text{m}$. This is reasonably large on the scale of thin films so that we only needed a few sections to produce foils that were thick enough to be free-standing.

2.2.2. Comparison to Knepper et al.

Knepper *et al.* [23] developed an empirical expression for the critical section thickness in dual-bilayer foils as described in the introduction to Sec. 2.2. The critical section thickness in this context was the largest thickness that each section could be without observing decoupling of the reaction between sections, and the formula they derived was

$$L_{\text{crit}} = A \alpha // \Delta v \quad (12)$$

where $A = 1.3 \pm 0.3$ is an empirical constant and Δv is the difference between the propagation velocities of the two sections in isolation. We can apply this formula to IMRMs by taking $\Delta v = v_{RM}$ since the inert layers cannot propagate on their own. For our particular system, we take $\alpha // = 0.67 \text{ cm}^2 \cdot \text{s}^{-1}$ for Al/Ni multilayers (this is the value used in [23] to derive Eq. (12)) and $v_{RM} \approx 13 \text{ m} \cdot \text{s}^{-1}$ for a 23 nm bilayer and obtain $L_{\text{crit}} = 6.7 \mu\text{m} \pm 1.5 \mu\text{m}$. This is in reasonable agreement with the result of the theoretical analysis in Sec. 2.2.1.

2.3. Final Design

The design details for all samples are given in Table 1. We fabricated a total of five IMRM foils ranging from 66% to 90% reactive material, as well as a pure Al/Ni foil (“Control”) and a pure Cu/Ni foil (“Inert”). The total sample thickness and number of sections was held constant (18 μm and five, respectively), while the section thicknesses were varied based on the desired volume fraction of reactive material. The maximum section thickness was set at 5.4 μm , well within the limit calculated.

3. Experimental

3.1. Fabrication

The samples tested were deposited onto polished brass substrates using DC magnetron sputtering from Al (1100 alloy [99 wt % Al, 0.87 wt % (Si, Fe), 0.12 wt % Cu]), Ni/V (93 wt % Ni, 7 wt % V), and Cu (OFHC grade [99.99 wt % Cu]) targets. Vanadium is added to the Ni target to render it nonmagnetic. Multilayers are produced by mounting the substrates on a cooled rotating carousel and passing them over alternating targets. By controlling the sputtering power and rotation rate, a wide range of component ratios and bilayer spacings can be obtained.

Sputtering was performed in a vacuum chamber evacuated below 3×10^{-6} Torr and then backfilled to 1.3 mTorr with Ar (99.999 % pure).

The samples were patterned into strips approximately 1.3 cm wide by taping the substrates prior to deposition. After sputtering, the brass substrates were removed from the vacuum chamber, the tape was removed, and the patterned material was peeled from the substrate to produce free-standing foils. The first layer of the first reactive section and the last layer of the last reactive section were aluminum so that the foils were terminated by aluminum on both sides.

3.2. Characterization

Heat flow and total enthalpy of reaction measurements were carried out using a power-compensated differential scanning calorimeter (Perkin-Elmer DSC 8000). The specific enthalpy of reaction was computed by integrating the heat flow data over the temperature range 380 K – 763 K and dividing by the sample mass. At least three DSC measurements were performed on each sample tested. The experimental volume fraction of reactive material, ϕ_{RMexp} , was calculated from enthalpy data by first calculating the mass fraction of reactive material as

$$w_{RMexp} = \frac{\Delta H_i}{\Delta H_{Control}} \quad (13)$$

where ΔH_i is the total enthalpy of the sample in question and $\Delta H_{Control}$ is the total enthalpy of the purely reactive “Control” sample, and then converting this mass fraction to a volume fraction using the densities of the inert (ρ_{IM}) and reactive (ρ_{RM}) components:

$$\phi_{RMexp} = \frac{w_{RMexp} \rho_{RM}}{w_{RMexp} \rho_{RM} + 1 - w_{RMexp} \rho_{IM}} \quad (14)$$

This approach was selected (as opposed to measuring the volume fraction directly using cross-sectional microscopy) because (1) it effectively samples a much larger volume of material than

can feasibly be done using microscopy, and (2) the result obtained is directly related to the relative heat output which is of most importance for IMRMs. However, we did verify that the results obtained using the two approaches are comparable.

