Reactive Multilayers Fabricated by Vapor Deposition:

A Critical Review

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Reactive multilayer thin films are a class of energetic materials that continue to attract attention for use in joining applications and as igniters. Generally composed of two reactants, these heterogeneous solids can be stimulated by an external source to promptly release stored chemical energy in a sudden emission of light and heat. In this critical review article, results from recent investigations of these materials are discussed. Discussion begins with a brief description of the vapor deposition techniques that provide accurate control of layer thickness and film composition. More than 50 reactive film compositions have been reported to date, with most multilayers fabricated by magnetron sputter deposition or electron-beam evaporation. In subsequent sections, we review how multilayer ignition threshold, reaction rate, and total heat are tailored via thin film design. For example, planar multilayers with nanometer-scale periodicity exhibit rapid, self-sustained reactions with wavefront velocities up to 100 m/s. Numeric and analytical models have elucidated many of the fundamental processes that underly propagating exothermic reactions while demonstrating how reaction rates vary with multilayer design. Recent, time-resolved diffraction and imaging studies have further revealed the phase transformations and the wavefront dynamics associated with propagating chemical reactions. Many reactive multilayers (e.g., Co/Al) form product phases that are consistent with published equilibrium phase diagrams, yet a few systems, such as Pt/Al, develop metastable products. The final section highlights current and emerging applications of reactive multilayers. Examples include reactive Ni(V)/Al and Pd/Al multilayers which have been developed for localized soldering of heat-sensitive components.

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Nomenclature

1-D	=	one dimensional
2-D	=	two dimensional
3-D	=	three dimensional
$\mathcal{A}$	=	Arrhenius prefactor
C	=	concentration
C_p	=	heat capacity at constant pressure
D	=	mass diffusion coefficient
D_o	=	diffusion prefactor
E_a	=	activation energy for atomic diffusion
f	=	fractional concentration of product phase
F_{ig}	=	threshold ignition fluence
g	=	geometrical term
n	=	composition of one reactant in a two-reactant system
R	=	gas constant
R_T	=	thermal resistance
t	=	time
T	=	temperature
T_{ad}	=	adiabatic temperature
T_f	=	flame temperature
T_{ig}	=	ignition temperature
T_{melt}	=	melting temperature
T_{max}	=	maximum temperature
T_o	=	ambient temperature
T_{onset}	=	onset reaction temperature
Q	=	quantity of heat
$\mathcal{Q}_L$	=	rate of heat loss
$\mathcal{Q}_{RX}$	=	rate of internal chemical energy release
$\mathcal{Q}_S$	=	supplied external power
v	=	propagating wave velocity
w	=	product phase thickness, premixed thickness
α	=	thermal diffusivity
δ	=	one quarter of bilayer thickness
H_o	=	heat of formation
H_{RX}	=	heat of reaction
λ	=	bilayer thickness
$\sim$	=	approximately

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1. Introduction

A reactive multilayer thin film is a relatively new form of energetic material that consists of a well-defined, heterogeneous structure and stored chemical energy. These metastable solids are composed of alternating, thin layers of at least two reactants, with total thickness in the range of ~ 0.1 to $300\text{ }\mu\text{m}$. In practice, the constituents are chosen based on their propensity to react with each other and generate heat. This means that the majority of reactant pairs that make up multilayers are characterized by a large heat of formation (H_o) and high adiabatic reaction temperature, T_{ad} [1,2]. The driving ‘force’ behind reactions in multilayers is the stability, or low free energy, of the products. The kinetics of mass diffusion, chemical reactions, and thermal transport along with various energy-loss mechanisms operate against thermodynamics and inhibit, or potentially extinguish, reactions.

The multilayers react either by thermal explosion or by a self-sustained propagating reaction. Thermal explosion occurs if the temperature of the reactants is raised rapidly to a characteristic ignition temperature (T_{ig}). It is described as an homogeneous reaction involving the simultaneous reaction of all constituents. Alternatively, an external source of energy, such as a focused laser beam or mechanical stylus, can be applied at a point to initiate a self-propagating reaction. In the latter mode, the external source mixes a small volume of reactants, which generates heat locally. The generated heat then spreads into neighboring, unreacted portions of the film, and causes additional mixing therein leading to a self-sustained reaction wave. Energy is often lost to surrounding material during

these events, primarily through conduction. As a result, the net forward heat transfer within the energetic solid is critical to self-sustained reactions.

A variety of two-component reactive multilayers have been reported. As discussed further in this review, known reactive systems include metal/metal, metal/semiconductor, metal/metalloid, metal/metal-oxide, and metal/organic multilayers. Reactions may involve the formation of a product that is composed of the two reactants ($A + B = AB$). Other reactive multilayers undergo metallothermic reactions ($A + BC = AC + B$), such as a reduction/oxidation (thermite) reaction. Reactive multilayers are deposited to different total thicknesses, depending on the specific goal(s) of an experiment or an application. For example, *in-situ* transmission electron microscopy (TEM) characterization of phase transformations requires a small number of reactant layers to achieve electron transparency [3], while joining applications benefit from multilayer heat sources that contain hundreds or even thousands of individual layers [4].

Most vapor-deposited, reactive multilayers discussed in the literature are not explosives. Rather, these materials exhibit less rapid, deflagration reactions in which a chemical reaction wave moves through the substance at subsonic rates. Detonation – a property of explosives - is characterized by a reaction wave that moves at rates exceeding the speed of sound in the solid. The heat generating, deflagration reactions of some multilayers are accompanied by gas emission. Nevertheless, deflagration reactions involve distinctly different reaction pathways compared to explosives. In particular, mass transport is a rate-limiting process in self-propagating formation reactions.

Detailed investigations of multilayer ignition and self-propagating deflagration reactions have benefited from vacuum deposition techniques. Vapor deposition methods

establish a well-defined heterostructure, with tailored interfacial area and minimal void volume, making these solids attractive for scientific study. The total interfacial area is indirectly controlled by the choice of layer thicknesses and the number of layers.

Interfacial area is not readily tailored by alternative fabrication methods, such as powder consolidation; therefore, direct correlation of material behavior to model predictions remains challenging for these other approaches. Furthermore, vacuum-based deposition methods provide a pristine environment for thin film growth and access to nanometer dimensions. Control of multilayer composition and structure enables researchers to tailor ignition sensitivity and reaction speed.

The structure of this critical review article is as follows. Section 2 begins with a brief summary of relevant research that preceded the discovery of reactive multilayer thin films. This background is included for those new to the field who may want to learn more about self-propagating, high-temperature synthesis (SHS) and self-propagating crystallization reactions. Section 2 also summarizes the vapor deposition methods used for reactive multilayer growth and the multilayer geometries that can be achieved. Section 3 describes the conditions required for initiating a high-temperature reaction in multilayers. Discussion includes ignition by uniform heating and local point stimulation. In Section 4, the dynamics of self-propagating reactions are discussed. This topic has been the focus of many laboratory experiments, model simulations, and theory development. Section 5 describes wavefront instabilities that develop during self-propagating chemical reactions. In particular, recent work has identified 1-D (oscillatory) and 2-D (spin) instabilities that are common to low exothermicity and/or kinetically-constrained reactive multilayers. Section 6 discusses the product phases that

form in several example multilayer systems. The surrounding, gaseous test environment often affects product phase. The paper ends with a discussion of mature and emerging applications of these materials followed by conclusions and envisioned future work.

The following notation is used throughout. The symbol “/” indicates a multilayer composed of two reactants, such as Ti/Al. With this notation, the numbers preceding the reactants’ chemical symbols indicate their relative amounts. For example, a 2Ti/Al multilayer contains twice as many moles of Ti compared with Al. The symbol “-” refers to a reactive system, as in Ti-Al.

2. Background

This section starts by discussing relevant research into self-propagating deflagration reactions that preceded the discovery of reactive multilayer films. After this brief review, sections 2.2 and 2.3 describe the vacuum deposition methods that have been used to deposit reactive multilayers, attainable multilayer geometries, and some key properties of as-deposited films.

2.1 Research leading to the discovery of reactive multilayers

Numerous studies of self-propagating, high-temperature reactions preceded the discovery of reactive multilayer thin films and, thus, form the basis of current research. In particular, the extensive work by Merzhanov et al. [5,6] beginning in the 1960s demonstrated combustion synthesis of different reactive powder compacts. Their original

work has had a lasting effect on reactive materials science as it launched a new field of study on gasless, deflagration reactions in solids. Building on earlier studies of metallothermic reactions [7-9] and previous combustion theory [10,11], Merzhanov et al. demonstrated how “autowaves” move rapidly through reactive bulk compacts composed of transition metals (Ti, Zr, Ta, Hf, etc.) and C or B. In a few systems, the temperatures of propagating, reaction fronts were found to be below the known eutectic temperatures for a given material system [6]. The Soviet teams also investigated ignition phenomena, which included both volumetric thermal explosion and initiation at a discrete point, edge, or face. Early model descriptions of ignition borrowed from previous research of propellants that account for heat generation and conduction [12]. These studies implemented zeroth-order reaction kinetics when modeling ignition, which means that no mass transport or phase transformations are assumed to take place within a sample. Continued research of SHS demonstrated a variety of different self-propagating reaction modes including steady, pulsating [13], spinning [14], chaotic [15], and repeated combustion [16]. The original theory put forth by Merzhanov for stable fronts was extended to explain these different, observed reaction modes [17-21].

Research on synthesis reactions and high-purity product phases has had a profound effect on the development and the application of vapor-deposited reactive multilayers [22]. Many of the intermetallic compounds produced in earlier SHS studies, such as TiB_2 [23], have reappeared as the subject of multilayer research. In addition, SHS [24,25] and earlier work on thermites [9] demonstrated how the heat released during a reaction could be used for joining dissimilar materials (a current activity with reactive multilayers). Similar to prior work with SHS, reactive multilayer joining does not require a vacuum

furnace and can be completed in air. For more discussion of SHS and the novel materials produced by this technique, interested parties are directed to several review articles [26-34] and other publications [35-37].

Prior research on self-propagating crystallization reactions also led to the discovery of reactive multilayer films. More than 100 years ago, Gore [38] and Cohen [39] showed that electrolytically deposited Sb undergoes a propagating, exothermic reaction when stimulated at a point. This behavior was explained later, in 1934, by Coffin and Johnston [40] as being due to rapid crystallization. In other words, these particular deflagration reactions are driven by the rapid, heat release rates associated with an amorphous-to-crystalline transformation. Beginning in the 1970s, several groups reported on self-propagating crystallization reactions in amorphous films grown by vapor deposition. Evaporated and sputter deposited films of Ge [41-44], GeTe [43], (In,Ga)Sb [45], Si [46], and silicon dioxide [47] undergo “explosive” crystallization (EC) reactions when stimulated at a point. Modern EC studies also identified various means for igniting amorphous films, including thermal [47], optical [43,46], and mechanical approaches [45,48]. It is important to note that “explosive” crystallization of amorphous films requires thick films, typically with thickness ranging from ~10 to 100 μm [48-51]. A sizeable thickness is attributed to the relatively small heats of crystallization [52,53].

It is apparent that these studies of self-propagating reactions led to the discovery of reactive multilayer thin films. Prentice first discussed the potential of reactive multilayers as ignitable heaters for power sources [54]. His 1979 patent, titled “Heat Sources for Thermal Batteries: Exothermic Intermetallic Reactions,” discusses alternating layers of sputter-deposited Ti and B which undergo a rapid, propagating, gasless reaction

[54]. A few years after this publication, Floro first demonstrated reactive multilayer thin films grown by vapor deposition [55]. With the title “Propagation of explosive crystallization in thin Rh-Si multilayer films”, Floro bridged the gap between previous research on crystallization reactions in homogeneous films and propagating formation reactions in heterogeneous multilayers [55]. Importantly, both the patent and the journal article associate alternating, nanometer-scale, layered structures with rapid, propagating synthesis reactions. A subsequent report by Wickersham and Poole [56] demonstrated how the reactivity of vapor-deposited multilayers varies with reactant layer thickness.

2.2 Vapor deposition methods and multilayer geometries

Sputter deposition [2, 56-62] and electron-beam evaporation [55,63-65] have been used to deposit the majority of reactive multilayer thin films, with most work in the past ten years relying on magnetron sputtering methods. The most common multilayer design is the planar configuration depicted in Fig. 1(a), in which alternating layers of two reactants are stacked with a single periodicity. The schematic drawing in Fig. 1(a) is an idealized depiction of a planar multilayer. Representative, sputter-deposited Pt/Al and Ti/Al multilayers are presented in Fig. 2. The combined thickness of two reactant layers, shown for Pt/Al, is referred to as the bilayer (BL) thickness. In most studies, the BL thickness is constant through the thickness of a given multilayer. The reactant layer thicknesses of these multilayers, however, are almost always different. Reactant thicknesses are typically chosen to achieve a particular, desired composition. For example, an equiatomic Ni/Al multilayer will require a Ni:Al thickness ratio of 1:1.51 if

both species are deposited with their theoretical bulk densities (9.13×10^{22} at/cm³ for Ni and 6.03×10^{22} at/cm³ for Al) [66].

Different source/sample geometries have been utilized for sputter deposition. This includes sputter-up [67], sputter-down [60,62], and side-sputter [68] arrangements. In each of these geometries, one or more substrates are moved between two, high-purity vapor sources and rotated to improve uniformity, if needed. Advanced sputter deposition systems afford complex multilayer designs such as those with graded-layer periodicity [69], dual periodicity [70], and more than two reactant species [71,72]. Non-planar multilayers have been fabricated on curved substrates [73,74]. Multi-axis stages allow for deposition onto rotating cylinders, particles, or other non-planar shapes [75].

Planar multilayers comprised of alternating metal and metal oxide layers present unique challenges [61,76-79]. In particular, care must be taken to prevent oxidation of the deposited metal reactant layers during film growth. Oxidation of the metal layers can take place through unwanted reactions with residual gases, the process gases used during reactive deposition, and oxygen evolved by sputtering metal oxide targets. High-purity, metal/metal-oxide multilayer growth has involved repeated cycling (on/off) of the metal oxide target power supply [61]. Using this approach, the power is turned off after the completion of a given oxide layer, and the chamber is evacuated before starting a subsequent metal layer. High-purity thermite multilayers have been deposited within a single chamber [61,76-78]. Alternatively, multilayers can be deposited within cluster tools that incorporate different sources in separate, interconnected deposition chambers.

Evaporative deposition methods provide an alternative approach to depositing planar multilayers. Like sputter deposition, multiple sources and sequential shuttering can be

used to tailor reactant layer thicknesses and net composition [80]. *In-situ* crystal monitors are used to accurately control the deposition rate and the layer thickness during electron-beam (e-beam) evaporation. Active cooling of substrates is utilized in some, but not all, deposition systems (includes sputtering and evaporation). The growth temperature and multilayer characteristics are, therefore, likely to vary across different deposition systems. As a word of caution, it should be noted that electron-beam evaporation of reactive multilayers can be complicated by premature hot particle ignition [55]. Particles may be emitted from e-beam evaporators during multilayer fabrication, strike a growing film, and induce a self-propagating reaction before the substrate and the film are removed from the vacuum apparatus.

A different approach to depositing reactive multilayers has recently been proposed [81]. Depicted in Figs. 1(b) and 1(c), “vertical multilayers” are oriented with at least one in-plane periodicity. Instead of sequential deposition of hundreds or thousands of layers, this new approach holds the promise of a single deposition step. Alternating volumes of different reactants could be created simply by depositing one reactant “layer” into a porous substrate (which is a second reactant). The porous starting material may also be a film, which has been etched to have a periodic or aperiodic array of holes.

Fully-dense, vertical multilayer structures have not yet been reported in the literature. However, less dense, reactive structures, described as reactive “nanorods”, have been fabricated using a single deposition step approach [82-85]. Shown in Fig. 3(a), as-produced structures resemble an array of core-shell nanocolumns. This particular example exhibits minimal coupling between individual energetic rods, although the array is bonded to a common substrate. Improved thermal coupling should come with greater

infiltration into porous starting materials. Several studies show that the produced nanorod arrays are, nevertheless, reactive and undergo propagating reactions [82,83,86]. One system has been ignited, as shown in Fig. 3(c) [85].

