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Numerical modeling of self-propagating reactions in Ru/Al nanoscale multilayer foils

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The Ru/Al system integrates high energy density and high product ductility and serves as an alternative for utilization as nanoscale reactive multilayer. We present a modeling study that relates the Ru-Al phase transformations occurring during self-propagating reactions with macroscopic reaction parameters such as net front velocity and reaction temperature. We coupled equations for mass and thermal transport and used a numerical scheme to solve the differential equations. We calculated the temporal evolution of the temperature distribution in the reaction front as a function of the multilayer bilayer thickness. The calculated net velocities were between 4.2 m/s and 10.8 m/s, and maximal reaction temperatures were up to 2171 K, in good agreement with measured data. Interfacial premixing, estimated to be around 4 nm, had a large influence on reaction velocities and temperature at smaller bilayer thicknesses. Finally, the theoretical results of the present study help to explain the experimental findings and guide tailoring of reactive properties of Ru/Al multilayers for applications. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928665]

Nanoscale reactive multilayers store large amounts of chemical energy and release it during self-propagating reactions.[1–3] The amount of stored energy and the reaction characteristics are given by the adequate choice of the constituents, the bilayer thickness, Λ, and the interfacial premixing, ω. After local ignition, a micron-scale reaction front travels along the multilayer with net velocities up to 90 m/s.[3] The foil rapidly heats up to temperatures >1273 K. This kind of energy release makes reactive multilayers attractive for utilization as localized heat sources where heating and cooling occur in less than 1 s. For example, components can be joined at micrometer scale with very limited thermal exposure.[4,5]

Researchers have studied the self-propagating reaction in various binary metallic multilayers and their transformation to intermetallic compounds.[2,3,6–13] Those phases are highly brittle.[14,15] However, product ductility is often desirable to ensure mechanical reliability during operation.[16] Thus, intermetallics formation narrows down materials selection. Recently, we identified potentially the best compromise between high energy density needed for joining at smallest scale and high product ductility for the Ru/Al system.[17] The product phase B2-RuAl is one of the few intermetallic compounds with substantial room temperature ductility.[18,19] As indicators for high energy density, we determined (1) the net velocity by following the front propagation in high-speed videos and (2) the peak temperature of the reaction via the measurement of the temporal temperature evolution. For the latter measurements, we used a one-color high-speed pyrometer. The emissivity was chosen to one enabling us to capture temperature profiles generally showing minimal temperatures. In addition, we

carefully cross-checked the peak temperatures via peak shift analysis in *in-situ* diffraction studies. Velocities as well as peak temperatures serve as reference in the present study. We measured maximal net velocities of 11 m/s and maximal peak reaction temperatures of 2173 K. In addition to the maximal reaction temperature, the diffraction experiments also revealed a one-step reaction mechanism to RuAl. We also utilized the observed transformation behavior to study the RuAl nucleation process at a single interface under rapid heating via atomistic simulations.[17]

Here, we aim to relate the RuAl formation mechanism to our macroscopically measured net velocities and peak temperatures. By doing so, we will provide consistency of the suggested formation mechanism and said reaction characteristics. In addition, the presented reaction modeling enables us to produce parameters for future theoretical studies where simpler configurations are considered. One example might be the assessment of component heating during joining where reactive multilayers act as local heating source. For the current study, we require reaction front modeling on an adequate time and spatial scale. Time and spatial constraints are determined by the lateral front dimensions (several tens of micrometers) and its fast propagation (several tens of m/s). Modeling has to consider the local balance of heat generation due to intermixing and phase formation and heat dissipation into the front surrounding. This balance determines the net propagation velocity and the temperature evolution which have been measured in our experiments. The temporal and spatial limitations of atomistic simulations impede modeling of a propagating front and are, thus, inadequate for our purposes. To overcome the limitations we

used numerical continuum simulations. The effort draws on the previously suggested direct RuAl formation. More specifically, we use (1) an estimated interdiffusivity to capture intermixing and (2) thermodynamic functions to describe the phase formation within the front. This enabled us to model front dimensions, front propagation, and temperature profiles, which were subsequently compared with experimental measurements.