Structural analysis was carried out using x-ray diffraction (Philips X'Pert) in a θ -2 θ configuration with Cu-K α radiation. Cross-sectional images were produced by mounting samples vertically in epoxy, polishing with a succession of abrasive papers and suspensions, and imaging the results in a scanning electron microscope (Tescan MIRA3).

For investigations of propagating reactions, samples were placed between two glass slides with one end protruding outside the glass. The exothermic reaction was initiated by applying an electric spark from a DC power supply (MPJA 14602PS) to the exposed end of the foil. The reaction then propagated into the part of the foil between the glass slides where characterization was conducted.

Temperature measurements were performed using a one-color (single wavelength) pyrometer (Kleiber KG740-LO) covering the temperature range 773 K – 2773 K. This instrument works by measuring the intensity of radiation from the sample at a single wavelength and inferring the sample temperature based on an assumed value for the emissivity of the sample. While the emissivity of our samples is not precisely known and may change during reaction, we found the consistency of results from this instrument to be superior to those obtained using a two-color (ratio) pyrometer [11] for these samples. The data from the pyrometer was analyzed assuming an emissivity of $\epsilon=0.10$. This is a reasonable value for polished Al (the deposited foils all had Al on the exterior) and matches the value used in previous work with a comparable instrument [26]. The flame temperature was taken as the maximum value of the temperature vs. time curve, and at least ten measurements were averaged for each sample tested.

High-speed videos of reaction propagation under glass were made using a high-speed visible-light camera (NAC Memrecam HX-6) equipped with a 150mm macro lens (Sigma) and mounted vertically. Frame rates varied between 5000 and 20,000 fps depending on the speed of the reaction studied. The position of the reaction front was extracted from the high-speed videos using the open-source program Tracker (<http://physlets.org/tracker/>), and the front velocity was obtained from a linear regression of the front position vs. time. At least three videos were analyzed for each sample tested.

The maximum reaction temperature was increased for some samples by raising the initial temperature of the reaction above ambient. For these experiments, two glass slides were placed on a small ceramic heater (Watlow ULTRAMIC) and allowed to equilibrate at the set temperature. To conduct an experiment, the test foil was placed between the glass slides on the hot plate and reacted within 10 – 20 seconds. This procedure was adopted to minimize variations in the initial temperature between experiments. The maximum initial temperature was limited to 473 K in order to minimize the amount of mixing that could occur prior to reaction initiation.

We found testing under glass slides to be more repeatable because (1) some samples were warped due to residual stresses and needed to be held flat, (2) many samples showed a tendency to curl unpredictably during reaction if unconstrained, and (3) the samples tended to oxidize when hot. For the Control sample studied in this work we compared tests under glass to tests in air and found no significant difference in the propagation velocity (12.5 ± 0.1 m/s under glass and 12.6 ± 0.1 m/s in air). The maximum temperature for foils tested in air was higher, but this is likely due to oxidation that occurs following passage of the reaction front. Fig. 3(a) shows a comparison of pyrometry plots under both conditions, and both traces are nominally identical up

until the end of rapid heating (presumed completion of the intermetallic reaction). After this point, heating continues for foils tested in air but more slowly than before. The additional heating is most likely due to oxidation as suggested by the surface oxidation that is visible in Fig. 3(b). Since this study was specifically concerned with the connection between the propagation velocity and the temperature of the flame front, we focused on samples reacted between glass slides to exclude any effects from oxidation.

4. Experimental Results

Experimental results for the volume fraction of reactive material, the maximum temperature, and the propagation velocity are summarized in Table 2. The design values of ϕRM in Table 1 match the measured values of ϕRM_{exp} in Table 2 to within 4% for all samples studied. As anticipated, the flame temperature of the reaction scales with ϕRM , ranging from 1962 ± 24 K for a fully reactive foil to 1303 ± 33 K for a 66% reactive foil. Propagation velocities scale similarly, ranging from 12.5 ± 0.1 m/s for the fully reactive foil to 0.73 ± 0.04 m/s for a 66% reactive foil.