Atomic layer deposition (ALD) has recently been used in the fabrication of reactive multilayers. ALD is a chemical precursor-based method that relies on successive, self-terminating gas-solid reactions to deposit a given layer. As such, it is uniquely suited for the deposition of thin, conformal films onto planar and non-planar substrates, including high aspect ratio, porous structures. One application of ALD has involved the deposition of ultrathin (0.5 nm) alumina interfacial barrier layers within sputter-deposited CuO/Al (thermite) multilayers [79]. Conformal, interfacial layers effectively prevented Al reactant diffusion at room temperature and resulted in reduced multilayer reactivity [79]. In a separate study, ALD was used to deposit a single SnO₂ layer onto Al nanoparticles to form “enhanced thermite” [87,88]. A TEM micrograph of a SnO₂-coated particle is included in Fig. 3(b) along with a demonstration of its reaction in 3(d). An idealized structure associated with this approach is depicted in Fig. 1(d). On a related note, chemical vapor deposition (CVD) has not been used to fabricate reactive multilayers although this technique has been suggested for fabrication [81]. CVD requires a relatively high growth temperature, which makes it unsuitable for producing many metastable, multilayer structures.

2.3 Properties of as-deposited multilayers (prior to ignition)

Vacuum deposition systems provide a pristine environment for the fabrication of high-purity, reactive multilayers. Modern systems provide an ability to layer pure

materials, such as Ti, Zr, and B, while minimizing the incorporation of impurities such as oxygen [89]. A representative, composition-depth profile of a bimetallic multilayer is included in Fig. 4 to highlight the level of purity that can be achieved by vacuum deposition techniques [90]. This particular Sc/Au multilayer was sputter deposited within a stainless steel chamber having a base pressure $< 1 \times 10^{-7}$ Torr using 10 mTorr of ultra-high-purity Ar. Depth-resolved, Auger electron spectroscopy (AES) shows that the film is clean with no detectable impurities (detection limits ~ 0.1 at.%) within the layers or at the many interfaces. High-purity multilayers have also been achieved using electron-beam evaporation [91]. The purity of monolithic films grown by ALD is discussed in several review articles [92,93].

The net composition of reactive multilayers can be tailored accurately if the densities of reactant layers are known. Sputter deposited and evaporated metal layers are often within a few percent of their theoretical bulk density. However, Si, Ge, B, and some oxide films are amorphous and require characterization of density in order to ensure composition accuracy. Layer thicknesses (and composition) may be selected to achieve a maximum heat of formation for a given reactive system. Alternatively, the composition of a multilayer may be tailored in order to achieve a particular product phase that has favorable mechanical properties.

Premixed material formed near multilayer interfaces is an artifact of deposition that can have a significant effect on multilayer performance [56]. The depiction of a planar multilayer in Fig. 1(a) suggests atomically sharp interfaces, which are rarely found in practice, irrespective of the deposition procedure. More often, there is a ~ 0.1 -10 nm thick layer of mixed reactants at each interface. An example of premixing along

interfaces is shown in Fig. 5. Premixing is a consequence of the growth process and can arise from diffusion at the growth temperature or ion-beam mixing in the case of sputter deposition. First-principles calculations predict that intermixing at Ni/Al interfaces occurs as Ni and Al atoms penetrate into subsurface volumes via interstitial and substitutional sites, respectively [94]. For the case of Al/CuO thermites, density functional theory suggests that intermixing occurs by Al penetration into CuO surfaces and, in turn, by Cu and O atoms penetrating Al after dissociative chemisorption of CuO [95]. Premixed reactant volumes are important to multilayer performance, because they reduce stored chemical energy that would, otherwise, contribute to high-temperature multilayer reactions.[1,2] Additionally, premixed interlayers may act as a diffusion barrier or even modify the thermal properties of exothermic multilayers.

Although rarely cited in studies of reactive multilayers, layer roughness and film stress are additional multilayer characteristics that can affect performance. A rough growth surface can lead to a decreased film density when voids form along columnar grain boundaries as a result of self-shadowing [96]. Deposition onto a severely roughened surface can further result in a distribution of reactant layer thicknesses rather than the single, intended value for each reactant [73]. A distribution of reactant layer thicknesses or a partially voided microstructure may one day provide advantages to a material designer who is interested in tailoring ignition sensitivity. However, the point-to-point variations in reactivity that are likely associated with these microstructural modifications must be understood and implemented in a way that is beneficial over the course of the application. Finally, film stress must be managed in order to produce a reactive multilayer. A large film stress can lead to decohesion from a substrate either by

buckling (when in compression) or cracking (when in tension) [97,98]. Extrinsic stress effects are largely offset by maintaining a low growth temperature, ideally near room temperature. Intrinsic stress originating from defects, premixing across interfaces, or other known mechanisms make these depositions extremely challenging. Many researchers rely on magnetron sputter deposition and/or substrate biasing to tailor film stress and prevent film decohesion [58,95].

3. Multilayer Ignition

Experimental and modeling studies have made great progress toward an improved understanding of reactive multilayer ignition. In particular, recent investigations of planar, bimetallic multilayers demonstrate how their ignition sensitivity is affected by layer periodicity, premixed volume fraction, and other material properties. Experiments also have demonstrated how the energy requirements for ignition vary with the method employed. The information learned from these studies has enabled researchers to tailor the ignition sensitivity of a few reactive systems.

3.1 Ignition by uniform heating

Thermal ignition tests reported in the literature have utilized a hot plate to rapidly and uniformly heat multilayers. This method involves placing a multilayer specimen (detached from its substrate) in contact with a surface fixed at a known, elevated temperature and observing the reaction [99-101]. Evidence for ignition includes a sudden, large rise in temperature and/or an accompanying bright flash. Samples that fail

to ignite when heated do not emit a burst of light and become discolored due to surface oxidation or phase transformations [99-101]. Threshold temperatures for ignition are determined by incrementing the hot surface temperature between experiments and using fresh multilayer samples in successive tests. With care, reproducible threshold temperatures have been obtained. Fritz et al. report that multilayers do not ignite when specimens are heated to temperatures just 1 K below T_{ig} [99].

Figure 6 is a plot of temperatures required for igniting different Ni₉₁V₀₉/Al 1100 [99], Co/Al [100], and Ni/Ti [101] multilayers. In this graph, the threshold values are referred to as conduction-ignition temperatures in order to identify the method of heating and the associated rates of temperature rise (estimated to be about 10² K/s [102]). The conduction-ignition temperatures of all three multilayer systems are between ~500 and 750 K. Ni(V)/Al 1100 multilayers have the lowest conduction-ignition temperatures of the three systems. Important to applications, the data in Fig. 6 show that the ignition sensitivity can be tailored within this range by changing multilayer design. T_{ig} of a given system increases moderately as the bilayer thickness is increased, consistent with an early model [103].

The three reactive multilayer systems shown in Fig. 6 are characterized by threshold temperatures that are significantly less than the reported ignition temperatures of bulk powder compacts having identical chemical composition. For example, equiatomic Ni-Ti compacts fabricated from micrometer-size Ni and Ti particles ignite at much higher temperatures, between 1183 and 1203 K [104,105]. Consolidated 10- m Co and Al powders ignite when heated to a temperature of 1243±10 K [106]. In part, one can attribute the lower ignition temperatures of reactive multilayers to their refined structure

and higher purity. These characteristics should lead to relatively large rates of heat release. Differences in experimental test procedures may also account for the dissimilarities, to some degree. A survey of the literature shows that a large range of heating rates have been used for thermal explosion tests of bulk solids [107-110], and, in general, the T_{ig} of a reactive material increases with heating rate [111,112].

It is interesting that Ni₉₁V₀₉/Al 1100, Co/Al, and Ni/Ti multilayers are ignited at temperatures below the melting points of the constituent layers and the eutectic temperatures. This implies that ignition can occur by solid-state diffusion; that is, melting is not required for these designs. This finding is important, because prior studies of SHS identify reactant melting as being critical to ignition [113]. To be fair, these prior studies involved powder compacts or foils having much larger layer spacings. The importance of large interface area (small reactant spacing) and intimate contact between layers is confirmed in a recent study of consolidated Ni/Al. Manukyan et al. ignited ball-milled Ni/Al nanolaminates at temperatures as low as ~500 K (similar to the lowest T_{ig} of Ni₉₁V₀₉/Al 1100), when utilizing heating rates of ~40 K/s [114]. The ignition temperature of coarse, ball-milled microstructures were higher, ~700 K.

Since the discovery of low ignition temperatures in nanolaminates and vapor-deposited multilayers, this behavior has been attributed to the interplay of refined layered structures and reaction kinetics. It was thought that reactive multilayers comprised of a reduced interfacial area (large bilayer thickness) should require higher initiation temperatures, because a coarse structure leads to lower rates of mixing at a particular temperature [100,101]. Conversely, small-period multilayers can be ignited at a lower

temperature when heated at the same rate, because atoms have a reduced distance of travel for reaction completion [103].

Fritz et al. built upon these general ideas and developed an analytical model to explain how ignition sensitivity varies with multilayer structure and associated physical properties [99]. This model description accounts for the heat of reaction (H_{RX}), mass diffusion prefactor (D_o), the activation energy (E_A) for atomic diffusion, and the thermal resistance (R_T) of multilayers [99]. Starting with the general expression

$$\frac{dT}{dt} = \frac{Q_s}{\rho V} + \frac{Q_{RX}}{\rho V} - \frac{Q_L}{\rho V} \quad \text{Eq. 1}$$

which relates the change in local temperature (T) of a multilayer to the supplied external power (Q_s), the energy released internally due to chemical mixing per unit time (Q_{RX}), and the rate of heat loss to surrounding material (Q_L); while assuming that Q_{RX} scales with the growth rate $\frac{dw}{dt}$ of the product phase, the authors derived the following expression for ignition temperature:

$$\frac{dw}{dt} \propto \frac{Q_s}{\rho V} \frac{2\Delta T}{E_A} \frac{1}{1 - \frac{Q_L}{Q_s}}$$

Eq. 2

In equation 2, other variables and constants include the bilayer thickness (λ), the thickness of the product phase (w), the atomic fraction of one of one of the reactants (n), the fractional concentration over which the product phase exists (f), the gas constant (R), and a geometrical term (g).

The prediction of T_{ig} as a function of λ is consistent with the experimental data shown in Fig. 6. Equation 2 specifies a logarithmic dependence on bilayer thickness, which is exhibited by each of the reactive multilayer systems. Logarithmic fits included in the plot of conduction-ignition temperature are shown with lines. Using the measured ignition temperatures and considering that heat loss likely involves a combination of convective and conductive sinks, Fritz et al. used Eq. 2 to determine an activation energy of 77.3 ± 1.3 kJ/mol (0.80 eV/atom) for $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ 1100 [99]. This value is similar to activation energies obtained by other methods [65,115-118], giving credence to the derived expression. With regard to the atomistic processes underlying ignition, it was surmised that grain boundary diffusion dominates thermal ignition of reactive $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ 1100 multilayers [99]. This prediction of defect-mediated mass transport is based on the determined activation energy being half of that associated with solid-state diffusion of Ni in Al [119].

As a final point regarding thermal ignition, it should be noted that simultaneous reactions have not been demonstrated in vapor-deposited multilayers. Thus, it is not clear whether thermal explosion (as described in the theory of SHS) has occurred in previous uniform heating tests of multilayers. Ignition tests involving uniform conductive heating may, instead, involve fast reaction waves that are nucleated at one or more sites. Perhaps reactions start at internal defects or regions of locally high internal stress. Thus, the term “ignition temperature”, which has been used to describe thermal explosions in bulk solids, should be applied with caution.

3.2 Point ignition and thresholds

A variety of different techniques have been used to ignite reactive multilayers at a discrete point. Common methods that provide a sufficient burst of energy include electrostatic discharge, mechanical impact, electrical heating, and laser irradiation. The ignition requirements vary with ignition method, multilayer chemistry, and multilayer design.

An improved understanding of point ignition is critical for current and future applications, such as joining. In joining applications, foils typically must reflect the shape of the parts to be joined. Mechanical punching and laser cutting are currently used to attain those desired preform shapes. These machining methods must not prematurely ignite reactive multilayers.

3.2.1 *Electrical ignition*

Reactive multilayers have been ignited by electrostatic discharge and direct current heating. Early work by Ma et al. first used an electrical spark to reliably trigger reactions in 3Ni/Al and Ni/3Al [63]. Subsequently, Gash et al. investigated the response of different Ni₉₁V₉/Al and Monel 400/Al multilayers to spark discharges and found that multilayers having periodicities ~10-100 nm were extremely sensitive [120]. (Monel 400 is Ni₇Cu₃) A miniscule spark energy of 40 mJ (2.5×10^{17} eV) was reported in the latter study, highlighting the challenges and necessary precautions for handling these materials.

The scientific study of electrical ignition has included determining the threshold current densities required to ignite planar multilayers and relating these values to initial

multilayer structures and their properties. Using the instrument depicted in Fig. 7(a), $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ 1100 multilayers were characterized by determining ignition threshold values [99]. Electrical testing involved contacting multilayers with opposing Cu electrodes and driving current through the exothermic multilayer for time periods ~ 50 s. With ramp rates of the order of 2×10^7 A/s, currents were incremented between 0 and 200 A to achieve the required amounts for initiating, self-sustained reactions. The initiated area was estimated by considering the elastic response of the reactants subject to Hertzian contact with the Cu electrodes [99].

Tests showed that the minimum current densities for igniting $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ 1100 vary with the contact area and the structure of multilayers [99]. For example, a reduced current density was required to ignite multilayers of a given design when the contact area was increased. This trend can be understood generally by referring to Eq. 1. As contact area is increased, there is a larger heat release rate and relatively less heat loss. With contact area fixed, threshold current densities increased significantly with layer periodicity as shown in Fig. 7(b). Multilayers having 100-nm bilayer thickness required 2X greater current density for ignition compared with a 50-nm periodicity multilayer. This behavior was explained in terms of less efficient reactions occurring in coarse bilayer designs. An increased mass diffusion length lowers the rate of interdiffusion, which in turn reduces the rate of effective heat generation at a particular temperature. Finally, the authors show in Fig. 8 that multilayers having larger premixed layer thicknesses require greater energy for ignition [99]. This trend is attributed to the reduced heat of reaction that comes with a significant volume of premixed Ni and Al and the effects of premixed layers on reactant diffusion.

It is likely that thermomigration plays the dominant role during these electrical ignition tests. Electromigration is not expected to be significant during electrical ignition, at least for the reported current densities. It is noted that the largest current densities ($\sim 10^6$ A/cm²) required for igniting Ni₉₁V₀₉/Al 1100 are above the threshold current density required for electromigration of Al atoms [121,122]. However, the effects of electromigration at 10^6 - 10^7 A/cm² are detected over the course of hundreds or thousands of hours, not over the millisecond timescales involved with ignition. For a discussion of electric field effects and the possible role of electromigration during SHS, the interested reader is directed to review articles [123,124].

3.2.2 Mechanical ignition

Planar multilayers have been ignited by mechanical loading at different strain rates. Wickersham et al. first reported the mechanical ignition of vapor-deposited Zr/Si multilayers [56]. This team repeatedly struck Zr/Si films adhered to glass substrates with a sharp tipped stylus to ignite the multilayers at a point. Mechanical impact led to subsequent, self-sustained reactions that moved completely through the multilayers. Since this initial report, others have utilized frictional testers [120], swinging lever arm devices [99], and drop tubes [99,120] to determine the requirements for mechanical ignition. Recent experiments [125] and model descriptions [126-128] have extended mechanical ignition studies to high strain rates, $\sim 10^7$ to 10^8 s⁻¹.

The threshold impact energies of planar Ni₉₁V₀₉/Al 1100 [99,120], Monel 400/Al [120], and Inconel 600/Al multilayers [99] have been determined via drop-tube testing.

As depicted in Fig. 9(a), this test involves dropping an impactor of known shape onto a specimen from increasingly greater heights (or with greater mass) and monitoring the sample for ignition. Sample foils are placed on a flat, hard surface prior to drop testing; base materials have included bulk metallic glass [99] and carborundum [120]. Experiments determine an average height (and load) required for ignition and, from this, an impact energy is calculated. A rigorous characterization of required impact energies utilizes the Bruceton up-down method to determine the mean height for ignition [120,129].