Next, we outline our approach. Figure S1 presents the typical microstructure of our as-prepared Ru/Al multilayers.[20] The sublayers are nearly uniform with approximately parallel interfaces. The inset shows details of the interface. While we cannot exclude atomic intermixing, we note the absence of phase formation. Hence, we describe the microstructure as flat sublayers with sharp interfaces. Intermixing will be included indirectly (see discussion below). To model the reaction, we utilize our previously developed numerical scheme[21] under the following assumptions: (1) propagation parallel to the interfaces, (2) one-dimensional, diffusion limited RuAl growth perpendicular to the interfaces, (3) physical quantities are functions of temperature and phase, and (4) adiabatic reaction conditions. Under these conditions, we couple the equation for heat conduction with laws describing intermixing and phase formation. We use the heat equation with a source term

$$\rho \times C_p \times \frac{\partial T}{\partial t} = \nabla \times (\kappa \times \nabla T) + \alpha \times \Delta H_r, \quad (1)$$

where ρ denotes the density, C_p is the heat capacity, κ is the thermal conductivity, T is the temperature, and t is the time. The percentage of the reaction product is denoted by α, and ΔH_r is the change in enthalpy due to the reaction. All phase changes are included using discontinuous thermal properties. Equation (1) neglects radiative heat losses. Jayaraman *et al.* report for Ni/Al multilayers negligible radiation effects for foils thicker than $8\,\mu m$.[22] We draw on their findings and chose a total thickness of $>6\,\mu m$ for our freestanding Ru/Al samples which is close to the critical thickness for Ni/Al foils. Consequently, we suggest that heat losses due to radiation do not dominate the propagation behavior in the Ru/Al samples and can be omitted in Equation (1).

The reaction enthalpy, ΔH_r, is a function of Λ and ω where premixing reduces the available chemical energy according to[23]

$$\Delta H_r = \left(1 - \frac{2\omega}{\Lambda}\right) \times \Delta H_f, \quad (2)$$

where ΔH_f denotes the enthalpy of formation of RuAl.

We use Equation (2) to estimate ω and draw on measured peak temperatures. The latter increase with Λ from 2029 K to 2218 K. Assuming that the individual temperatures equal the respective adiabatic temperatures (calculated using $\Delta H_r(\Lambda)$ in Equation (2)), we found the best match between experiment and theory for $\omega = 4\,nm$. The adiabatic temperature $T_{ad}(\Lambda)$ increases with Λ from 1982 K to 2214 K. $\omega = 4\,nm$ is consistent with premixing zone sizes of other metallic multilayers, such as that of Ni/Al.[24] Thus, we perform numerical modeling at $\omega = 4\,nm$.

Next, we made use of $T_{ad}(\Lambda)$ when calculating the growth percentage α at every time step. We define the incremental increase of $d\alpha$ through the incremental growth dX of the product phase via

$$d\alpha = \frac{dX}{\Lambda/2}. \quad (3)$$

To evaluate Equation (3), we assume parabolic growth kinetics for RuAl

$$X = \sqrt{\frac{2 \times D \times t}{\beta}}, \quad (4)$$

where β is a growth factor determined by the concentration profile around the growing RuAl and can be taken as ~ 0.2,[21] and D is the interdiffusivity of the intermetallic. The best match with the experimental net velocity data was obtained for $D_0 = 1.91 \times 10^{-7}\,m^2/s$ and $Q = 105\,kJ/mol$, where D_0 and Q are the pre-exponential factor and the activation energy, respectively, in the Arrhenius dependency of D. Comparing the effective activation energy used in the fit with the measured bulk activation energy Q_{bulk} for Ru diffusion in Al (199 kJ/mol),[25] it is found that $Q/Q_{bulk} = 0.53$. Since the Ru/Al multilayers are nanocrystalline and contain a high fraction of grain boundaries, we assume that grain boundary diffusion dominates. Under these conditions, the activation energy Q for atomic transport is generally lower and the ratio Q/Q_{bulk} takes values between 0.4 and 0.6.[26] Consequently, the activation energy of 105 kJ/mol used in the present study to model the atomic diffusion in Ru/Al multilayer is in reasonable agreement with the estimations based on literature data. We also adopted an empirical approach to model the Λ-dependence of the measured net front velocity v using

$$v = \sqrt{D_0 \times \exp\left(-\frac{Q}{R \cdot T_{ad}(\Lambda)}\right)} \times \frac{A}{\Lambda} \times \left(1 - \frac{B}{\Lambda}\right) \quad (5)$$

to cross-check the interdiffusion parameters. The parameters A and B are calibrated constants. In our case $A = 2.77 \times 10^7$ $nm^2 \cdot s^{-1}$ and $B = 15.39\,nm$. Note that $T_{ad}(\Lambda)$ enters Equation (5) through the Arrhenius-dependency of the interdiffusivity. Equation (5) is an empirical relationship drawing on the analytically deduced proportionality between v and $D^{0.5}$ (Refs. 8 and 27) and on an earlier reported empirical equation.[24] However, the advantage of Equation (5) is the explicit dependency of interdiffusivity.