Differential scanning calorimetry traces for all samples listed in Table 1 are shown in Fig. 4. The shapes of the heat flow traces are very sensitive to the chemistry and bilayer spacing of the reactive sections of the sample. Looking at the Control sample, we see a characteristic profile consisting of a sharp first exothermic peak around 493 K, a very broad middle peak around 533 K, and a somewhat broad third peak around 623 K. This profile agrees with those observed previously for sputtered Al/Ni at very small bilayers [23], and is reproduced across all samples implying that the same reactions are occurring in all of them. The sample-to-sample variations in the magnitude and position of the latter two peaks are most likely due to small variations in the bilayer spacing and/or chemistry of the reactive component between

depositions. There are more systematic trends in the total area under the curves and the position of the first peak. The total area decreases with decreasing mass fraction of reactive material as we would expect, while the temperature of the first peak increases. We believe the temperature increase can be attributed to stresses caused by the coefficient of thermal expansion (CTE) mismatch between Al/Ni and Cu/Ni. Al/Ni has a higher CTE than Cu/Ni, so at any temperature above the deposition temperature (~ 348 K) the Al/Ni sections will be in compression and the Cu/Ni sections will be in tension. Atomic diffusion tends to be inhibited by compression [27], an effect which would delay intermixing and product growth and shift the exothermic peaks to higher temperatures. The magnitude of the compressive stress should scale inversely with the thickness ratio of reactive to inert material, shifting the peaks to higher temperatures as the volume fraction of reactive material is reduced, thus matching the observed behavior. While interesting, this effect is unlikely to be relevant in the self-propagating regime since most of the reaction occurs above the melting point of Al.

A cross-sectional scanning electron micrograph of the hottest IMRM sample (IMRM 1) after reaction is shown in Fig. 5. Clearly the bulk organization of the sample into inert and reactive sections remains intact through the reaction. While detailed analysis is difficult using SEM, we examined high-magnification images of the inert/reactive interface (inset) and concluded that any interaction between the sections appears to be limited to a distance of ~ 200 nm. To explore this in more detail, we performed x-ray diffraction (XRD) on the as-reacted samples. The inert material introduces Cu and an excess of Ni into the system, so the presence of Al-Cu or Ni-rich Al-Ni intermetallic phases in the IMRM reaction products would indicate possible chemical contamination of the reactive material. We observed no evidence of these phases in any of the samples tested. A post-reaction XRD scan of IMRM 1 is shown in Fig. 6.

One set of peaks in Fig. 6 is due to B2 AlNi (the reaction product of 1:1 Al:Ni multilayers) and the other set of peaks comes from an fcc phase with a lattice parameter of approximately 0.356 nm. This is intermediate between that of Cu and Ni, suggesting that these peaks arise from a solid solution of Cu and Ni formed when the Cu/Ni multilayers are heated by the reaction. If unintended products are present, we conclude that they are in such small volume fractions as to be undetectable by XRD.

The maximum reaction (“flame”) temperatures are plotted in Fig. 7 versus the experimental volume fraction of reactive material. The data correspond well with predictions, suggesting that the temperatures measured are accurate and lending support to our choice of emissivity for pyrometry analysis. Flame speed is plotted versus flame temperature in Fig. 8. Velocities generally increase with temperature. One sample (indicated by an open symbol in Fig. 8) exhibited a phenomenon known as unsteady propagation [28] where rather than a smooth flame front aligned perpendicular to the propagation direction we observe a multitude of transverse bands that propagate parallel to the front. This is typical of samples propagating close to the point of extinction. Following other recent investigations into this phenomenon [28,29], the value reported is the “bulk propagation rate” perpendicular to the direction of band propagation.

5. Analysis

The maximum temperatures and flame speeds for IMRM samples decrease systematically with increasing inert volume fraction, while DSC data indicate that all samples have nominally the same bilayer spacing and chemistry within the reactive sections. X-ray diffraction and cross-sectional microscopy both indicate that the inert material is functioning as intended and is not contaminating the reactive material. This validates our design considerations and confirms that the general concept of inert-mediated reactive multilayers – decoupling the reaction temperature

and velocity from the sample chemistry and bilayer spacing – is sound. We now turn to the potential scientific application of these materials. Continuum modeling results [30] suggest that the majority (>90%) of mixing in self-propagating reactions occurs in the upper third of the temperature range traversed. If this is true, we expect that varying the maximum temperature of the reaction should have a significant impact on the mechanism and kinetics of mixing. Since mixing is a critical factor in determining the propagation velocity, we should be able to detect changes in the mixing kinetics by examining how the velocity scales with flame temperature.

To do this, we draw on theories that predict how the velocity should scale with flame temperature assuming a mixing mechanism with simple Arrhenius scaling. By applying these theories to velocity versus temperature data, we can estimate the activation energy for the mixing process as a function of temperature. This has the benefit of requiring far fewer assumptions about materials properties than the traditional approach of fitting a curve to velocity versus bilayer data (e.g., [31]).