The drop-tube test data included in Fig. 9(b) shows that increased amounts of energy are required to ignite multilayers having coarser bilayer designs. Energies required for point ignition were generally in the range of 2.5 to 8 mJ (1.6×10^{17} to 5.0×10^{17} eV) for the Inconel 600/Al films, with no detectable difference for two different impactor shapes [99]. Gash et al. show a similar trend for drop-tube ignition of large bilayer thickness $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ and Monel 400/Al multilayers [120]. Friction testing of multilayers has also produced similar trends [120].

Evidence of premix thickness effects was revealed by a swinging lever arm apparatus as depicted in Fig. 9(a). The amount of energy required to ignite 90- μm $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ 1100 multilayers having a 50-nm bilayer thickness increased as premix thickness was systematically raised from 2.4 to 5.7 nm [99]. This general trend is consistent with the electrical ignition test results shown in Fig. 8. As such, it is expected that premixed layers affect ignition by slowing the rate of reactant mixing and lowering the total amount of released heat.

Experiments and modeling of mechanical ignition have extended to high strain rate mechanical loading, up to rates of 10^8 s^{-1} . Experiments involving laser-driven compression (shockless loading) of large periodicity Ni/Al multilayers resulted in material mixing, but propagating intermetallic reactions did not ensue [125]. Additional experiments involving thinner bilayer ($\sim 50 \text{ nm}$) foils, however, reacted fully when subjected to shock compression [125]. In the latter experiment, complete reaction to a stoichiometric B2 cubic NiAl intermetallic was attributed to the combined effects of shock-wave loading and heat generation associated with a self-sustained, propagating reaction [125]. Molecular dynamics (MD)[126-128] and numerical modeling [130] of shock propagation in Ni/Al multilayers has provided insight into the complex interplay of various mechanical, thermal, and chemical processes that underly ignition at high strain rates. Detailed MD simulations by Zhao et al. demonstrate that shock loading in a direction normal to the multilayer interfaces reacts material starting at interfaces closest to the impact surface [126-128]. Model simulations further predict that the density of a multilayer structure can affect the heat release rate in a unique way: according to the model, structures containing pores should undergo reactions with higher heat release rates than fully dense structures [127]. Higher heat release rates are predicted to arise from the enhanced mechanical mixing of reactants associated with pore collapse and higher shock temperatures. Wavefront speeds are predicted to be $\sim 200 \text{ m/s}$ for this case [127].

3.2.3 Laser ignition

Optical ignition provides advantages for scientific study and applications. Focused laser light can be used to ignite a multilayer at a discrete, microscopic point without the

need for contacting electrodes or heaters. In addition, modern pulsed lasers provide a well-controlled pulse of energy, which leads to reproducible ignition [131-133].

Since Clevenger et al. first reported on focused laser-light ignition of planar 2Ni/Si multilayers [64], studies have attempted to determine thresholds for initiation and relate these to properties and design. A common test approach for determining threshold ignition fluences (F_{ig}) involves single-pulse irradiation at a known energy. As depicted in Fig. 10(a), a single light pulse is directed through a lens to a point at the specimen surface. Threshold fluences are determined by starting with a low pulse energy and incrementing the energy (in fresh material or neighboring areas) until a self-sustaining reaction is observed.

Research has shown that threshold fluences are affected by multilayer design and properties. For example, a study of Pt/Al demonstrates that the energy required for optical ignition varies significantly with capping-layer material [131]. Aluminum-capped Pt/Al multilayers required larger fluences for ignition than those having Pt capping layers, and this difference was attributed to the higher reflectance of Al (0.88) versus that of Pt (0.70) at the selected wavelength (800 nm). Additionally, ignition fluence varies with the internal structure of multilayers [134]. The external energy required to ignite Pt/Al generally increased with bilayer thickness, consistent with electrical and mechanical point ignition. Figure 10(b) shows this trend for two different pulse durations (100 fs and 30 ns) over a range of bilayer thicknesses.

Also evident in Fig. 10(b), the two thinnest bilayer structures (20 and 32 nm) required similar or slightly higher fluence for ignition compared with the thicker (40 nm) bilayer structure. This deviation from the overall trend is attributed to the volume of premixed

reactants at interfaces. As described earlier, the thinnest bilayer structures have a large number of interfaces per unit volume, and premixing results in significantly less stored energy for these designs. Thus, more energy from an external source is required to initiate self-propagating reactions in heavily premixed multilayers. It is noted that Pt/Al multilayers having bilayer thickness < 20 nm did not ignite even when using the maximum laser energy. Premixing also leads to decreased steady-state velocities, as revealed in Fig. 10(b).

The ignition threshold fluence varies considerably with reactive multilayer composition, as indicated in Fig. 11. For example, Picard et al. showed that the nanosecond-pulse fluences required to ignite Ni/Ti, Pt/Al, and Co/Al foils vary over two decades when utilizing an 8 μ m spot size [135]. The most exothermic pair, Pt/Al ($H_o = -100$ kJ/mol; -1.04 eV/atom), was ignited with fluences as low as ~ 3 J/cm², while the least energetic system, Ni/Ti ($H_o = -34$ kJ/mol; -0.35 eV/atom), required $F_{ig} > 10^2$ J/cm² [135]. Although a number of physical and chemical properties affect ignition, these experiments with freestanding foils highlight the importance of stored chemical energy density on ignition. The described trends are consistent with the dependence of T_{ig} on H_{RX} expressed in Eq. 2.

The fluence required to ignite a particular multilayer also varies with the characteristics of the laser pulse. Important beam parameters include the spot size, the pulse duration, and the incident wavelength. Figure 11 demonstrates the relationship between ignition fluence required to ignite a given multilayer and laser beam size. For each of the three reactive systems in Fig. 11, the threshold laser fluence increases as the spot size is reduced from 108 to 8 μ m. Ignition fluence also varies significantly with

pulse duration when other parameters are held constant. The plot in Fig. 10 shows systemic differences between femtosecond-pulse and nanosecond-pulse laser ignition thresholds. With wavelength and spot size held constant, a larger femtosecond-pulse fluence was required for ignition compared with nanosecond stimulation. The differences in F_{ig} for fs vs. ns pulses are large for coarse multilayer designs, but still evident in thin bilayer designs (affected by premixed reactants). Although a precise explanation of these behaviors is still forthcoming, it is expected that differences in heat-affected depth, material loss (via ablation or evaporation), and changes in reflectivity are responsible. From the perspective of laser machining reactive foils into different shapes for joining or power source applications, these results are interesting. The femtosecond-pulse ignition fluences are greater than the femtosecond ablation threshold ($\sim 0.14 \pm 0.003$ J/cm²; 8.74×10^{17} eV/cm²) for Pt layers [134]. However, the nanosecond-pulse ignition fluences are less than the nanosecond threshold fluence for removing Pt ($\sim 0.49 \pm 0.026$ J/cm²; 3.06×10^{18} eV/cm²) [134]. Thus, one strategy for laser machining reactive multilayers involves femtosecond pulses [136].

4. Self-sustained Reactions

Different planar multilayers and related structures (arrays of coated nanorods, powders, etc.) undergo self-sustained, exothermic reactions. Sustained deflagration reactions are characterized by a high-temperature wavefront that propagates rapidly

through a multilayer and transforms reactants into product phases. These reactions are driven by a reduced free energy associated with product formation.

Self-propagating reactions do not inherently rely on combustion with air or other gaseous environments. Reactions primarily involve the internal mixing of reactant species that compose the multilayers. Thus, self-propagating, high-temperature reactions can be completed in vacuum or in an inert-gas environment. Self-propagating reactions often proceed through the entire multilayer, and reaction waves may even bypass obstructions such as particles, as demonstrated first by Floro [55]. In other multilayers, particularly those machined to narrow widths, self-propagating reactions may be extinguished after a finite distance. Critical to applications, a large number of multilayer systems do not require preheating above room temperature to ensure complete, self-sustained reactions. In fact, a few systems undergo propagating reactions when reactants are precooled below room temperature [71].

4.1 Planar multilayers exhibiting self-propagating reactions

More than 50 different planar multilayer compositions have been reported to undergo self-sustained reactions. Systems include aluminides, borides, carbides, silicides, titanides, zirconides, and thermites as specified in Table 1. Each of the material systems listed in Table 1 are ignited at a point, with the ambient temperature (T_o) at room temperature (~ 298 K). For a detailed description of the multilayers used in testing, the reader is encouraged to investigate the associated references listed in the right column of the table.

The majority of work to date has involved bimetallic systems. It is known that different bimetallic compositions of a given multilayer system are reactive. For example, the Ni-Al system has been evaluated for 3:1, 3:2, 1:1, 2:3, and 1:3 Ni/Al ratios, and each exhibits a rapid, propagating exothermic reaction that moves through the entire substance [58,63-65]. Reactive Pt-Al [60], Ti-Al [59,145,146], Ni(V)-Zr [142,153], and Zr-Al [147] multilayers also span large ranges of composition. In some studies, an alloy target is used for deposition. Examples include Monel 400 and Inconel 600, which are layered with Al [1,2,99,138,139]. Material may also be added to a target material to improve the deposition process or add functionality to multilayers. Vanadium is often incorporated into Ni targets to 9 at.% (or greater) in order to make these non-ferromagnetic and boost target utilization [70,140-142].

The thickness of multilayers fabricated by vapor deposition varies widely, according to the goals of a particular experiment. In applications that involve multilayer heat sources, such as joining or power sources, multilayers may exceed 100 μ m total thickness. In contrast, thin multilayers, ~100-200 nm, are typically used in dynamic TEM experiments [3,140,151]. It is noted that the minimum total thickness for self-propagating reactions has not been determined rigorously for any materials system. The maximum thickness of reactive multilayers is limited by the amount of available material, one's ability to manage residual film stress, and possible changes in tooling factor that occur during long depositions which would move a process out of calibration.

Table 1 also specifies the form of multilayers used for testing. Many multilayers exhibit complete, self-sustained reactions when adhered to substrates (see the example in Fig. 12). Alternatively, some multilayers only react if they are detached from substrates

and mounted as freestanding foils. Ni/Ti is one system that must be separated from its substrate in order to react, at least when deposited to a 5 μm total thickness and tested at $T_o \sim 298\text{ K}$ [101]. This particular reactive material is otherwise overwhelmed by the conductive, heat-sinking properties of adjoined substrates. Multilayers have been removed from substrates by peeling, solvent dissolution of underlying organic release layers [61,63,85], dissolution of substrates (e.g., NaCl)[3,140], and flexure [73].

The heat evolved from multilayers is often measured by scanning calorimetry and differential thermal analysis. H_o values specified in Table 1 (with parenthesis) are in good agreement with values reported elsewhere [155-158]. Heats of reaction (H_{RX}) are similar to H_o in some cases. Characterization generally involves slow heating rates (temperature rise of $\sim 1\text{ K/s}$), which are far below the rapid heating rates required for self-propagating reaction fronts. Two exceptions include recent nanocalorimetry studies at heating rates of 10^4 K/s [159] and 10^3 K/s [160]. Of all the systems listed in Table 1, $\text{Cu}_4\text{O}_3/\text{Al}$ is the most energetic on a molar basis. It has a heat of reaction equal to $-151.7 \pm 35\text{ kJ/mol}$ (-1.57 eV/atom). The 2Ni/Si system described by Clevenger et al. is the least energetic system ($H_{RX} = -17\text{ kJ/mol}$; -0.17 eV/atom) that exhibits a self-sustained reaction [64]. Michaelson et al. demonstrated the variation of stored chemical energy with multilayer composition for the Zr-Al system [161].

The speeds of propagating reactions in planar multilayers range from approximately 0.1 to near 100 m/s. Surveying the systems listed in Table 1, it is apparent that, in general, highly exothermic systems propagate at increased rates. Rapid reactions with speeds $> 10\text{ m/s}$ have been observed in 2Ni/3Al [58], Pt/Al [60], Ni(V)/1100 Al [70], Ru/Al [144], 3Nb/Si [67], Zr/2Al [147], Zr/3Al [147], Sc/Au [90], Y/Au [90], Ti/2B

[148], CuO/Al [76], and Ti/C [146] multilayers of different total thicknesses. Equiatomic Pt/Al self-propagates at the highest reported rates, up to 100 m/s, even when adhered to substrates [60], while low exothermicity Ni/Ti [101] is an example system that propagates at low rates. Speeds less than 1 m/s are rarely reported in planar multilayers, except for multilayers configured in special ways (see Section 4.5).

Two patents issued to Barbee and Weihs in 1996 demonstrate how the average propagation speed and ignition sensitivity of a given multilayer system can be tailored via design [1,2]. These initial reports showed that the propagation speeds of Monel 400/Al multilayers can be tuned using their bilayer thickness [1,2]. The authors explained how changes to bilayer thickness result in different volume-specific interface areas, which ultimately affects heat release rates. They also identified other characteristics, including interfacial structure, layer stress, and crystal structure, as being critical to reaction rates. In Fig. 13, the measured propagation speeds for the Monel 400/Al system are displayed along with measured values for other reactive systems. Multilayers were tested as freestanding foils in air with $T_o \sim 298$ K.

The results in Fig. 13 demonstrate several key trends discussed initially by Barbee and Weihs [1,2]. For a large range of bilayer thickness, a given multilayer system reacts at higher speeds for thinner bilayers. The speed of 1.6- μ m thick Pt/Al, for example, increased from approximately 9 m/s when the bilayer thickness was 1600 nm to ~ 74 m/s when this dimension was 40 nm. This trend is explained by the relative rates of heat release at a given temperature, enabled by refined multilayer structures [1,2,162,163]. Heat release rates are increased with large interfacial area, akin to SHS powder compacts. Reactant atoms are required to diffuse less distance on average and can mix at a higher

rate when bilayer thickness is reduced; thus, the stored chemical energy is released more rapidly. Counter to this trend, the reaction wave velocity decreases for extremely small periodicity multilayers. For the Monel 400/Al multilayer data, the propagation velocity decreases with reduced bilayer thickness when this dimension is less than ~ 11 nm. This deviation from the trend at higher bilayer thicknesses is attributed to premixed reactants [56]. Reactant species are premixed along multilayer interfaces as described in Section 2.3, and this significantly reduces the amount of stored energy, according to the relationship [1,2]:

$$\cdot \quad \text{Eq. 3}$$

As in Eq. 2, w is the premix thickness and λ is the bilayer thickness. Thus, when premixed thickness is a sizeable fraction of the bilayer thickness, a multilayer will have a significantly reduced amount of stored chemical energy and a decreased wavefront temperature. Barbee and Weihs showed a 40% reduction in H_{RX} for 9-nm thick Monel 400/Al bilayers, compared with multilayers having a bilayer thickness of 65 nm [1,2]. A significant volume of premixed reactants should also affect the mass-transport properties of multilayers.

In addition to the effects on heat of reaction and mass transport, the thermal properties of multilayers impact reaction rates. It is expected that many of the differences in average reaction speed shown in Fig. 13 are affected by the thermal properties of the different multilayer systems. Such differences are likely responsible, in part, for the relatively low rates in Ti-B and Ti-C multilayers listed in Table 1. Ti/2B has the largest

heat of reaction (-110 kJ/mol; -1.14 eV/atom)[148] and the second highest adiabatic temperature (3498 K)[158] of all bimetallic systems listed in Table 1. Nevertheless, the propagation speeds of Ti/2B multilayers are less than those of Pt/Al and a few other bimetallic pairs. Poor thermal conductivity together with low mass diffusivity could explain the low reaction speed of Ti/2B multilayers. Equiatomic Pt/Al multilayers (with $H_{RX} = -100$ kJ/mol; -1.04 eV/atom and $T_{ad} = 3073$ K) are expected to be more thermally conductive than Ti/2B based on the bulk properties of the reactants. Similarly, differences in thermal and/or mass transport may explain the relatively low propagation speeds of Ti-C multilayers [146]. The Ti-C system has nearly the same heat of formation (-92 kJ/mol; -0.95 eV/atom)[155] as Pt-Al, but an even larger T_{ad} (3523 K) [158].