The physical and thermodynamic information required to solve the coupled Equations (1), (3), and (4) for Ru/Al multilayers were obtained from the literature or databases and are summarized in Table SI and Table SII (see supplementary material[20]). We implement temperature dependent physical and thermodynamic data. The enthalpy of the individual phases is approximated by third order polynomials. Finally, we implicitly discretize Equation (1) in a forward time Crank-Nicolson finite difference scheme. For symmetry reasons, we modeled the reaction behavior in half bilayers. The cell had a length of $120\,\mu m$. The grid size and the time step were set to 200 nm and 0.5 ns, respectively. The simulations captured maximal the first $6\,\mu s$ of the reaction. The

reactions were started at the edge of the domain by applying a constant temperature boundary condition set at adiabatic temperature, which was removed once the thermal front started propagating. For details of the implementation, the reader is referred to our previous work.[21]

Figure 1 shows the simulated temperature profiles of the reaction front for the bilayer thicknesses of 22, 44, 88, and 178 nm. The comparison with the adiabatic reaction temperature of 2247 K reveals that the maximal reaction temperatures of the simulated profiles are generally lower and decrease with decreasing Λ. We explain both observations by the increasing impact of the pre-mixing effect with decreasing Λ. As noted earlier, pre-mixing often occurs during deposition and reduces the stored chemical energy in the multilayer by the heat of mixing of the multilayer. Assuming a constant premixing width, ω, for all periods, the volume fraction of intermixing increases for smaller Λs. Consequently, the stored energy is reduced more severely for the latter cases. This was also confirmed by calorimetric studies in other systems such as Ni/Al.[24] In addition to the lowered temperatures compared to the theoretical adiabatic temperature, Figure 1 also reveals steeper temperature profiles for smaller Λs corresponding to faster wave propagation. For increased velocities, heat has less time to diffuse forward resulting in reduced thermal profiles.

By tracking the temporal evolution of a specified temperature (here we used the 1200 K-position) in the profiles, we calculated the instantaneous and the net front velocity for each bilayer thickness. Figure 2(a) plots the instantaneous velocity with time and shows a similar evolution for all Λs. Initially, the instantaneous velocity quickly drops to a minimum and, subsequently, increases again, goes through a maximum, and reaches the steady state value. The instantaneous velocities show oscillations around an average velocity value. Similar oscillations were present in our previous theoretical study on self-propagating reactions in Ni/Al multilayers where we used the same model than for the present study. Parametric studies enabled Gunduz *et al.* to prove that the oscillations are a numerical artifact.[21] Thus, we assume that discretization causes the oscillatory behavior in Figure 2(a) rather than physical effects. However, it is possible that oscillations occurring in the Ru/Al system at larger bilayers may
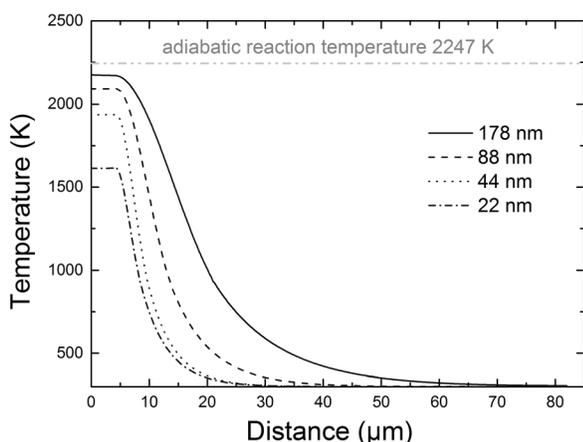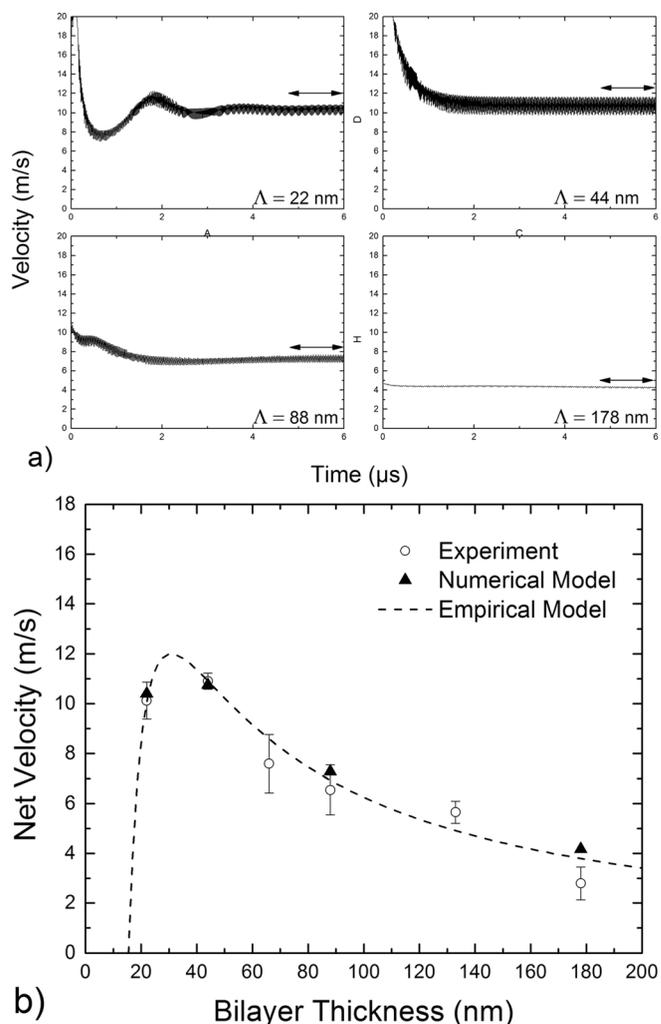