5.1. Analysis Approach

Several models [31–33] have been developed to describe the propagation velocity of laminar reactive materials. They are derived by solving a boundary value problem for the coupled thermal and atomic diffusion equations. All of the models feature the activation energy for atomic diffusion in a similar role to that occupied by the activation energy for chemical reaction in gas-phase combustion [33], and all predict that velocity should have an inverse dependence on the bilayer spacing. Aldushin and Khaikin [32] presented the earliest model reaching this conclusion, assuming that the rate-controlling mixing process was interdiffusion through a product phase at the interface. Armstrong [33] obtained a similar result by assuming mixing into a homogenous solution. Mann *et al.* [31] extended the Armstrong analysis to non-ideal multilayers, enabling predictions of the velocity “fall off” that is observed experimentally at

small bilayers in samples with initial intermixing. Any of these models would be sufficient for our analysis. Here we choose to neglect the effects of intermixing and start with Armstrong's result [33] for a quadratic dependence of heat release on concentration:

$$\nu_f^2 = 6\lambda^2 R T_f^2 A \delta^2 \exp(-E/T_f) \quad (15)$$

Here ν_f is the flame speed, λ the thermal diffusivity, R the gas constant, T_f the flame temperature, A the Arrhenius prefactor, E the Arrhenius activation energy, δ one-quarter of the bilayer spacing, and T_0 the initial temperature. Of these parameters R is a physical constant, λ and δ are constant by design in IMRMs (see Sec. 2), and A and E are constant for a given mixing mode. Moving non-constant terms to the left-hand side and taking the natural logarithm,

$$\ln \nu_f^2 T_f - T_0 K^* T_f^2 = \ln 6\lambda^2 R A K^* \delta^2 E - E/T_f \quad (16)$$

Here K^* is a reference value with dimensions of T^{-2} that we add when taking the natural logarithm to make its argument non-dimensional. From Eq. (16) we can obtain the activation energy as

$$d \ln \nu_f^2 T_f - T_0 K^* T_f^2 / d(1/T_f) = -E/R \quad (17)$$

That is, a plot of $\ln \nu_f^2 T_f - T_0 K^* T_f^2$ versus $1/T_f$ (all experimentally measured quantities) should have a slope proportional to the activation energy for the mixing process. Some may note the similarity of Eq. (17) to the so-called ‘‘Zeldovich method’’ [34,35] which was derived for gaseous flames but has also been applied to condensed-phase reactions. That theory implies a simpler relationship but has in common the factor of ν_f^2 :

$$d \ln \nu_f^2 / d(1/T_f) = -E/R \quad (18)$$

The reason for the similarity is no doubt the parallel form of the equations for gaseous and condensed-phase flames as observed by Armstrong [33]. Here we use Eq. (17) because it was specifically derived for laminar materials.

Before proceeding we note that the analytical models described, and the analysis approach derived from them, are oversimplifications. They assume composition-independent diffusivities, temperature-independent materials properties, and homogeneous mixing from reactants to products. While in-depth investigations invariably find that the actual situation is more complex, there is also substantial data showing that at the very high heating rates observed during self-propagating reactions the assumption of mixing characterized by a single Arrhenius activation energy is reasonably accurate [14–16]. More philosophically, we note that ascribing an “activation energy” to a process is simply an attempt to quantify the extent to which it depends on temperature. Given that temperature is an important parameter in reactive material performance, an Arrhenius activation energy is a valuable tool whether it ultimately refers to diffusion in a solid, diffusion in a liquid, interfacial detachment, or (as is most likely here) some combination of these processes.

5.2. Analysis Results

Taking the data obtained from the IMRM samples (Table 2) and calculating quantities as prescribed in Eq. (17) with $K^* = 1 \text{ K}\cdot\text{s}^{-2}\cdot\text{m}^{-2}$, we obtain the plot shown in Fig. 9. While the data show considerable scatter, there is a clear negative slope as predicted (the activation energy is a positive quantity). However, the data are not well approximated by a straight line as we would expect for a single controlling process. Instead, the best fit is a curve as shown by the dashed line, implying perhaps multiple rate-controlling processes operating in different regions of the temperature range. To study this result in more detail we divided the data into three

temperature regimes and approximated the best-fit curve using three straight lines as shown in Fig. 9. Each line segment gives a different activation energy. Next, we explore these values and propose possible rate-controlling mechanisms to explain them.