When comparing reaction speeds, it is also important to understand that they vary with multilayer thickness and ambient temperature, T_o . The reaction speeds of a given multilayer materials system decrease when total thickness is reduced or when they are adhered to heat-sinking substrates [164]. A multilayer undergoes a slower reaction when total thickness is reduced, because less heat is pushed forward for reaction. In addition, radiative heat losses become increasingly important as the volume/surface area ratio is reduced [165]. The initial temperature can be equally important. Besnoin et al. predicted a factor of three increase in the average flame speed of Ni/Al upon increasing T_o from 245 to 325 K [166]. Experiments with 7.5- μ m thick Co/Al multilayers demonstrate a 2 m/s increase in reaction wave velocity at 473 K compared to values at ~298 K [137].

4.2 Characteristics of steady reaction fronts

Many systems listed in Table 1 exhibit steady reactions, which are characterized by a smooth wavefront morphology and a constant reaction propagation speed [30,31]. A smooth wavefront is evident at different length scales. As shown in Fig. 12 for a Pt/Al multilayer, the wavefront appears smooth when imaged by high-speed optical microscopy. Similarly, a smooth wavefront is observed in Ti/2B when imaged with nanometer spatial resolution using dynamic TEM, as in Fig. 14 [151]. In this case, a narrow, uniform reaction zone ($\sim 1\text{ }\mu\text{m}$ in width) is present along the boundary between reacted TiB_2 and the unreacted Ti/2B multilayer. Behind this boundary, a granular structure is formed upon resolidification [151].

A constant speed is revealed in plots of wavefront position vs. time. In Fig. 15, representative data is shown for 1.6- μm thick Pt/Al multilayers with bilayer thicknesses ranging from 320 to 1600 nm. These measurements (made outside the ignition volumes) show speeds, which are constant over several millimeters. Remarkably, steady propagation also occurs in the 1600-nm thick bilayer design, consisting of just one layer each of Pt and Al.

Multilayers exhibiting steady propagating reactions are heated rapidly for short periods of time. A few studies have measured the rate of temperature rise associated with a passing wavefront and estimate this to be $\sim 10^6\text{ K/s}$ [167,168]. Peak temperatures in steady reaction wavefronts vary with reactive multilayer composition, but are generally well above 1000 K. A survey of bimetallic systems reveals a low flame temperature of $\sim 1250\text{ K}$ in $2\text{Ni}_{.91}\text{V}_{.09}/\text{Zr}$ [142,153], and a high flame temperature of 1875 K for $\text{Zr}/3\text{Al}$ [141]. Much higher temperatures can be expected in Pt/Al and various thermite

systems when reacted near adiabatic conditions. The peak temperature associated with a wavefront decreases significantly in multilayers that have a large volumetric fraction of premixed reactants. A recent study of the Zr/2Al system reports a near-constant wavefront temperature of ~1700 K for multilayers having bilayer thicknesses > 11 nm [147]. Yet, thinner bilayers undergo propagating reactions at temperatures as low as 1425 K. The downturn in flame temperature correlates with a decreased propagation speed at small bilayer thickness [147].

4.3 Model descriptions of steady propagating reactions

Analytical and numeric models have provided an improved understanding of the various thermochemical and thermophysical processes that underly steady propagating reactions in multilayers. Initial analytical models, assuming constant thermophysical properties and ideal layered structures, demonstrated a fundamental relationship between propagation speed and multilayer structure [162,163]. More recent, refined studies account for heat losses [165], premixed reactants at interfaces [139], phase transformations [166], pressure effects [169], and temperature-dependent properties [170-173].

Armstrong and Koszykowski started with a one-dimensional analytical model to describe propagating reactions in layered reactive solids.[162,163]. The authors assumed that the two constituents within the layered structure would co-diffuse, react to form a single product phase, and evolve heat to drive reactions. They used the equation

$$\rho \frac{dT}{dt} = \rho C_p \frac{dT}{dt} - \nabla \cdot (\kappa \nabla T), \quad \text{Eq. 4}$$

to describe thermal conduction and the relationship

$$\nabla^2 T = \nabla \cdot (\nabla T) \quad \text{Eq. 5}$$

to describe interdiffusion. In this first study, mass transport was assumed to follow a single Arrhenius dependence on T but was independent of composition (C). Other variables included in these equations are the volumetric heat generation rate (dQ/dt), heat capacity at constant pressure (C_p), thermal diffusivity (α), and mass diffusivity (D). By setting the rate of heat generation proportional to the rate of concentration change, the authors derived an expression for the propagating wave velocity (v),

$$v^2 = \frac{3}{2} \frac{D}{C_p} \left(-\frac{dQ/dt}{dT} \right) \frac{1}{T_{max} - T} \quad \text{Eq. 6}$$

that has been the foundation for subsequent investigations of reactive multilayers. Other variables in Eq. 6 include the Arrhenius prefactor (A), the maximum temperature attained during steady reaction (T_{max}), and one quarter of the bilayer thickness (δ).

The dependence on bilayer dimension specified by Armstrong et al. has been validated through multiple experiments. Considering the data presented in Fig. 13 for large bilayer thicknesses (> 40 nm for Pt/Al; > 20 nm all others), there is a general increase in reaction speed as bilayer thickness is reduced. This trend is due to the increased heat release rates that are enabled by refined multilayer structures. However,

this initial modeling approach did not include the effects of premixing. Therefore, comparisons cannot be made to the trends exhibited by ultrathin bilayer films.

More recently, models have included the effects of premixed reactants and heat losses. Gavens et al. built on the earlier approach by Armstrong et al. and accounted for the presence of premixed reactants by varying the initial composition profile [58]. Their approach successfully reproduced the general trends of reaction speed vs. bilayer thickness for a wide range of thicknesses, and confirmed that the reduced amount of stored chemical energy associated with premixed reactants leads to decreased reaction rates [1,2,56]. Jayaraman et al. implemented a numerical approach to investigate the effects of conductive and radiative heat losses on propagating reactions [165]. Focusing on the Ni/Al system, their model predictions showed that conductive heat losses reduce the propagation speed of steady reactions. Jayaraman's study specifically investigated the conductive losses due to thin overlayers (with different thermal properties), similar to filler metals used in joining experiments. This modeling study also predicted that significant conductive heat losses could result in unsteady reaction modes (1-D instabilities) [165]. Radiative losses were reported to be negligible for the modeled geometry when reaction speeds were large, but become increasingly important when flame speed decreases.

The effects of heat losses have been investigated further by considering the heat sinking ability of thick (semi-infinite) substrates [164,175-178]. A numerical approach was used to model reactions in planar Al/CuO multilayers adhered to composite substrates [178]. Films were reacted on oxide-capped silicon wafers, wherein the thickness of the oxide was varied systematically to study the likelihood of propagating

reactions. The experiments and the associated model description confirmed that reactions are less likely to quench when oxide layer thicknesses are large [178]. Quenching was more likely to occur the closer the reacting multilayer was to thermally conductive silicon. A separate, semi-analytical model was developed to account for the combined effects of heat sinking substrates and premixed reactant layers. With this approach, Zaporozhets et al. specify the criteria for reaction extinction on substrates and provide a modified expression for wavefront velocity [177].

Molecular Dynamics simulations have contributed to studies of reactive multilayers [179-183]. In particular, MD has been vital for investigating the diffusivity of reactants at high temperatures, information that is not readily available through experiments. Rizzi et al. have used MD simulations to estimate the diffusivity of species in Ni/Al multilayers at temperatures, ~ 1500 K, similar to peak temperatures in wavefronts [182]. Additional simulations have characterized the effects of pressure on high-temperature reactions in Ni/Al by showing that pressure-dependent melting can influence reaction rates [169,180]. Alawieh et al. have combined the information learned from their own MD simulations with inferred rates of mixing characteristic of reactions at lower temperatures to determine a wide ranging temperature dependence of diffusivity for the Ni(V)-Al system [174]. With this relationship for $D(T)$, the authors were able to accurately reproduce key characteristics of steady propagating reactions including propagation speed and its dependence on bilayer thickness. Their predicted wavefront velocities are included in Fig. 16 together with experimental results from Knepper et al. [70]. Excellent agreement with experiments is found using a reduced model approach incorporating the determined $D(T)$. Two sets of modeling results are included; both account for the effects of premixed

width (w) on D_o and E_a . Interestingly, large discrepancies in predicted flame velocities compared to experimental results were discovered when implementing only the MD simulation results [174]. This was thought to be due to an overestimation of the atomic intermixing rates [174].

4.4 Phase evolution during steady propagating reactions

Several studies have investigated phase evolution in reactive multilayers. Primarily, these experiments utilize slow heating (with $dT/dt \sim 1\text{-}10\text{ K/s}$) to induce changes in phase and structure [69,78,91,117,152,161,184-188]. Phases are examined either during heating using a method such as hot-stage x-ray diffraction (XRD) [58,189] or after rapid quenching following an observed exotherm [161]. Despite providing information about the thermodynamics and kinetics of reactions in multilayers, a slow heating approach may provide a false picture of the phase evolution occurring at high heating rates $\sim 10^6\text{ K/sec}$. In particular, it is known that the phases formed in the Ni-Al system upon slow heating are not the same as those formed during self-propagating, high- temperature reactions [3,63,140]. Van Heerden et al. further show that a quenched, self-sustained front can also develop different phases compared with those formed during unarrested, propagating reactions [190]. For these reasons, several groups have turned to high temporal resolution techniques for the direct assessment of rapid, structural transformations.

Synchrotron x-ray microdiffraction analysis and dynamic TEM (DTEM) have been used to study structural evolution during the passage of a self-sustained, high-temperature reaction wave. Both characterization techniques provide time-resolved information

concerning the reaction pathway at relevant heating rates; each technique is capable of detecting reactant melting and the formation of intermetallic compounds. Synchrotron x-ray methods provide images of reaction fronts and complimentary diffraction information from thick multilayers [142,168,191-193]. Temporal resolution as small as ~ 55 s was reported for this approach [142,168]. DTEM is a related pump-probe method that provides images and diffraction information with ~ 15 ns temporal and 10 nm spatial resolution [3,140,151]. Evaluation requires a much thinner specimen (< 200 nm in total thickness), which is electron transparent. While this thickness is sufficient to self-propagate reactions in some reactive multilayers (Ni/Al, Pt/Al, Co/Al), it has prevented our study of the low exothermicity Ni-Ti system.

Rogachev et al. first utilized synchrotron x-ray microdiffraction for the study of phase transformations in 18- μ m thick Ti/Al multilayers [192]. This original study demonstrated that a single product phase, TiAl, formed within 40 ms of wavefront arrival. Trenkle et al. have since shown that $2\text{Ni}_{.91}\text{V}_{.09}/3\text{Al}$ 1100 multilayers undergo a series of phase transformations [168]. Within ~ 55 s after the arrival of the reaction wave, $2\text{Ni}_{.91}\text{V}_{.09}/3\text{Al}$ 1100 multilayers form cubic NiAl and an amorphous phase that is thought to be an Al-rich liquid with Ni [168]. Upon cooling, NiAl undergoes a peritectic transformation to Al_3Ni_2 and Al_3V (which remain to room temperature). These studies point to interesting details about the nucleation of phases when subjected to extremely high heating rates. As noted by the authors, little time was available for the nucleation of Al_3Ni_2 during heating, and the low melting temperature of this phase was passed rapidly [168]. It was surmised that NiAl is a preferred intermediate phase because of its high-temperature stability over a large composition range and its relatively simple crystal structure [168]. NiAl was the

only intermediate intermetallic phase observed during propagating, high-temperature reactions, in contrast to the formation of Al_9Ni_2 during slow heating [142]. More recently, x-ray microdiffraction has been used to characterize rapid phase transformations in $\text{Zr}/3\text{Al}$ [147], $\text{Zr}/2\text{Al}$ [147], and $9\text{Ni}_{.91}\text{V}_{.09}/11\text{Zr}$ multilayers [142]. Similar to the progression in $2\text{Ni}_{.91}\text{V}_{.09}/3\text{Al}$, reactive $9\text{Ni}_{.91}\text{V}_{.09}/11\text{Zr}$ multilayers developed a phase mixture, consisting of equiatomic intermetallic ZrNi and an amorphous phase, soon after the arrival of a self-propagating wave [142].

DTEM has provided additional details regarding the phase transformations occurring in Ni-Al [3,140] and Ti-B [151] multilayers. The phases formed in Ni-Al multilayers have been studied for three different compositions, 2:3, 1:1 and 3:2 Ni:Al atomic ratios. Thin (125 nm) Ni-Al multilayer foils were initiated by an IR laser pulse in the electron microscope, and fast self-propagating reactions were imaged in regions away from the laser-heated zones. Single diffraction patterns show that a B2 cubic NiAl phase is formed in all three foil types within ~ 15 ns of wavefront arrival [140], and the images of reaction fronts showed interesting differences in structure evolution, according to multilayer composition. In particular, the 2:3 and 3:2 composition multilayers exhibited dark striations behind the reaction fronts that were attributed to transformations occurring within a two-phase field, liquid + NiAl , during cooling [3]. Observing the reacted zone microseconds after the front has passed and the region has cooled, the striations disappear without detectable artifacts due to their prior existence [3,140]. A cellular morphology is not observed, however, in Ni/Al multilayers [142]. It was surmised that a dual-phase solid/liquid cellular structure was less likely to form in equiatomic multilayers, because NiAl is the only stable phase for this composition at reaction temperatures [142].

Dynamic TEM studies of Ti-B multilayers show similar, fast reaction times. High-magnification images of reactive Ti/2B multilayers revealed a thin ($< 1\ \mu\text{m}$ wide), diffuse zone near wavefronts, which suggests that TiB_2 forms in less than 100 ns [151]. Striations were not observed immediately after the passage of reaction fronts in Ti/2B, in contrast to those observed in 3:2 and 2:3 Ni/Al multilayers. Instead, as shown in Fig. 14, the reacted material developed a granular topography with local thickness variations in TiB_2 grains. The estimated adiabatic temperature ($\sim 3500\ \text{K}$) [158] for this system suggests that both reactants melt near the propagating front; however, no liquid phase has been detected.

Despite revealing unprecedented information regarding phase transformations, DTEM and temporally-resolved synchrotron x-ray microdiffraction have not provided a through-thickness, time-resolved map of phase formation with respect to initial interfaces within multilayers. A recent high-rate quench experiment suggests that there is still much to learn about preferred sites for intermetallic nucleation and the role of crystal nuclei shape for enabling high-rate reactions. By evaluating arrested reaction fronts in Ni/Al multilayers [167], Rogachev et al. suggest that rapid self-sustained reactions may only occur because the solid NiAl product phase does not form a continuous, planar layer along interfaces. Instead, NiAl forms initially-separated spherical grains, which would permit the continued, high-rate dissolution of Ni into liquid [167].

4.5 Propagating reactions in less-dense structures including particle arrays

Other non-planar, reactive multilayers undergo rapid, self-propagating, high-temperature reactions. Listed in Table 2, these structures include vertical multilayers, arrays of coated nanorods, and ALD-coated particles. Zhang et al. have produced one of the most dense vertical multilayers which they refer to as a honeycomb structure [83]. Their approach involved electron beam-evaporation of Al into a prefabricated, 2-D periodic, porous NiO structure. Reactive nanorod arrays that resemble an arrangement of core-shell structures have also been produced by similar methods [82,86,194,195]. Calorimetry and ignition tests demonstrate that these forms of reactive materials contain large amounts of stored chemical energy. Several of the materials listed in Table 2 ignite and undergo high-temperature, exothermic reactions.

Additionally, planar reactive multilayers have been broken into coarse fragments and arranged into dense structures that ignite and self-propagate. Monel 400/Al and $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ multilayers were broken into $\sim 400\text{ }\mu\text{m}$ pieces and arranged by compaction for testing [120]. Similarly, $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ 1100 particles were stripped from nylon-mesh substrates by folding/stretching and tested as a powder compact [73,74]. Particle compacts exhibit relatively slow reaction velocities ($\sim 1\text{ cm s}^{-1}$) compared with fully dense, planar multilayers. The coupling of heat through adjacent particles is described as a series of repeated events involving the ignition of a given particle, a propagating reaction within the particle, and the subsequent heating of an adjacent multilayer fragment [73]. Despite this complexity, the propagation speeds of reactive multilayer powder compacts can be tailored by changing average bilayer thickness during magnetron sputter deposition.