a)

b)

FIG. 2. (a) Variation of instantaneous velocity for the considered bilayer thicknesses. The simulation was stopped after steady state was reached. The time interval in the steady state regime indicated by the arrows denotes the period of averaging to calculate the nete velocity. (b) Net velocities according to (a) compared with the experimentally determined front velocities.[17] The curve of the empirical modeling (Equation (5)) is also shown.

have some physical significance, similar to experimental observations for other systems.[6,9] Latest experiments revealed front instabilities also for Ru/Al multilayers where faster transverse bands oscillate in-plane perpendicular to a net reaction front. The underlying physical principles causing the evolution of these bands are currently still an open research topic where several mechanisms have been proposed.[28,29] To study oscillatory behavior, we need to describe the processes within the reaction front (1) on a smaller length scale and (2) in two dimensions. We currently expand our model accordingly and will present the results in a separate study focusing on the oscillations in Ru/Al multilayers.

To compare the calculations with our experimental data, we calculate v. For a given bilayer thickness, we averaged the instantaneous velocity over about 1.5 μs within the steady state regime (indicated by the arrows in Figure 2(a)). Figure 2(b) plots v together with the measured net velocities as a function of Λ. We note the good agreement between modeled and measured velocities for the studied Λ range. With decreasing bilayer thickness, v increases up to 11 m/s

FIG. 1. Front temperature profiles across the foil as a function of bilayer thickness Λ. The adiabatic reaction temperature of 2247 K is also indicated.

for $\Lambda = 44$ nm before it starts to drop down for $\Lambda < 44$ nm. Figure 2(b) also shows the results of the empirical fit using Equation (5) which is in good agreement with the numerical model and the measurement. The fit also reproduces the transition in the net velocities with decreasing Λ and enables us to estimate the transition point to be about 30 nm. This transition was also experimentally demonstrated for a number of other reactive multilayer systems.[6,9,11,24,30] Researchers generally assume for bilayer spacings larger than the transition point that the increase in the atomic diffusion distances perpendicular to the interfaces slows down the net velocity. At smaller bilayer thicknesses, however, the loss of chemical energy due to interfacial intermixing (fabrication induced pre-mixing) becomes increasingly substantial as the fraction of the intermixed zone at the interfaces increases. Consequently, the net velocity decreases again below a critical Λ value (here, about 30 nm) defining the transition point.