5.2.1. High Temperature Regime (1650 – 1950 K)

The activation energy obtained from the measured data in the high temperature range is $26.0 \text{ kJ/mol} \pm 0.37 \text{ kJ/mol}$. Du *et al.* [36] obtained an identical value in experiments where they measured the diffusivity of Ni in molten Al. This agreement is strong support for the hypothesis that at high temperatures (typical of relatively unmediated Al/Ni reactive multilayers) the rate-limiting process is diffusion of Ni in molten Al. It also suggests that at these temperatures the solid product (AlNi) either does not form until relatively late in the reaction or does not present a barrier to diffusion, since diffusion through AlNi should give rise to a much larger activation energy [37,38]. This result is consistent with *in situ* experiments [11,12] which have established the presence of molten Al in the reaction fronts of Al/Ni multilayers. Molecular dynamics simulations also support this conclusion. Adiabatic (NPH) simulations have found that aluminum melts early in the reaction and mixing occurs primarily into the melt [13–15]. Xu *et al.* [16] used isothermal (NPT) simulations to assess the dominant transport mechanism in Al/Ni multilayers and its thermal sensitivity between 1700 K and 2000 K, and concluded that the rate-controlling process was diffusion of Ni in molten Al with an activation energy of 35.77 kJ/mol.

5.2.2. Intermediate Temperature Regime (1450 – 1650 K)

In this temperature regime a linear fit to the data yields an activation energy of $103.8 \text{ kJ/mol} \pm 1.47 \text{ kJ/mol}$. This value is too large to be due to diffusion of Ni in liquid Al and too small to be due to solid-state diffusion of Ni through an intermetallic product. More likely processes are the detachment of Ni atoms from the Ni lattice (or an Al-Ni solid solution), or diffusion through said solution. Based on the minimal modeling data available at these

temperatures [16] a detachment process (i.e. interface-limited dissolution) seems most likely. Xu *et al.* [16] found that in the temperature range 1300 K – 1600 K dissolution of Ni into molten Al was the rate-limiting process. They analyzed mixing in this regime using the simple dissolution model of Noyes and Whitney [39] and obtained an activation energy of 101 kJ/mol. This result is a good fit to both the activation energy obtained and the temperature range considered here. While the Noyes and Whitney model has been interpreted as applying to both transport-limited [40] and interface-limited [41] kinetics, in the present context the latter interpretation is clearly preferable since the activation energy is higher than that expected for diffusion in the liquid.

5.2.3. Low Temperature Regime (1250 – 1450 K)

In the low temperature regime we observe the most aggressive scaling of velocity with temperature, characterized by an activation energy of 376.6 kJ/mol $\pm$ 5.47 kJ/mol. This is significantly larger than the other two values reported and, if accurate, can only reasonably be attributed to solid-state diffusion. The aluminum layer is still molten in this regime, but a solid intermetallic phase growing at the Ni/molten Al interface could present a significant barrier to diffusion. Given the activation energy obtained and the temperatures considered, the most likely phase is B2 AlNi. Experimental values of activation energy for diffusion of Ni in AlNi at high temperatures vary considerably depending on the precise composition of the AlNi phase but generally fall in the range 200 – 360 kJ/mol [37,38]. The intermetallic phase that forms at these low reaction temperatures could also be the closely related Al₃Ni₂ structure. This phase has never been observed experimentally during a self-propagating reaction due to its relatively low decomposition temperature (1406 K [42]), but it may be stable during self-propagation in the most mediated samples because of the reduced flame temperature. Diffusion data on this phase is unavailable but would likely be comparable to that for AlNi given their structural similarity.

There is substantial modeling support for the formation of solid phases at the Ni/Al interface at moderate temperatures. NPT molecular dynamics simulations at relatively low temperatures (800 – 1000 K) [13,17] clearly show the formation of solid AlNi at the Ni/Al interface. The Al_3Ni_2 phase has not been observed, but this phase is known to be unstable for the family of MD potentials [20–22] used in all simulations described. Xu *et al.* [16] also observed the temporary formation of AlNi intermetallic at the interface in isothermal simulations from 1300 – 1600 K. While they were unable to extract an activation energy for diffusion through this phase, their data clearly showed a substantial decrease in the mixing rate associated with its presence, consistent with our results.