5. Instabilities and Secondary Reactions

Self-sustained, exothermic reactions are often characterized by an unsteady propagating wavefront and large temperature variations near the reaction boundary. Reports of 1-D (auto-oscillatory) instabilities are limited to a few systems, yet 2-D (spin) instabilities have recently been observed in multiple reactive multilayer systems. In addition, a few reactive bimetallic multilayers have been found to react twice when tested in air. An initial, self-propagating intermetallic reaction wave is followed by an oxidation front. In certain materials systems, the oxidation front is separated from the intermetallic front in time and space and it moves at a constant, yet slower, rate.

Unsteady behaviors and secondary reactions are important to applications. Variable microstructures produced by auto-oscillatory reaction waves could affect the mechanical properties of multilayer-joined assemblies. Two-dimensional instabilities may abruptly terminate at asperities, particles, etc. leading to incomplete heat release. However, secondary combustion reactions could provide enhanced functionality. Reactive multilayers that harness additional energy from air have been proposed as a means to counteract pathogenic microorganisms (akin to a biocide) [73].

5.1 1-D (oscillatory) instabilities

Oscillatory reactions have been reported for a few reactive multilayer systems, including Ni/Al [196] and the trilayer system Zr-Al-CuNi [71]. In both studies, oscillatory reactions were inferred from the product microstructure and/or the resultant morphology. As shown in Fig. 17, Zr-Al-CuNi multilayers develop a regular, banded microstructure after reaction. This structure is similar, in several respects, to products

formed in bulk materials that undergo pulsating SHS reactions [197]. The banded product microstructure of this foil is composed of dark and light phases, with the former having a larger grain size. Electron microprobe analysis revealed two different compositions: $\text{Zr}_{35}\text{Al}_{29}\text{Cu}_{14}\text{Ni}_{22}$ (dark) and $\text{Zr}_{41}\text{Al}_{25}\text{Cu}_{17}\text{Ni}_{17}$ (light) [71]. It was suggested that the temperature oscillations associated with pulsating reaction fronts correspond to the banded microstructure, with regions of hotter material likely forming coarser microstructures [71]. The banded microstructure periodicity, $\sim 10\text{-}14\text{ }\mu\text{m}$, generally matched the surface ripple wavelength [71]. Experiments involving lower ambient temperatures, $T_o = 253\text{ K}$, clearly show the bands of coarse microstructure correlated with minima in the rippled surface morphology.

Oscillatory reactions in planar multilayers have been predicted based upon numeric and analytical models [198-200]. The calculations of Jayaraman et al. demonstrate large variations in the temperature, the reaction zone width, the flame thermal width, and the instantaneous propagation speeds of unsteady fronts [198]. The origin of auto-oscillation is attributed to the sensitivity of reactions subject to small changes in temperature. Oscillatory reactions undergo a series of momentary “amplifications” in which the front moves ahead of the peak temperature [198]. Subsequently, the temperature decreases due to thermal diffusion and the peak temperature position catches the wavefront, which starts the process anew.

Several characteristics of multilayers are expected to affect oscillatory behavior. Jayaraman et al. has predicted that the ambient temperature, the interfacial roughness, compositional inhomogeneities, and the premixed thickness can influence the oscillatory behaviors in Ni/Al multilayers [198]. For example, the magnitude of power associated

with the oscillations is predicted to increase with decreasing ambient temperature (T_o) as highlighted in Fig. 18 showing the evolution of maximum total power (triangles) and reaction wavefront position (circles) for T_o equal to (a) 248 K, (b) 273 K, and (c) 323 K. Oscillations are predicted for the lower two ambient temperatures, but steady reactions are expected at the highest temperature. Further model simulations show that oscillatory reactions become more prevalent with increasing premixed thickness. Increasing the thickness from 1.5 to 3.5 nm resulted in increased oscillation magnitude and period. In general, these models show that the magnitude of the oscillations increases as δ and T_o decrease and as w increases. Additionally, the oscillation period is expected to increase as δ and w increase and T_o decreases. The widths of the oscillations are predicted to be in the range of 1 to 100s of μm .

5.2 2-D (spin) instabilities

Other planar multilayer systems exhibit a 2-D instability. This distinctly different instability is characterized by the repeated propagation of narrow, reaction bands along previously reacted portions of a multilayer. The term “spin” is adopted from the studies of SHS in bulk materials to describe this instability. Previous work by Filonenko [14] and others [15] involving SHS of cylindrical compacts showed that 2-D reaction instabilities involve burning along a spiral path. Initiated on one face, the reaction in bulk samples propagated along a helical path, with the reaction zone remaining in contact with previously reacted volumes. In some cases, the burning spot moved in a single rotation direction. Other samples were observed to have multiple reaction spots traveling

in opposite rotation directions. The term “spin” depicts the geometrical path along which the reaction moves.

Multilayers that exhibit a 2-D instability have many of the same features as spin combustion in bulk SHS samples. Ignited at a point, the reaction front appears to spiral out from the initiated volume with thin bands that move along the circumference of the previously reacted material. When observed in plan view, bands may move in a single rotation direction as shown in Fig. 19(a) for a 66.4-nm BL Co/Al multilayer or in opposite directions (generally for thicker bilayer Co/Al structures) as in Fig. 19(b). Like SHS spin reactions, the reaction front stalls in the net forward (radial) direction. However, material continues to react as narrow reaction bands propagate along the warm boundary of previously reacted material. When viewed over a limited area in plan view, such as that shown in Fig. 19(a), the bands appear to move transverse to the net forward direction. The band widths vary with bilayer thickness, but are generally ~ 10 to $200\text{ }\mu\text{m}$ [201]. Bands moving in opposite directions show a different behavior than those moving in a single rotation direction. Multiple bands collide and advance the reaction front in the net forward direction, but, after moving a distance of $\sim 100\text{ }\mu\text{m}$, reactions return to trace boundaries of stalled fronts [201]. This behavior is similar in many respects to spin band collisions and reaction advancement at collision sites for SHS powder compacts described by Mukasyan et al. [15].

Large, microscopic variations in temperature are associated with spin instabilities. As demonstrated in Fig. 19(b) for Co/Al multilayers, high-speed thermal imaging reveals temperatures $\sim 1100\text{ K}$ within reaction bands and much cooler ($< 725\text{ K}$) neighboring (trailing) volumes. A few milliseconds after the passage of a reaction band, the foil is

heated to higher average temperatures. Interestingly, the initially cooler (dark) volumes between bands increase to higher temperatures, ~ 1450 K, than surrounding material that was reacted as part of a spin band.

Systems that are known to exhibit 2-D instabilities include Co/Al [100], Ni/Ti [202], Sc/Cu [90], Sc/Ag [90], Zr/Al [147], and Ni/Al [203]. From the data in Table 1, these systems have a low exothermicity on average. Highly exothermic Pt/Al ($H_o = -100$ kJ/mol; -1.04 eV/atom) multilayers do not exhibit an instability, irrespective of bilayer thickness, at $T_o = 298$ K. Reaction kinetics also influence the characteristics of spin waves. Freestanding, $7.5\text{-}\mu\text{m}$ thick Co/Al multilayer foils tested at $T_o = 298$ K exhibit a 2-D instability when the bilayer thickness is ≥ 66 nm, yet multilayers having smaller bilayer thicknesses are characterized by a steady reaction front. A bilayer thickness dependence has also been discovered for $\sim 10\text{-}\mu\text{m}$ Ni/Al; multilayers having a periodicity > 125 nm exhibited a 2-D instability [203].

A phenomenological model has been proposed to explain the large temperature variations near a reaction front. Reeves and Adams have experimentally mapped the temperatures near reaction wavefronts in Co/Al multilayers and interpreted the extent of local reaction based on the measured onset reaction temperature (T_{onset}) [137]. Their results, presented in Fig. 20, illustrate the temperature, the composition, and the phase variability expected near a reacting front. In Fig. 20(a), the predicted momentary temperature and composition profiles are shown just before the arrival of a spin band. Although the reaction front associated with the previous band has stalled, heat continues to diffuse forward and the temperature is elevated slightly in the net forward direction (x). The elevated temperatures in front of a stalled front are important, because they

likely define the width of the subsequent band. It was surmised [137] that the next reaction band would move in a region preheated by the previous spin band. The width of a given spin band should therefore be related to the relative rates of forward heat transfer, which are material dependent. Interestingly, it was found that the subsequent reaction band does not pass through the entire preheated zone. The momentarily dark zones between bands are regions where the $T > T_{\text{onset}}$ and diffusive reactions of Co and Al are likely. It is predicted that these zones are characterized by the formation of intermediate phases that inhibit fast reactions and a decreased amount of stored chemical energy.

Utilizing a 3-D numeric model, Alawieh et al. predict 2-D instabilities in Ni/Al multilayers and confirm that the thermodiffusive properties of multilayers play a critical role in the formation of spin bands [204]. In particular, 2-D instabilities were predicted when the thermal conductivity was allowed to vary with temperature and direction [204], but models that incorporated a constant thermal conductivity did not result in unsteady propagating reactions. The results shown in Fig. 21 are time-lapse simulations of a propagating reaction wave in Ni/Al. Model simulations show stalled reaction fronts in the net forward direction and spin bands that move along the boundary of previously reacted material, consistent with experimental observations. The temperature varies near the reaction front with decreased temperatures in regions between bands.

Continuing investigations of stability boundaries for a given reactive multilayer system may develop a more detailed understanding of the processes that underly 2-D instabilities. Rogachev et al. have previously demonstrated unsteady reactions in some Ti/Al and Ti/3Al multilayers [145]. As shown in the upper plot of Fig. 22, Ti/Al and Ti/3Al multilayers transition to a steady reaction front and increased reaction speed when

T_o is increased above ~ 350 K. Reeves et al. [137] have shown that certain Co/Al multilayer foils undergo a transition to steady propagation with increasing T_o . Displayed in the lower plot of Fig. 22, Co/Al multilayers with BL = 33.2 nm exhibited steady propagating reactions at all temperatures [137]. Conversely, large bilayer thickness ($\lambda \geq 100$ nm) multilayers were unsteady at all T_o values. However, several multilayers (with BL = 66.4 nm, 75 nm, and 87.5 nm) transitioned from initially unsteady behavior to steady propagating reactions at elevated initial temperatures [137]. Example transitions are shown in Fig. 23 using high-speed, plan-view optical microscopy.

5.3 Secondary combustion reactions

Planar, bimetallic multilayers reacted in air often undergo two distinct propagating reactions. First, a rapid, propagating, intermetallic formation reaction moves through the multilayer. Following this, an oxidation reaction occurs which transforms a portion of the hot intermetallic compound to metal oxide. Using high-speed optical microscopy, the oxidation process can appear to overlap the intermetallic wave or a distinct oxidation wave, separate from the intermetallic front, can propagate at a slower rate than the first wave [90].

An example of two propagating fronts, moving left to right, is included in Fig. 24 for a 2.5- m thick Sc/Cu multilayer with bilayer thickness of 41.2 nm. The first four high-speed, plan-view photographic images reveal spin waves propagating through the multilayer due presumably to the mixing of Sc and Cu to form ScCu, since a similar reaction wave occurring in vacuum produces this product phase. Following the initial wavefront, an additional, bright oxidation reaction wave passes through the material. The

oxidation front does not appear when Sc/Cu is reacted in vacuum and is associated with combustion in air. The net forward velocities of the intermetallic and oxidation fronts were ~ 0.92 m/s and 0.036 ± 0.012 m/s, respectively [90]. Also evident in the last four high-speed images, the well-defined, periodic morphology formed by the reaction bands is disrupted by the passing oxidation front. There have been no reports of instabilities in secondary combustion reaction waves occurring in multilayers.

Ni/Ti multilayers are affected by secondary oxidation reactions in different ways. Presented in Fig. 25, the effects of oxidation on 5- m thick Ni/Ti multilayers vary with bilayer thickness. Multilayers with small bilayer thickness (103 nm) exhibit a small increase in average propagation speed when tested at 637 Torr vs. 10 mTorr [202]. Presumably, the added heat of oxidation reaction promotes mass transport, thus mixing of Ni and Ti becomes more efficient. Ni/Ti multilayers with large bilayer thicknesses are also affected by oxidation. These multilayers exhibit an unsteady intermetallic wavefront that is characterized by increased propagation speed (in the net forward direction) when oxygen is present. Thicker bilayers also exhibit an increased frequency of transverse bands when reacted in at 637 Torr as evidenced by the number of ‘steps’ in the plot of Fig. 25. Analysis of high-speed movies explains the increased frequency of spin bands as being due to a larger transverse-band nucleation rate at the foil edges. That is, the presence of oxygen does not increase the transit speed of reaction bands. These effects appear to be limited to multilayers that undergo slow intermetallic reactions. Conversely, the intermetallic waves in the Sc/Cu example far outpace the slower oxidation front giving it little chance to interfere with the intermetallic wavefronts.

6. Product Phases and Microstructures

This section reviews the product phases and microstructures that result from rapid, high-temperature formation reactions and secondary oxidation reactions. Typically, product phases are identified after reactions are completed and the energetic material has cooled to room temperature. Common methods used for phase identification include x-ray and electron diffraction. Product phase formation is critical to applications such as joining, because the reacted multilayer is part of the final, bonded assembly. Reactive multilayers may provide access to novel, metastable compounds that have unique properties and structure.

6.1 Single phase products

Research on bimetallic multilayers for joining applications has targeted single-phase products having B2 (CsCl type) structures, because this structure offers moderate ductility and strength. Toward this end, a single B2 phase has been achieved in a few different reactive systems. Figure 26 shows the characteristic B2 XRD patterns for reacted CoAl, ScAu, ScCu, YAu, and YCu multilayers [90,100]. The B2 phase is the equilibrium structure for each of the equiatomic compounds. The Sc- and Y-containing multilayers required reactions in vacuum to prevent oxidation, in order to form the targeted single phase. CoAl forms a single B2 phase regardless of reaction environment (air vs. vacuum) or reaction mode (homogeneous vs. self-propagating). The finding of a single product phase for Co/Al is interesting, because it implies that the 2-D spin instability exhibited by this system has little effect on the final phase. Presumably the

extended time at elevated temperature after the passage of an unsteady reaction front homogenizes any initial microstructural variations that may have formed. The single phase, equiaxed grain structure of CoAl shown in Fig. 19(c) is unlike the modulated microstructure produced in Zr/Al/CuNi [71]. Other multilayers that form a single B2 phase (not included in Fig. 26) are Ru/Al [144] and Ni/Al [68]. Ni(V)/Al also forms a majority B2 phase, but the ~9 at.% V added to Ni targets reacts to form a minority phase of Al₆V [68,98].

A different product phase has been reported for 3Ni/Al[63], Pt/Al [60], Ti/2B [148], Zr/2Si [56], Ni₉₁V₉/Zr[153], and 7Ni₉₁V₉/2Zr[153] multilayers. Many of these systems (e.g., 7Ni₉₁V₉/2Zr) form a single product phase irrespective of their bilayer thickness. For some materials systems, it is essential to react multilayers in vacuum or an inert gas environment to achieve a single product phase. Otherwise, reactions in air result in secondary combustion and a mixture of metal oxide and intermetallic phases.

6.2 Multi-phase products

Some reactive multilayers form multiple product phases as a result of self-propagating reactions. The reasons underlying their formation vary with reactive system and include: incomplete reactions, multiple phase stability, and 1-D (auto-oscillatory) instabilities. Secondary combustion reactions can also lead to a complex mixture of phases, as described in Section 6.4.