Since the premixing effect draws upon the loss of chemical energy due to atomic intermixing, we expect an impact on the reaction temperatures when Λ is varied. Based on the modeling of the temperature profiles in Figure 1, we, thus, determined the theoretical peak temperatures as a function of Λ. Figure 3 shows the result together with experimentally measured reaction temperatures. Both data sets exhibit an asymptotic trend of increasing reaction temperatures with Λ. The asymptotic behavior is consistent with the decreasing volume fraction of premixing for larger bilayer thicknesses. The associated increase in stored chemical energy leads to higher reaction temperatures. Although the model systematically underestimates the measurement it correctly reproduces the experimental trend. For the largest bilayer thickness of 178 nm, the modeled reaction temperature takes a value of 2171 K which is close to the adiabatic reaction temperature of 2247 K. Thus, we expect that premixing effects become negligible for Ru/Al multilayer for periods >178 nm. We further note an increasing difference between the modeled and the experimental maximal temperatures. We assume that the integration of the premixing effect in our numerical model causes 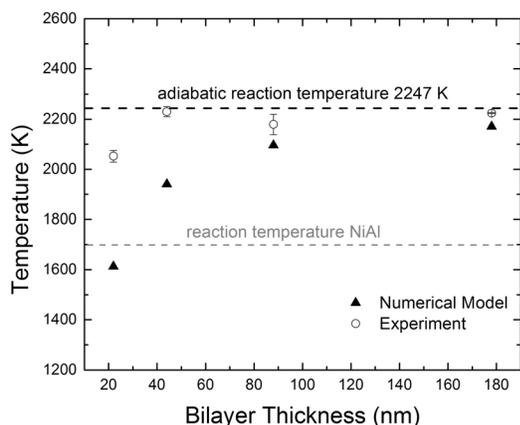the increasing deviation from the experiment. Premixing is accounted for via Equation (2), which approximates the composition profile across the interface with a step function. The latter drops to zero when the intermixing distance is equal to bilayer thickness and, in consequence, attributes no residual energy to the premixed zone. Instead of stepwise changes in composition, gradual profiles across the interface are more realistic for some binary systems. The intermixing zone should also store residual energy. Calorimetric experiments for Ni/Al multilayers indicate that Equation (2) underestimates the actual stored energy especially for samples with small periods.[21] Measured heats of reaction are considerably higher and functions assuming a gradual composition change across the interface show improved fitting of the measured data in the small Λ range. However, in the case of Cu/Zr multilayers the measured heat of reactions in the small Λ range can be better fitted under the assumption of a stepwise composition change.[23] For larger Λs, the functions are equal. Both examples demonstrate: (1) the adequate choice of the function forms depends on the considered material system and (2) the estimated heat of reactions based on the step profile assumption may be interpreted as lower bounds. Since we do not have experimental evidence for which function would replicate the pre-mixing effect best for the Ru/Al multilayers, we chose the conservative approximation of the step profile used in Equation (2). By doing so, we probably underestimate the heat of reactions and consider the modeled reaction temperatures presented in Figure 3 as lower bounds; especially for the bilayer thicknesses of 22 and 44 nm. The general lower modeled reaction temperatures compared with the measured ones support this hypothesis.

Figure 3 also compares the Ru/Al reaction temperatures with those for Ni/Al foils. Although both systems have the same chemical energy density of ~ 8 kJ/cm^{-3}, Ru/Al multilayers reach higher temperatures (as much as 300 K, see Figure 3). This is due to the melting of NiAl which consumes some fraction of the stored chemical energy and limits the reaction temperature. Conversely, for Ru/Al reactions, the adiabatic temperatures are lower than the RuAl melting point, so compound melting does not limit the reaction temperature resulting in the significantly higher peak temperatures.

In conclusion, we modeled the self-propagating reactions in nanoscale Ru/Al multilayers. Modeling draws on independently determined physical and thermodynamic data. We inferred the interdiffusivity from our measurements of net front velocity and peak temperature. Finally, we were able to model temperature profiles for various bilayer thicknesses enabling us to theoretically study the effect of multilayer period on net velocity and maximal reaction temperature. For the studied range of bilayer thicknesses, the results from the model agree very well with the experiment. The present study provides the necessary fundamentals for our current research effort dedicated to the open-research topic of reaction instabilities.

FIG. 3. Variation of the simulated maximal reaction temperature with bilayer thickness. The measured maximal reaction temperatures[17] and the adiabatic reaction temperature for Ru/Al multilayers are presented for comparison. The measured reaction temperature for Ni/Al foils is also shown as a benchmark value.

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