It is worth noting that the activation energy reported for this low-temperature regime is particularly sensitive to a single data point, IMRM 5. Since this sample is also the only one that exhibits unsteady propagation it is reasonable to ask whether any conclusions should be drawn from it at all. There are two perspectives on this. On one hand, as we have noted the analysis approach we are using relies on an already simplified model for uniform flame propagation and unsteady propagation is undeniably an even more complex phenomenon. This argues against inclusion since the assumptions made are unlikely to hold for unsteady propagation. On the other hand, it can be argued that regardless of the specifics of the propagation process (uniform versus unsteady) the bulk propagation rate will still be governed by the balance between atomic and thermal diffusion. In this case its scaling should remain relevant even when the propagation becomes unsteady. At the moment it is impossible to say for sure which of these perspectives is more accurate. The latter view is more consistent with the limited experimental data available [28,29], but additional work would be needed to verify this for the Al/Ni system. Because of this uncertainty we have included the IMRM 5 data point in our analysis but also mark it as a

potential outlier. If it were to be ignored, the best interpretation of our results would be to discard the low-temperature regime entirely since the results in the other two temperature ranges are sufficient to describe the rest of the data.

6. Discussion

In Fig. 10, we present schematic drawings of the processes described in Sec. 5.2 and how they may relate to the microstructure of reactants and products within a single bilayer during the reaction. We conclude our analysis by considering why it might be reasonable to expect such variations in the rate-controlling process as the reaction temperature changes.

As already noted, if diffusion in the liquid is to be rate-controlling at the highest temperatures it seems likely that AlNi is either forming only very late in the reaction or is forming in such a way as to not present a barrier to mixing. There are several reasons why AlNi might not form promptly when the flame temperature is high. First, the melting temperature of AlNi is 1911 K [42] and consequently the driving force for nucleation of AlNi is quite low at the temperatures considered. High flame temperatures also correlate with high heating rates and relatively steep concentration gradients which may further reduce the thermodynamic driving force for nucleating a new phase [43]. The combination of these factors may delay the formation of AlNi until the majority of the mixing has occurred. This is illustrated in Fig. 10(a) which depicts mixing dominated by diffusion of Ni into liquid Al with no product phase present.

As flame temperatures decrease, the factors described above that inhibit nucleation become less relevant and it seems more likely that AlNi could nucleate relatively early in the reaction. For this reason Fig. 10(b) includes the possibility of solid product grains at the interface even if they are not directly implicated in the mixing process at these temperatures. The suggested location and morphology of these grains is guided by the results of MD simulations and cross-sectional microscopy on quenched reactions [17–19] showing

hemispherical AlNi grains that have evidently nucleated at the Ni surface and grown into the Al. Such a morphology might be expected because the solid Ni surface presents a low-energy nucleation site and growth into the liquid is preferred because of easier atomic transport.

Whether or not a solid phase is present, our analysis suggests that the dissolution process is still rate-limiting at intermediate temperatures (1450 K – 1650 K). In Sec. 5.2.2, we attributed the measured activation energy specifically to the interface-limited process of detaching Ni atoms from the lattice. While this hypothesis is impossible to prove with the data currently available, it seems reasonable if we note that most of the high temperature regime (1650 K – 1950 K) is above the melting temperature of Ni (1706 K) while the entire intermediate temperature regime is below it. The rate of detachment from the lattice is directly related to the energy required to remove an atom from it [41], a value which will drop significantly as we approach the melting temperature. This observation would explain why at high temperatures we appear to have diffusion-limited mixing while at the intermediate temperatures the detachment process is dominant.

Finally, in the lowest temperature regime analyzed (1250 K – 1450 K) we propose that solid product has most likely formed and constitutes an obstacle to mixing as illustrated in Fig. 10(c). Our rationale for depicting the product layer as fine-grained and continuous as opposed to large-grained and discrete as in Fig. 10(b) lies in the expected balance between nucleation rate and growth rate. The nucleation rate for a given phase tends to increase as temperature is reduced because the driving force for nucleation scales with undercooling. In contrast, the growth rate tends to decrease as temperature is reduced because the atomic transport required for growth is thermally activated. For this reason one expects a smaller number of larger grains when the temperature is higher and a larger number of smaller grains when the temperature is

lower. We suggest that in the low temperature regime the nucleation rate is sufficiently high compared to the growth rate that after a small amount of mixing a large number of product nuclei form at the Ni/Al interface and rapidly impinge on each other, effectively forcing all subsequent mixing to occur via solid-state diffusion through them. Contrast this with the picture of the intermediate temperature regime (Fig. 10(b)) which shows larger discrete grains due to the higher temperature, with areas for detachment and dissolution between the grains.