Several multilayer systems react incompletely to form multiple product phases. Ma et al. studied thin (0.06-0.30 μ m) Ni/3Al multilayers and discovered a mixture of Al₃Ni₂, Al₃Ni, and Al phases after the passage of self-propagating reactions [63]. Subsequent

annealing to 750 K transformed this mixture of phases into a single equilibrium phase, Al_3Ni [63]. In other systems, such as Ni-Zr, multiple phases are present after reaction because more than one phase is stable for the chosen composition. Barron et al. investigated various compositions of the Ni-Zr system and found that multilayers with a composition of 2Ni/Zr formed a mixture of $\text{Ni}_{10}\text{Zr}_7$ and Ni_3Zr phases [153]. This mixture is consistent with published Ni-Zr phase diagrams [142], as the 2Ni:Zr composition lies in a zone of dual phase stability.

The product phases can vary significantly with bilayer thickness, even when the net composition is fixed. For example, the low exothermicity system Ni/Ti forms a variety of different phases depending on bilayer thickness [101]. When multilayer periodicity is small ($\lambda \leq 13$ nm), Ni and Ti react and form single-phase B2 NiTi (austenite). As shown in Fig. 27, multilayers with BL thickness ≥ 28 nm form a mixture of phases including NiTi_2 , monoclinic B19' NiTi (martensite), and austenite. The XRD data presented in Fig. 27 further suggests that the relative amounts of austenite decrease with increasing bilayer thickness as the concentration of NiTi_2 and B19' martensite increases. Presumably, the incomplete blending of reactants in thicker bilayers is a result of limited reaction kinetics. Additional evidence for incomplete blending in coarse reactive Ni/Ti multilayers is obtained by cross sectional TEM as shown in Fig. 27. The micrograph reveals discontinuous layers of Ti-rich precipitates (possibly NiTi_2), with an out-of-plane periodicity that is approximately the same as the original bilayer thickness, immersed within a matrix of NiTi.

As discussed in Section 5.1, reactive multilayers may undergo a 1-D (auto-oscillatory) instability that is characterized by a pulsating reaction front with large

temperature variations in time and space, which can lead to a regular, banded microstructure like that for Zr/Al/CuNi shown in Fig. 17. The multilayer develops after reaction with two different phases [71]. Similar phase modulations have not been detected in multilayers that undergo a 2-D spin instability.

6.3 Metastable products

Only a few reactive multilayer systems are reported to form metastable phases as a result of self-propagating reactions. One example is sputter-deposited 3Nb/Si [66], which reacts to form a mixture of Nb₅Si₃, Nb, and Nb₃Si. The latter intermetallic compound is a high-temperature phase that is metastable at room temperature. In a separate study, Pt/Al multilayers [60] reacted in a self-propagating mode and formed a metastable rhombohedral PtAl phase [205]. This single product phase is a complex metal alloy having a 76-atom unit cell as depicted in Fig. 28. The XRD pattern obtained from rhombohedral PtAl (included in Fig. 28) is unlike that of equilibrium PtAl, which forms a cubic FeSi-type structure. Rhombohedral PtAl films were transformed to the equilibrium cubic phase upon slow heating to ~900 K [60]. Although the reasons underlying metastable PtAl phase formation are still unknown, previous work postulates that the rapid cooling rate (-3.9×10^8 K/s) could be responsible for rhombohedral PtAl [60].

6.4 Effects of surrounding gaseous environment

The gaseous environment surrounding a reacting multilayer can affect product phase and microstructure. In particular, several bimetallic multilayers reacted in air form a mixture of intermetallic compounds and metal oxides.

Crystalline oxide phases form in Zr/Al, Sc/Au, Sc/Cu, Sc/Ag, and Ni/Ti multilayers ignited in air [90,101,141]. Oxide phases tend to form in the near-surface regions of reacting multilayers, and one or both metal species present in multilayers can react with oxygen [141]. The XRD patterns included in Fig. 29 demonstrate the effects of surrounding gas environment on Sc/Cu phase formation. The bottom XRD pattern shows the characteristic peaks of Sc and Cu prior to reaction, whereas the top pattern reveals a single product phase (ScCu) after reaction in 0.1 mTorr. From the middle pattern, the same Sc/Cu multilayer reacted in air (637 Torr) forms a mixture of off-stoichiometric, Cu-rich intermetallic compounds, such as Cu_2Sc , and crystalline Sc_2O_3 and $\text{ScO}_{0.95}$. Comparing the middle and top XRD patterns, there is no evidence for crystalline oxide phases after reaction in vacuum. The formation of Sc_2O_3 is not surprising considering the stability of this compound ($H_o = -1908 \pm 2$ kJ/mol; -19.7 eV/atom) [206], compared with that of equiatomic ScCu ($H_o = -20.9$ kJ/mol; -0.22 eV/atom)) [157].

Oxidation of bimetallic multilayers can be extensive [141]. A study of 40- μm thick Zr/Al shows that multilayers reacted in air absorbed approximately 30 at.% O, while forming crystalline ZrO_2 near the surface [141]. Oxygen penetration depths were large, ~ 10 μm , and a mixture of Al_2Zr , Al_3Zr , Al_4Zr_5 , and Al_3Zr_5 was formed below the ZrO_2 outer layer. It was noted that, according to published Ellingham diagrams, the oxidation of Zr is favored over the oxidation of Al at high temperatures [141].

7. Brief Summary of Applications

Reactive multilayer thin films have been proposed for several applications. This includes use in joining components [207,208], defeating harmful microorganisms [73], igniters [209-213], flares, power sources [54,214], car airbag initiators [215], and pattern recording [216]. Of these, reactive multilayer joining technology has received the most attention. A bimetallic multilayer composed of $\text{Ni}_{0.91}\text{V}_{0.09}$ and Al has been developed and commercialized for localized soldering and brazing applications. It is currently used to bond sputter targets to copper backing plates.

7.1 Joining

The arrangement used for reactive multilayer joining involves sandwiching a bimetallic multilayer heat source between component materials as shown in Fig. 30 [207]. The aligned structure is uniaxially compressed with pressures between ~ 0.1 and 10 MPa, and a reaction is initiated at one or more points in the multilayer. The heat evolved from propagating reactions is promptly coupled to adjacent layers, where the temperature is elevated for a short amount of time. In many uses, a low melting temperature filler metal or alloy is placed, prior to ignition, between the heat source and the components to be joined. The purpose of fillers is to promote bonding to components and the reactive multilayer. Reactive multilayer joining is relatively simple and fast, and it avoids the use of large, costly furnaces. Materials can be bonded in air or in inert gas atmospheres; often this is accomplished without preheating the assembly.

Weihs, Knio, and their colleagues have championed $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ for reactive multilayer joining and developed a commercial product known as NanoFoil[®] [4,68,217-

228]. This planar multilayer is currently fabricated by magnetron sputter deposition and is available in different thicknesses, from 40 to 150 nm. NanoFoil[®] is characterized by a heat of reaction between -44.3 and -52.2 kJ/mol (-0.46 and -0.54 eV/atom), and it is readily ignited at a point by a focused laser beam, electrical impulse, or other source of energy. The multilayer reacts in a self-propagating mode at speeds of about 7 m/s to form B2-structure NiAl, a relatively ductile intermetallic compound. As outlined in Table 3, NanoFoil[®] and a few other multilayers have been used to join a range of materials including metallized ceramics, bulk metallic glasses, stainless steel, titanium alloys, and polymers. Joining has mostly involved localized soldering, although brazing and welding are reported [208,217,218]. Large area (~1 m²) sputter targets have been bonded to copper backing plates using Ni₉₁V₀₉/Al multilayers and low melting point solder layers [227,228]. Small area (~1 mm²) joined structures include quartz strain gauges and IR emitters bonded to metal membranes [62].

Reactive multilayer joining is optimized to *i.*) heat neighboring materials for successful bonding and *ii.*) maintain relatively low temperatures in the bulk of adjacent components. For soldering, a sufficient amount of heat is conducted into fillers in order to melt them. Numerical models estimate that NanoFoil[®] is heated internally at rates of ~10⁶ K/s, while adjacent metals (such as fillers) experience a lower rate of temperature rise, ~10³ K/s [139,165,166]. The time spent at elevated temperature varies with the joining experiment, but models suggest this to be less than 1 s in some cases [220]. Thin reactive multilayers do not provide excessive amounts of heat; therefore, the bulk of a joined component remains at relatively low temperature. Two demonstrations of joining with this approach include the welding of a bulk metallic glass, Zr₅₇Ti₅Cu₂₀Ni₈Al₁₀

[217,218], and the soldering of heat spreaders to temperature-sensitive integrated circuit dies [225]. In the first example, small volumes of the amorphous metallic glass were raised to temperatures above its melting point for a length of time that was sufficient for bonding [217,218], yet the bulk amorphous structure of the components and its related mechanical properties were preserved [217]. In the second study, semiconductor dies were soldered to heat spreaders using NanoFoil[®], and the resultant joint was characterized by low thermal resistance and good thermal fatigue resistance [225,226].

The physical dimensions of a reactive foil and the filler are critical to successful reactive multilayer joining. Wang et al. showed that the minimal thickness of $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ required to form a good bond varied with the component material according to its thermal properties [220]. For example, a thicker $\text{Ni}_{91}\text{V}_{09}/\text{Al}$ multilayer was required to join Al than for bonding stainless steel, as the former efficiently pulled heat away from the reaction zone and adjoining solder. The thickness of solder or other filler material is also selected carefully based on several criteria. Sufficient heat must be provided to melt the solder and heat the volume of material near a solder/component interface to establish a good bond. Thus, the solder is typically thin, as specified in Table 3. Solder flows during joining, and a portion of molten material may even flash to the outside of a joined assembly. With pressure applied, solder also flows into cracks formed in the reacted multilayer. The resultant, composite structure shown in Fig. 31 (cross section) is a typical, well-bonded joint.

Reactive multilayers are often coated with thin layers of metal or alloy (e.g., Sn, AuGe) prior to removal from the vacuum deposition system. These layers protect multilayers against surface oxidation and are, therefore, important to creating a strong,

tough bond. A 0.5 to 3.0 μm -thick layer of InCuSil[®]-ABA[™] is currently applied to both sides of the NanoFoil[®] to promote solder wetting during the exothermic reaction. Also, the component surfaces are often metallized to achieve a strong bond [68]. In a few experiments, reactive multilayers have been used to bond directly to bare (non-metallized) components. This has included direct attachment to parylene-C and polyetheretherketone (PEEK) [100,234].

New approaches to reactive multilayer joining are emerging. For example, Braeuer et al. utilized 1.6- m thick Pd/Al multilayers to join Si dies and wafers [143]. This highly exothermic pair was sputter deposited onto Si with a bilayer thickness of ~ 180 nm, coated with a Sn capping layer, and pressed to a mating Si piece. When ignited, this multilayer provided a sufficient amount of heat to melt and flow the Sn overlayer. The joined assemblies exhibited good adhesion strengths, $\sim 77 \pm 5$ MPa, and cracks were not observed in either the PdAl or Sn layers [143]. Continued research into solder-based processes seeks solutions for fabricating hermetic seals, with leak rates $< 10^{-10}$ atm cc s⁻¹ [222,223,244].

Recent studies have also investigated brazing as an alternative method for obtaining higher bond strengths [230,231]. Brazing fillers potentially offer greater strength; however, the high melting temperatures (> 723 K) of these alloys present formidable challenges for joining with thin multilayers. Suryanarayana et al. have overcome this problem by combining the internal energy released from reactive Ni/Ti with external microwave sources to join diamond to tungsten carbide for down-hole tooling [208]. Microwaves heated the sandwiched structure and likely ignited the reactive multilayer located at the center of the assembly. A related approach combines the energy of reactive

multilayers and external heating sources with a large, applied pressure to diffusion bond metals and alloys. This approach does not require a braze or solder insert and often uses the multilayer as a “reactive filler”. High strengths have been obtained when using Ni/Ti, Ni/Al, and Ti/Al multilayers [239,241,242,245].

7.2 Igniters

Reactive multilayers are also potential igniters. This means that multilayers can stimulate a second reaction in a neighboring propellant, pyrotechnic, or other energetic material [146,209-213,246]. This includes ignition of material that lies across a small air gap as well as material that is initially in contact [209,246]. Planar Ni₉₁V₉/Al 1100 [209,212,213], Monel 400/Al [120], CuO_x/Al [246], and Ti/2B [210,211] multilayers show promise as igniters. Reaction initiation has involved direct current (Joule) heating [212], heated underlying metal traces [246], and semiconductor bridges (SCB) [154,210,211,247] for subsequent ignition of energetic materials, including nitrocellulose [246] and Fe₂O₃/Al sol-gel coatings [209].

More complex multilayers, such as hydrogen-containing thermites, have also been proposed [215]. Gas-containing reactive films were explored for car airbag deployment systems, in which the emitted gas causes bag deployment. A two-step fabrication process has been described for H-containing thermite multilayers. First, alternating layers of Ti or Zr and CuO or Fe₂O₃ are deposited by sputter deposition. Then, the metal layers are partially filled with H (interstitially) to concentrations of at least 50 at.% [215]. A

maximum temperature of ~398 K was used during the plasma hydrogenation treatment, which is low enough to preserve the stored chemical energy of the thermite.

Structures composed of reactive nanorod arrays have been proposed as igniters and for use in propulsion [85]. To date, studies have focused on a few thermite systems such as Al/CuO, grown by electron-beam evaporation, on porous substrates. These structures have been reliably initiated by underlying Au/Pt/Cr thin film microheaters. Propagating reactions were accompanied by a bright flash of light, which was attributed to a high reaction temperature > 2300 K. Zhang et al. report the ejection of hot particles over several millimeters for the ignition of neighboring materials [85].

7.3 Power sources

In 1979, Prentice described the potential use of vapor-deposited reactive multilayers as heat sources in thermal batteries [54]. Prentice recognized that exothermic intermetallic reactions provide certain advantages including gasless reactions and rapid reaction rates [248]. Drawing on previous work with SHS [249] and Hardt's model descriptions [37,248], Prentice identified principal parameters that underly self-sustained reactions, such as thermal and mass diffusivities, heat of reaction, and composition. Critical to their application as heat sources, the author described how the deposition of alternating reactant layers, such as Ti/2B, could be used to achieve required heat output.

More recently NanoFoil[®] has been evaluated as an alternative heat source for thermal batteries [214,250]. This bimetallic multilayer has the potential to replace traditional Fe/KClO₄ pellets, which have similar mass specific heats of reaction and are toxic [250].

Ni₉₁V₀₉/Al multilayer heat sources were configured within 2-cell and 4-cell batteries and ignited at their edge using heat paper [250]. With pressure applied normal to their face, multilayers reacted to completion and remained conductive. Thus, Ni₉₁V₀₉/Al provided heat and a pathway for mobile electrons. The battery constructed with NanoFoil[®] heat sources operated for a few minutes.

8. Conclusions

Reactive multilayers fabricated by vacuum deposition are currently a subject of intense scientific study. Multiple research teams are investigating the fundamental processes that underly ignition and self-sustained, high-temperature reactions. Such studies are challenging yet intriguing, because reactions occur far from equilibrium. As a reaction front progresses through a multilayer, the constituents are self-heated at high rates to temperatures in excess of 1000 K.

Planar, bimetallic multilayers have received the most attention to date. Almost all bimetallic multilayer investigations described in the literature are carried out with a constant layer periodicity (for a given film), and the total heat output of the multilayers is tailored by the choice of the number of repeat bilayer units. Periodic, planar multilayers have been ignited by rapid, uniform heating, which may involve a thermal explosion. Additionally, planar multilayers can be initiated at a point by applying an external stimulus, such as a hot tip or mechanical stylus. The ignition sensitivity of planar multilayers has been tailored primarily by adjusting the bilayer thickness. This design parameter establishes the interfacial area of multilayers, which has a pronounced effect

on heat release rate and the ability to start a reaction. Ignition thresholds have been determined for electrical, mechanical, and optical initiation. Engineers now have an opportunity to tailor the sensitivity of a given reactive material via bilayer thickness. Alternatively, one can elect an alternative multilayer system to gain access to a different range of ignition characteristics.