We conclude by briefly comparing our assertions to the results of other recent experimental studies on the Al/Ni reaction, namely those of Rogachev and co-workers obtained by quenching of self-propagating reactions [17–19]. These studies have consistently implicated mixing into an Al-rich melt as the rate-controlling process for propagation. This conclusion was first reached based solely on cross-sectional microscopy [19], where the morphology of product AlNi grains in quenched samples (discontinuous at the interface as in Fig. 10(b)) suggested that mixing was driven by continuous dissolution of Ni into the melt. Subsequent work comparing quenched microstructures to MD simulations [17,18] reinforced this conclusion. The discussion in [19] notes that the dissolution process might be transport or interface limited. Our results indicate that transport-limited dissolution is most likely at the flame temperature of unmediated Al/Ni, but we also suggest a transition to interface-limited dissolution at intermediate flame temperatures. Thus our results can be seen as consistent with quenching experiments for both intermediate and high flame temperatures.

7. Conclusions

In this paper we described a new class of reactive materials termed “inert-mediated reactive multilayers” (IMRMs) that use inert material to decouple the effects of chemistry and maximum temperature in a reactive multilayer. We presented general considerations for the choice of reactive and inert materials and their section thicknesses, and then detailed the results

obtained from IMRMs with reactive sections composed of 23-nm-bilayer 1:1 Al:Ni and inert sections composed of 2:3 Cu:Ni. We evaluated these materials under both slow heating and self-propagating conditions. With slow heating (differential scanning calorimetry) we observed predictable scaling of the specific heat output and consistent reaction peaks across all samples. Self-propagating reactions were ignited in all samples – the coldest at a volume fraction of 66% reactive and a maximum temperature 650 K below that for an unmediated foil. X-ray diffraction and cross-sectional electron microscopy on self-propagated samples confirmed that there is little, if any, interaction between the reactive material and the inert material during the self-propagating reactions, even at the highest temperatures. Both the flame temperature and propagation velocity decreased as the volume fraction of reactive material in the samples was reduced. A detailed analysis of the temperature and velocity data yielded experimental values for the activation energies of the processes controlling mixing, which were then used to propose possible reaction mechanisms as a function of temperature. The results are found to be in general agreement with those from recent molecular dynamics and quenching studies.

This work presents several intriguing possibilities for future studies. First, the results for the Al/Ni system could be expanded, either by extending the approach to lower temperatures or performing more tests over a narrower temperature range. This might be done to explore specific mechanisms or the steady-to-unsteady propagation transition in more detail. One could also apply the IMRM concept to other reactive multilayer chemistries (particularly those that we might expect to have significantly different mixing mechanisms, e.g. Ni/Zr) to see how their temperature-dependent activation energies differ. Finally, time-resolved characterization techniques like *in situ* x-ray diffraction could be applied to identify more precisely when product or other intermediate phases form. In summary, we conclude that inert-mediated reactive

multilayers provide a flexible experimental approach for those wishing to investigate reactive multilayers in the self-propagating state without employing quenching.

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Figure Captions

Fig. 1. A cross-sectional schematic of the generic design for an inert-mediated reactive multilayer (IMRM) showing alternating sections of reactive material (dark/light banded) and inert material (gray) with corresponding section thicknesses SRM and SIM . The multilayer bilayer spacing is also labeled.

Fig. 2. Graphical outline of the procedure used to derive the maximum temperature difference ΔT_{max} between inert and reactive sections as described in Sec. 2.2.1. A simplified IMRM structure is considered (a). The plots depict the spatially varying rate of heat release $Q_{rxn,z}$ (b), the spatially varying effective heat release relative to the average (c), and the steady-state component of the solution to the heat equation (d).

Fig. 3. Comparison of reactions performed under a glass slide versus in air. In (a), temperature versus time traces for a Control sample reacted under glass and in air show that samples reacted in air stay hot significantly longer. In (b), a visual comparison of Control samples reacted in different ways suggests that surface oxidation is the origin of the extended reaction in air.

Fig. 4. Differential scanning calorimetry curves for the samples tested in this work. The curves are labeled with the sample ID and, in parentheses, the *mass fraction* of reactive material in each (area under the curve is proportional to the total energy output per gram of sample).