Multilayers ignited at a point undergo self-sustained, high-temperature exothermic reactions. Self-sustained reactions are characterized by a propagating reaction wavefront that moves through the energetic multilayer. The relatively high rates of reaction (up to ~ 100 m/s) in vapor-deposited multilayers are attributed to the combined effects of thin layers and favorable reaction kinetics. Key factors include a large interfacial area per unit volume (small reactant layer thicknesses), high purity, and minimal void volume. In practice, the wavefront velocity of a given reactive multilayer system is tailored by adjusting the bilayer thickness. Coarse multilayers (typically $\lambda > 1000$ nm) that have a small interface density (large effective diffusion lengths) are characterized by relatively slow reaction propagation rates. Thin multilayer designs fabricated with a larger interface area per unit volume (reduced effective diffusion length) generally attain higher propagation speeds. These trends, however, do not continue for ultrathin bilayer designs. Multilayers fabricated with extremely small bilayer thickness ($\lambda \leq 40$ nm) are often affected by the premixed reactants that form along interfaces. When bilayer thickness is of the order of the premixed interlayer thickness, there is considerably less unreacted material available for high-temperature reaction compared with coarse multilayers. As a result, wavefront velocity, flame temperature, and heat output are reduced or reactions do not propagate at all.

Ni/Al and Ni₉₁V₀₉/Al multilayers are the most studied materials system. Much has been learned about the key properties of these multilayers and the atomic-scale processes that underly their performance. The conduction-ignition temperatures of Ni₉₁V₀₉/Al (and other multilayers) are in the range of ~500 to 750 K when bilayer thickness is less than 1 μ m. Ni/Al and Ni₉₁V₀₉/Al multilayers undergo a steady formation reaction for almost all planar designs, with average propagation speeds in the range of ~1 to 15 m/s. Detailed, time-resolved studies of rapid, propagating reactions in equiatomic Ni/Al show that the sequence of phases formed in a propagating reaction front is unlike those developed during slow heating (~ 1 K/s). Slow heating of Ni/Al starts with the formation of a metastable compound, Ni₂Al₉; however, this phase does not develop in rapid, propagating wavefronts. Instead, a B2 (CsCl type) NiAl phase is present within ~15 ns of wavefront arrival. Elegant analytical and numeric models have elucidated the interplay of different chemical, thermal, and mass transport processes during propagating reactions in Ni/Al and other n Ni/ m Al compositions. Consistent with experimental observations, steady reaction fronts are predicted for most Ni/Al multilayers, although oscillatory reactions are possible. Predicted propagation speeds of Ni/Al multilayers closely match those measured in the laboratory. This includes the speeds of the thin bilayer thickness designs that are affected by premixed reactants at interfaces.

Many other reactive multilayers exhibit steady propagating reactions, which are characterized by a smooth wavefront morphology and constant propagation speed. A smooth wavefront and an abrupt reaction front boundary are evident at the micrometer scale when examined optically and at nanometer length scales when probed by dynamic TEM. Conversely, low exothermicity and/or kinetically-constrained multilayers often

exhibit unsteady propagating reactions. Both 1-D (auto-oscillatory) and 2-D (spin) instabilities have been reported for different planar reactive multilayers. A 1-D instability is characterized by a pulsating wavefront and a fluctuating radial front velocity. This instability leads to a banded microstructure through the thickness of a reacted film or foil. A 2-D (spin) instability has been observed in Co/Al, Sc/Cu, and other low exothermicity, bimetallic systems. This instability is characterized by the passage of narrow reaction bands along the forward boundary of stalled fronts. Numeric models demonstrate that the thermodiffusive properties of multilayers are intimately tied to the development of wavefront instabilities. Recent research has begun to investigate the stability criteria for different planar multilayers.

The product phases that result from self-propagating formation reactions have been characterized by diffraction and imaging analyses. Many reactive multilayers, such as Co/Al, form equilibrium product phases. One system, Pt/Al, forms a previously unreported, metastable phase with a complex, large unit cell. When reacted in air, a few bimetallic multilayers form a mixture of intermetallic compounds and secondary oxide phases. Oxidation occurs soon after the mixing of reactant metals and can be observed as a second, distinct, propagating reaction front. Oxygen penetrates to depths of the order of microns, despite the short heating times.

Reactive Ni₉₁V₀₉/Al multilayers are currently used for industrial joining applications. The heat released from an exothermic multilayer is used to rapidly and reliably bond dissimilar components via soldering, brazing, and welding. Reactive multilayer joining is particularly beneficial for joining heat-sensitive components and structures, because the thermal penetration depths are small. A commercial joining application involves the

bonding of sputter targets to copper backing plates via soldering. Reactive multilayer bonding can be completed in air and does not require a large, expensive vacuum furnace.

Other forms of reactive multilayers are emerging, but little is known about their performance. Examples include core-shell structures, such as reactive nanorods, that are fabricated by evaporating a single “layer” of reactant into a porous substrate. The first studies of these structures demonstrate stored chemical energy, ignition, and self-sustained propagating reactions. Fully dense, vertical multilayers with 1-D and 2-D periodicity have been proposed, but have not been realized to date. Improved processes are needed to infiltrate porous substrates, attain increased density, and improve internal coupling. Atomic layer deposition has also been used to coat powders to fabricate nano-thermites.

9. Future Directions

Future research of planar multilayers will likely involve the continued study of dynamic processes underlying ignition and self-propagating reactions, because these are essential to all envisioned applications. Details of rapid mixing, phase transformations, heat release, and the effects of cooling on phase formation have been investigated for a few Ni-Al compositions, but very little information has been reported for other reactive bimetallic and thermite systems. There are many interesting questions that remain. For example, little is known about the reaction rates of thermite multilayers and how this relates to film microstructure and properties. The role of underlying reduction-oxidation reactions on ignition sensitivity and propagation rate has yet to be explained for these

reactive materials. Similarly, studies of reaction wavefront instabilities are in their infancy. It is not yet known whether 1-D instabilities are common to reactive planar multilayers, as it appears that 2-D instabilities are more prevalent. Reaction-front instabilities have not been reported in thermite multilayer systems. Much is to be learned about final phase formation. For example, Pt/Al forms a metastable, large unit cell when reacted on substrates. It is proposed that this is due to rapid cooling rates; however, the reasons underlying its formation are not known. There are many additional reactive chemistries that could be the subject of future investigations. In particular, other metallothermic systems, such as metal/metal-chalcogenide, metal/metal-hydride, and metal/metal-pnictogenide multilayers, could undergo propagating reactions and offer enhanced functionality.

Studies of planar and vertical multilayers could certainly benefit from the characterization of their thermal properties. Thermal processes play into ignition, self-propagating reactions and wavefront instabilities, and an improved understanding of the static and dynamic thermal behaviors should improve our understanding of reactivity. Almost all prior studies use a rule of mixtures to estimate the thermal conductivity of planar multilayers; yet it is understood that this could be a very poor estimate. Excellent progress has been made in the field of nanoscale thermal transport [251], and newly-developed techniques and theory can be applied to the study of reactive multilayers.

Non-planar reactive structures, including vertical multilayers, are an intriguing form of reactive material. A 2-D periodic structure has the potential for even higher propagation speeds, provided that interfacial area can be increased. However, much work is needed to fully infiltrate porous substrates and increase density for reliable

ignition and self-sustained reaction. Techniques such as ALD provide excellent conformality but are slow. CVD methods offer good conformality, but are limited by relatively high deposition temperatures. Ultimately, other methods such as electrodeposition may prove useful.

Applications of these materials continue to emerge. For example, it is envisioned that the secondary combustion reactions exhibited by some bimetallic multilayers may prove useful for counteracting harmful microorganisms. Additional energy could be harvested from air-induced oxidation reactions to increase overall reaction times and improve performance. In this and other applications, the long-term stability of vapor deposited multilayers will be important, and thus they require additional study. Only one report describes the long-term aging characteristics of planar multilayers. Nathani et al. [252] used differential scanning calorimetry (DSC) to characterize the changes in intermixing between nanoscale layers of sputter-deposited $\text{Ni}_{0.91}\text{V}_{0.09}/\text{Al}$ 1100 multilayers. The authors reported that, after three years of room temperature storage, these multilayers exhibit a 1.19-nm increase in the intermixing thickness [252]. Further, it was surmised that for multilayers with bilayer thickness > 35 nm, this small change does not lead to measurable changes in the total heat of reaction. Therefore, reactive multilayers with nanometer-scale layer thicknesses can exhibit long-term stability at room temperature.

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Table 1: Summary of multilayers that exhibit propagating reactions at $T_o \sim 298$ K and their properties. This table lists the overall multilayer thickness, the form used during velocity testing (foil, film, or both), the measured heat of reaction H_{RX} or heat of formation (H_o), with the latter in parenthesis, and reaction speed. Each material was ignited by an external source.

	Composition	Thick. (m)	Form	H_{RX} or H_o (kJ/mol at)	Speed (m/s)	Refs.
<u>Aluminides</u>						
Co/Al	Co + Al	7.5	Foil	-39 to -45	0.5-9	100,137
Inconel 600/Al	Alloy ^a + Al	80-120	"	-44.0 ± 0.2^b	.	99,138
Monel 400/Al	Ni ₇ Cu ₃ +Al	10-100	"	(-50 to -55)	0.5-17	1,2,139
Ni/Al	3Ni + Al	5	"	.	0.08-0.25	65
"	3Ni + Al	0.06-0.3	"	.	4	63
"	Ni + Al	5	"	.	0.62-1.96	64
"	2Ni + 3Al	11	"	(-51.5 ± 1.3)	1.1-10.1	58
"	Ni + 3Al	0.06-0.3	"	.	4	63
Ni(V)/Al	3Ni ₉₁ V ₉ + 2Al	0.125	"	.	~13	140
"	2Ni ₉₁ V ₉ + 3Al	10	"	.	.	141
Ni(V)/Al 1100	Ni ₉₁ V ₉ + Alloy ^c	5-36	"	-57.0 ± 1.7^b	2.1-13	70
"	"	90	"	(-48.6 ± 2.1^b)	.	99,138
"	"	30	"	.	3.9	142
"	"	0.125	"	.	.	140
"	2Ni ₉₁ V ₉ + 3Alloy ^c	30	"	.	2.8	142
"	"	0.125	"	.	.	140
Pd/Al	Pd + Al	1.8	Film	.	≤ 75	143
Pt/Al	3Pt + Al	1.6	Foil	-33 to -51	6-14	this work
"	2Pt + Al	1.6	"	-47 to -61	14-53	"
"	Pt + Al	1.0-3.6	Both	-88 to -90	25-90	60, this work
"	Pt + 2Al	1.6	Foil	-56 to -71	16-56	this work
"	Pt + 3Al	1.6	"	-46 to -56	7-19	"
Ru/Al	Ru + Al	6.0	"	(-48)	2-11	144
Ti/Al	Ti + Al	28	Foil	-35^b	0.08	59,145
"	Ti + 2Al	.	Film	.	≤ 0.5	146
"	Ti + 3Al	18	Foil	.	0.16	146
Zr/Al	Zr + Al	40	"	.	.	147
"	Zr + 2Al	16-50	"	-51 ± 4	0.8-11.5	147
"	Zr + 3Al	16-50	"	-46 ± 3	5-11.5	147
Zr/Al/CuNi	19Zr+16Al+ 15(NiCu)	~40	"	-39.2^b	.	71
<u>Borides</u>						
Ti/B	Ti + 2B	3.0	Foil	-110	0.05-15	148
"	Ti + 2B	1.57	Film	.	10-39	149
"	Various	5-7	"	.	.	150
"	Ti + 2B	0.25	"	.	~14	151
"	2Ti + 3B	0.25	"	.	~14	"
<u>Carbides</u>						
Ti/C	16Ti + 9C	.	Film	.	5	146
"	3Ti + 2C	.	"	.	8.2	"
"	13Ti + 12C	.	"	.	16.6	"
"	12Ti + 13C	.	"	.	18	"
"	19Ti + 31C	.	"	.	10.1	"

”	7Ti + 13C	.	”	.	7.8	”
<u>Silicides</u>						
Nb/Si	~3Nb + Si	25	Foil	.	0.3-3.8	67
Ni/Si	2Ni + Si	0.7, 1.6	”	-17 ^b	22-27	64
”	Ni + 2Si	0.16-0.58	”	.	.	”
Rh/Si	37Rh + 63 Si	0.75	Film	.	.	55
”	21Rh + 29Si	0.46, 0.6	”	.	.	”
Ti/Si	5Ti + 3Si	1-3	Foil	.	.	62
V/Si	V + 2Si	0.07-0.25	”	.	.	152
Zr/Si	Zr + 2Si	0.3-10	Film	-39.4 ^b	.	56
<u>Titanides</u>						
Ni/Ti	Ni + Ti	5.0	Foil	.	0.1-1	101
<u>Zirconides</u>						
Ni(V)/Zr	Ni ₉₁ V ₀₉ + Zr	17	Foil	-35.8 ± 4	0.7	153
”	2Ni ₉₁ V ₀₉ + Zr	17	”	-36.0 ± 4	0.52	”
”	7Ni ₉₁ V ₀₉ + 2Zr	17	”	-34.0 ± 4	0.58	”
”	9Ni ₉₁ V ₀₉ + 11Zr	30	”	.	0.4	142
<u>Bi-metals</u>						
Ag/Sc	Ag + Sc	2.5	Foil	.	0.2 0.45	90
Ag/Y	Ag + Y	2.5	”	.	0.4-0.75	”
Au/Sc	Au + Sc	2.5	”	.	8-40	”
Au/Y	Au + Y	2.5	”	.	9-13	”
Cu/Sc	Cu + Sc	2.5	”	.	0.4-0.9	”
Cu/Y	Cu + Y	2.5	”	.	0.18-0.4	”
<u>Thermite</u>						
Cu ₄ O ₃ /Al	2Cu ₄ O ₃ + 5Al	14	Foil	-151.7 ± 35 ^b	1	77
CuO/Al	CuO + Al	1-3	Both	-42.6 to -71.0 ^b	.	61
CuO/Al	CuO + Al	3.2	Film	.	2-61	76
CuO/Al	CuO + Al	1.3	”	.	.	154
<u>Organics</u>						
Fluorocarbon/ Mg	Mg + 2F	350	Film	.	.	154
PTFE TM /Mg	Mg + 2F	0.85	Film	.	.	154

^a Author states composition of this alloy to be >72 wt.% Ni, 14-17 wt.% Cr, 6-10 wt.% Fe with Mn, Si, Cu, C and S as remainder.

^b Values were reported in alternate units and converted to kJ/mol. at. in this report for consistency.

^c Author states composition of this alloy to be ~99 wt.% Al, 0.87 wt.% (Si,Fe), and 0.12 wt.% Cu.

Table 2: Alternative structural forms of reactive multilayers including layered nanorods, vertical bilayers (BL), and layered nanoparticles with their properties. Each system is reported to exhibit a self-propagating reaction when ignited in air. Thickness corresponds to rod length or average diameter of near-spherical particles.

	Targeted Composition	Thick. (m)	Method of Deposition	Tested Form	H_{RX} (kJ/g)	Refs.
<u>Aluminides</u>						
Ni/Al	3Ni + 2Al	0.06	Evaporation	Rods	.	80
<u>Thermite</u>						
Co ₃ O ₄ /Al	8Al + 3Co ₃ O ₄	5-15	Evaporation	Rods	-3.635	86
CuO/Al	3CuO + 2Al	< 2.0	”	”	-2.5	82
Fe ₂ O ₃ /Al	Fe ₂ O ₃ + 2Al	0.5, 2.0	”	”	.	194,195
NiO/ Al	.	~1.0	”	Vertical BL	-1.02	83
SnO ₂ /Al	3SnO ₂ + 4Al	< 0.10	ALD	Particles	.	87

Table 3: Summary of joining experiments involving vapor-deposited, planar multilayers. This Table lists the multilayer thickness, the joined materials, the method of joining (soldering, brazing, welding, direct attach, etc.) and the filler material. The bilayer thicknesses of these multilayers vary.