Fig. 5. Backscattered scanning electron micrograph of sample IMRM 1 after reaction. The boundaries between sections remain intact, with the reactive material appearing dark and the inert material appearing light.

Fig. 6. X-ray diffraction scan for the hottest IMRM sample (IMRM 1) after reaction in the self-propagating mode. The splitting of AlNi peaks observed at higher scattering angles is due to the Cu-K α 2 line at 1.544 Å.

Fig. 7. Plot of maximum temperature versus the volume fraction of reactive material. Samples that were preheated prior to reaction are not included (see Table 2). The dashed line is the predicted adiabatic reaction temperature assuming no phase changes, an initial temperature of 293 K, an adiabatic temperature change of 1660 K for a 100% reactive sample, and the bulk, room temperature heat capacities for Al, Ni, and Cu. The solid line is an improved prediction obtained when we incorporate the fact that the inert sections should melt around 1578 K.

Fig. 8. Plot of flame speed versus flame temperature. The open data point indicates that the sample (IMRM 5) exhibited unsteady propagation.

Fig. 9. Arrhenius plot for the samples tested in this work, analyzed using Eq. (17). Vertical error bars indicate the uncertainty obtained by propagating uncertainties in velocity and temperature through the calculation. The open data point indicates that the sample (IMRM 5) exhibited unsteady propagation. The dashed curve is a best-fit with the form $y = y_0 + A \exp(-x/t)$ and coefficients $y_0 = -2.70632$, $A = -0.08677$, $x_0 = 5.14643 \times 10^{-4}$, and $t = 6.42372 \times 10^{-5}$ ($R^2 = 0.764$). To obtain activation energies we approximate this curve using three straight line segments as shown.

Fig. 10. Proposed dominant mixing mechanisms based on the activation energies obtained in Fig. 9 and subsequent discussion in Sec. 5.2.

Table 1 Design table for the materials fabricated and tested in this work. Properties shown are the total thickness (t_{tot}), the volume fraction of reactive material (ϕ_{RM}), the number of each type of section, the section thicknesses S_{RM} and S_{IM} , and the bilayer spacing in each section (λ).

Sample ID	t_{tot} (μm)	ϕ_{RM}	Reactive Sections (1:1 Al:Ni)			Inert Sections (2:3 Cu:Ni)		
			#	S_{RM} (μm)	λ (nm)	#	S_{IM} (μm)	λ (nm)
Control	18	1.00	1	18	23	-		
IMRM 1		0.90	3	5.4		2	0.9	75
IMRM 2		0.82		4.92			1.62	106
IMRM 3		0.75		4.5			2.25	75
IMRM 4		0.70		4.2			2.7	75
IMRM 5		0.66		4.0			3.0	28
Inert	10	0	-			1	10	107

Table 2

Table 2 Experimental results for the tested foils, showing the experimentally measured volume fraction of reactive material calculated from DSC heats (ϕ_{RM}^{exp}), the maximum temperature (T_{max}), and the propagation velocity (v). Values obtained by pre-heating are indicated by a non-zero value of T_{plate} – samples with no T_{plate} value were reacted at room temperature. Uncertainties are one standard deviation on either side of the mean.

Sample ID	ϕ_{RM}^{exp}	T_{plate} (K)	T_{max} (K)	v (m/s)
Control	1.00	-	1962 ± 24	12.5 ± 0.1
IMRM 1	0.89 ± 0.003	473	1756 ± 13	13.1 ± 0.03
IMRM 1	0.89 ± 0.003	-	1647 ± 12	9.77 ± 0.1
IMRM 2	0.78 ± 0.004	473	1623 ± 18	9.02 ± 0.2
IMRM 2	0.78 ± 0.004	-	1478 ± 13	5.14 ± 0.02
IMRM 3	0.77 ± 0.004	-	1471 ± 25	4.44 ± 0.06
IMRM 4	0.71 ± 0.003	473	1452 ± 22	6.38 ± 0.1
IMRM 4	0.71 ± 0.003	423	1415 ± 29	4.99 ± 0.1
IMRM 4	0.71 ± 0.003	-	1341 ± 16	4.56 ± 0.2
IMRM 5	0.67 ± 0.003	-	1303 ± 33	$0.727 \pm 0.04^{\text{a}}$

^a This sample exhibited unsteady propagation. The reported velocity is the “bulk velocity” down the foil (perpendicular to the direction of band propagation).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10