Reactive Foil	Multilayer Thickness (m)	Joined Materials	Joining Method	Filler Material (wt%)	Refs.
Co/Al ^a	30	PEEK ^b	Attach	.	100
”	”	Sapphire w/Au	Solder	Pb ₃₆ Sn ₆₂ Ag ₀₂ (25 m)	”
Cu/Al (16at. %Cu)	50	Al-5wt %Mg + 27wt% Al ₂ O ₃ composite	Diff. Weld	.	229
Inconel 600 ^c /Al	87-274	Zr metallic glass	Weld	.	217,218
Ni ₉₁ V ₀₉ /Al ^d	80-260	Ti6Al4V ^e	Braze	Ag ₅₉ Cu _{27.25} In _{12.5} Ti _{1.25} (25-30 m)	230
”	~180	SiC; Ti6Al4V ^e	Braze	Ag ₅₉ Cu _{27.25} In _{12.5} Ti _{1.25}	231
”	~200	Al; Al ₂ O ₃	Solder	Sn _{96.5} Ag _{3.5}	232
”	50-180	Stainless steel w/Au	”	Au ₈₀ Sn ₂₀ (25 m)	68
”	20-180	Al 6061-T6 ^f w/Au	”	Au ₈₀ Sn ₂₀ (25 m)	220
”	60	Stainless steel w/Au	”	In (25, 50 m)	224
”	60	Si w/Au; Cu w/Ni	”	In (120 m)	225
”	~80	Indium tin oxide; Cu	”	Sn _{96.5} Ag _{3.5}	227
”	60, 250	Al 7475 ^g w/Au	”	Sn _{96.5} Ag _{3.5} , Sn ₂₀ Au ₈₀ , Au ₈₈ Ge ₁₂	233
”	40,80	Parylene-C ^h	Attach	none	234
”	60	Si, w/Au	Solder	Au ₈₀ Sn ₂₀ (25 m)	235
”	40,60,80	Si, w/Au	”	Sn _{96.5} Cu ₃ In _{1.5} (25 m)	138
”	40,60,80	Si, w/Au	”	Bi ₅₇ Sn ₄₂ Ag ₁ , Sn ₆₃ Pb ₃₇ Sn _{3.8} Ag _{95.5} Cu _{0.7}	236
Ni/Al	3-3.5	γ-TiAl	Diff. Bond	.	237
”	20-30	TiAl; TiC cermet	”	.	238
Ni/Ti	.	WC; diamond	Braze	Ag _{68.8} Cu _{26.7} Ti _{4.5}	208
”	~2.5	TiNi; Ti6Al4V ^e	Diff. Bond	.	239
Pd/Al	1.8	Si w/Au; Al ₂ O ₃ w/Au	Solder	Sn	138
”	”	Si w/Au; glass w/Au	”	”	”
”	”	Si w/Au; Si w/Au	”	”	”
Ti/Al	2	γ - TiAl	Diff. Bond	.	240-242
Ti/Al	20	γ - TiAl	Diff. Weld	.	243

- ^a Co/Al foils were coated with Au or GeoroTM (Au₈₈Ge₁₂).
- ^b PEEK is polyether ether ketone
- ^c Composition of this alloy is >72 wt.% Ni, 14-17 wt.% Cr, 6-10 wt.% Fe with Mn, Si, Cu, C and S as remainder.
- ^d NanoFoil[®] is a registered trademark of Indium Corp. NanoFoil[®] is generally coated with InCuSil[®]-ABATM (Ag₅₉Cu_{27.25}In_{12.5}Ti_{1.25}).
- ^e This alloy has a chemical composition of 6 wt. % Al, 4 wt. % V, 0.25 wt. % (maximum) Fe, 0.2 wt. % (maximum) O and the remainder Ti.
- ^f This is a precipitation hardened aluminum alloy containing Mg and Si as major alloying elements. T6 refers to the temper of this alloy.
- ^g This alloy includes 6.2 wt.% (maximum) Zn, 2.6 wt. % (maximum) Mg, 1.9 wt. % (maximum) Cu, 0.25 wt.% (maximum) Cr, smaller amounts of Mn, Fe, Si, and Ti with the remainder Al.
- ^h Parylene-C is a trade name for a chemical vapor deposited poly (p-xylylene) polymer.

FIGURES

Fig. 1. Schematic illustrations of reactive multilayers: (a) a planar two-reactant multilayer, (b, c) vertical multilayer structures with 1-D and 2-D periodicity, respectively, and (d) a coated particle with core/shell structure.

Fig. 2. Cross sectional TEM images of planar reactive multilayers fabricated by magnetron sputter deposition: $\sim 1.6 \mu\text{m}$ Pt/Al (bright field) and $\sim 3.8 \mu\text{m}$ Ti/Al (high-angle annular dark field) on silicon dioxide substrates. Each multilayer has a fixed bilayer thickness (94 nm for Pt/Al and 57.5 nm for Ti/Al).

Fig. 3. Non-planar reactive structures fabricated by vapor deposition including (a) reactive Al/CuO_x nanorods deposited by electron-beam evaporation [85], and (b) nanothermite particles composed of an Al core and SnO₂ film [87]. Macroscale images on the right show exothermic reactions for (c) nanorods and (d) nanothermite particles. Scale bars were not provided for (c) and (d) in original publication.

Fig. 4. AES composition-depth profile obtained from a Sc/Au film deposited on a SiO₂ substrate, prior to ignition [90]. This multilayer was deposited by magnetron sputtering in a sputter down configuration. See text for details.

Fig. 5. A cross sectional TEM image, and accompanying energy dispersive x-ray spectroscopy composition maps, obtained from a Pt/Al multilayer near the initial Pt - Al interface (closest to substrate). Mixing has resulted in an amorphous interfacial layer estimated to be ~10 nm thick. The deposited thicknesses of the Pt and Al layers were 31 and 34 nm, respectively. Images and maps were captured using a Titan G2 80-200 aberration-corrected transmission electron microscope operating at 200 kV.

Fig. 6. Conduction-ignition temperatures of planar 90- m thick Ni₉₁V₀₉/Al 1100 (▼) [99], 7.5- m thick Co/Al (Δ) [100], and 5.0- m thick Ni/Ti (●) [101] multilayers as a function of bilayer thicknesses. Experiments involved rapid, uniform heating on a grounded hotplate. Al 1100 is specified to be ~99 wt.% Al, 0.87 wt.% (Si, Fe), and 0.12 wt.% Cu [99].

Fig. 7. (a) Apparatus used to determine the minimum current density required for igniting planar reactive multilayers [99]. Tests involved direct current heating through spherical-tipped Cu electrodes. (b) Current densities required to ignite 90- μm thick $\text{Ni}_{.91}\text{V}_{.09}/\text{Al 1100}$ foils. Results are shown for multilayers of different periodicity; premixed thickness was fixed at 2.25 nm.

Fig. 8. Current density required to ignite 90- μ m thick, planar Ni_{0.91}V_{0.09}/Al 1100 multilayer foils. Multilayers were deposited and heated to attain different intermixed thicknesses prior to ignition [99]. Bilayer thickness was fixed at 50 nm for all test samples, and the pulse duration was set to 50 μ s. Error bars represent one standard deviation.

Fig. 9. (a) Schematic of drop-tube and swinging-arm techniques used for mechanical ignition testing [99]. (b) Plot of impact energy required to ignite Inconel 600/Al 1100 multilayer foils with different bilayer thicknesses. Drop tests utilized a 1.6 mm radius WC sphere and a Rockwell hardness indenter with a 0.2 mm radius and a tip angle of 120° . Total foil thickness varied from 80 to 120 μm as bilayer thickness was increased. Inconel 600 contains >72 wt.% Ni, 14-17 wt.% Cr, 6-10 wt.% Fe with Mn, Si, Cu, C and S as remainder.

Fig. 10. (a) Schematic illustration of the laser-ignition technique used to initiate multilayers at a point. (b) Laser ignition threshold fluences and steady-state reaction propagation speeds ($\blacktriangle$) for planar Pt/Al multilayers with different bilayer thickness [134]. Pulse durations used for single-pulse laser threshold tests were 30 ns ($\bullet$) and 100

fs ($\square$). Tested multilayers were capped with Pt. The Al/Pt layer thickness ratio was fixed at 1.1 for each multilayer.

Fig. 11. Ignition threshold fluences for Pt/Al (= -100 kJ/mol; -1.04 eV/atom), Co/Al (= -60 kJ/mol; -0.62 eV/atom) and Ni/Ti (= -34 kJ/mol; -0.35 eV/atom) multilayers plotted versus reaction enthalpy [135]. Results are shown for two different laser spot diameters (8 and 108 μm), specified as $1/e^2$ widths. Laser pulse duration was fixed at ~ 30 ns.

Fig. 12. High-speed photographic images of a propagating reaction front in an ~ 1.6 - m thick, equiatomic Pt/Al film with a bilayer thickness of 21 nm. Images are plan views with the ignition point on the left. The Al/Pt layer thickness ratio was fixed at 1.1 for this multilayer.

Fig. 13. Reaction speeds of different bimetallic and metal/metalloid multilayer foils vs. bilayer thickness. Planar multilayers include: 7.5- μm thick Co/Al ($\blacktriangle$) [100], 5- μm thick 3Ni/Al ($\times$) [65], 5- to 36- μm thick $\text{Ni}_{91}\text{V}_{09}$ /Al 1100 ($\blacklozenge$) [70], Monel 400/Al ($\triangle$) [1,2], 1.6- μm thick Pt/Al ($\blacktriangledown$), 3.0- μm thick Ti/2B ($\bullet$) [148], 25- μm thick 3Nb/Si ($\blacksquare$) [67], 5.0- μm thick Ni/Ti ($\square$) [101], and 2.5- μm thick Sc/Au ($\triangledown$) [90]. Foils were ignited in air and T_0 was $\sim 298\text{ K}$.

Fig. 14. Dynamic TEM images before and during the passage of a high speed (14 m/s) reaction front in 0.25- m thick Ti/2B [151]. The multilayer was ignited by a laser pulse outside the field of view.

Fig. 15. Plot of reaction front position versus time for 1.6- m thick Pt/Al foils with bilayer thicknesses ranging from 320 to 1600 nm. The foils were ignited in air at a point with $T_o \sim 298$ K.

Fig. 16. Average axial self-propagating flame velocity in Ni/Al multilayers as a function of one-quarter bilayer thickness (δ) and bilayer thickness (λ) [174]. The blue dots correspond to experimental observations, while the open circles and red triangles correspond to predicted values obtained from a reduced continuum model. The open circles correspond to data obtained using a premixed width of 0.8 nm, whereas the red triangle data points were obtained for a premix width of 0.91 nm.

Fig. 17. Cross sectional SEM image of a planar Zr-Al-NiCu multilayer foil reacted at $T_o \sim 298$ K [71]. Images show a banded microstructure in cross section after the passage of an oscillatory front. The reaction direction is from left to right. The multilayer was clamped between two copper blocks and ignited at a point using a 30 V spark.

Fig. 18. Predictions of oscillatory reactions in reactive Ni/Al multilayers as a function of ambient temperature (T_o), from [198]. In this figure, maximum total power (triangles) and reaction front position (circles) are plotted as a function of time following ignition. Results are shown for a single multilayer with $\delta = 40 \text{ nm}$ and $w = 3 \text{ nm}$.

a. Time lapse optical images in plan view

b. Thermal image of front

c. SEM of sectioned CoAl

Fig. 19. (a) Time lapse, plan view images showing a spin reaction front in a 7.5- μm thick Co/Al foil (66.4 nm bilayer thickness). (b) Overlapped optical and thermographic images of a reacting 7.5- μm thick Co/Al multilayer (250 nm bilayer thickness) demonstrating large temperature variation near a spin front. (c) Cross sectional SEM image showing a ~30 μm-thick Co/Al multilayer (with $\lambda = 33.2$ nm) after reaction. The microstructure is

composed of large, equiaxed CoAl grains with no evidence of a banded microstructure. A rippled surface morphology is evident.

a. Forward heat transfer forms diffusion zone

b. Subsequent transverse band passage

Fig. 20. Predicted temperature (T) and reactant concentration [C] profiles plotted as a function of position across an unstable, propagating reaction front. This figure includes times when (a) diffusion is occurring adjacent to a previously reacted area and (b) after the arrival of a transverse band in the pre-heated area shown in (a). A spatial description

of phase changes is also depicted in schematic cross sections representing $\frac{1}{2}$ bilayer of material, from [137]. The melting temperature (T_{melt}) indicated with a dotted line is that of Al. The insets include high-speed, plan view optical micrographs of a propagating reaction front in a 7.5- μ m thick Co/Al multilayer as it undergoes a 2-D instability.

Fig. 21. Model prediction of a 2-D instability in a planar Ni/Al multilayer [204]. The local surface temperature is represented by the color code shown on the right. The computations were performed using a temperature-dependent thermal conductivity model. Point ignition occurred near the bottom left corner of the images.

Fig. 22. Plots demonstrating stability boundaries for planar Ti/Al and Ti/3Al [145] as well as Co/Al multilayers [137]. In the top plot, the burning rates of Ti-Al (with different total thicknesses) are plotted vs. T_0 . The bottom plot shows the reaction propagation speeds of a 7.5- μ m thick Co/Al multilayer for different T_0 . The bilayer thicknesses are specified in the legends.

Fig. 23. Plan-view optical images of reaction fronts in 7.5- μm thick Co/Al multilayer foils with bilayer thicknesses of (a) 33.2 nm, (b) 75 nm, and (c) 250 nm. Results are shown for $T_o = 298\text{ K}$ and 448 K. Stable propagation is observed for the 33.2-nm multilayer at both temperatures. The 75-nm bilayer Co/Al foil undergoes steady propagation when $T_o = 448\text{ K}$, whereas the 250-nm bilayer Co/Al exhibits a 2-D instability for both temperatures. Each multilayer was ignited in air at a point outside the field of view.

Fig. 24. Plan view optical images showing a propagating intermetallic reaction front, for times up to 8 ms following point ignition in a 2.5- m thick Sc/Cu foil, followed by a slower propagating oxidation front. The reaction waves are moving from left to right. The Sc/Cu foil was ignited in air at $T_o \sim 298$ K.

Fig. 25. Reaction front position as a function of time for Ni/Ti multilayer foils with bilayer thicknesses of 473 nm or 103 nm. Results are shown for reactions at pressures of 637 Torr and 10 mTorr [202].

Fig. 26. X-ray diffraction patterns obtained from CoAl, ScAu, ScCu, YAu, and YCu foils after self-propagating reactions in medium vacuum, ~ 0.1 mTorr [90,100]. Each pattern is indexed to the corresponding B2 (CsCl type) structure.

Fig. 27. X-ray diffraction patterns obtained from reacted 5.0- μm thick, freestanding Ni/Ti multilayers with bilayer thicknesses ranging from 6.5 to 125 nm [101]. The cross sectional, high-angle annular dark-field (HAADF) TEM image at the bottom of the figure shows a foil (originally with bilayer thickness = 83.3 nm) after reaction in vacuum to form multiple phases, including B2 NiTi, B19' NiTi and NiTi₂. The fine scale (< 100 nm wide) precipitates that appear dark in this image are Ti rich and have an out-of-plane periodicity that is similar to the original bilayer thickness. Each Ni/Ti multilayer was ignited at a point in medium vacuum (~ 0.1 mTorr) with $T_o \sim 298$ K.

Fig. 28. X-ray diffraction pattern obtained from a reacted Pt/Al multilayer film (bilayer thickness = 48.8 nm) and an corresponding simulated pattern [60]. The inset shows the 76-atom unit cell of metastable, rhombohedral PtAl. This Pt/Al multilayer was initiated at a point with $T_o \sim 298\text{K}$.

Fig. 29. X-ray diffraction patterns obtained from 2.5 nm Sc/Cu (bilayer thickness = 164 nm) prior to reaction (bottom pattern), after reaction in 637 Torr of air (middle pattern) and after reaction in 0.1 mTorr (top pattern). Sc₂O₃ forms when reacted in air, but is absent after reaction in vacuum. Each freestanding Sc/Cu multilayer was ignited at a point with $T_o \sim 298\text{K}$.

Fig. 30. Schematic illustration of the methodology used for reactive multilayer soldering.

Fig. 31. Cross sectional SEM images showing Si wafers bonded using 60- m thick reactive NanoFoil® [143]. Local soldering was accomplished using a bonding pressure of 0.5 MPa (top image) and 5.0 MPa (bottom image).