# IDENTIFYING THE ROLE OF PRESSURE ON THE RESPONSE OF REACTIVE MATERIALS TO THERMAL INITIATION: A MOLECULAR DYNAMICS STUDY

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## ABSTRACT

Molecular dynamics (MD) simulations using a first principles-based Embedded-atom-Method (EAM) potential are used to simulate the exothermic alloying reactions of a NiAl bilayer at 1500 K and 1100 K. Both microcanonical (NVE) and isoenthalpic (NPH) MD simulations are used to demonstrate the influence of pressure on atomic mixing and subsequent alloying reaction. The NVE simulations, in which the volume is fixed and in which pressure increases as the exothermic reactions cause an increase in the system temperature, have a much slower reaction rate than those of the NPH-MD simulations in which the pressure is maintained at 1 bar. The mechanism of the mixing is the same for all simulations: As mixing and reaction occurs at the interface, the heat generated first melts the Al layer, and subsequent mixing leads to further heat generation after which the Ni layer melts, leading to additional mixing until the alloying reactions are completed. The results indicate that pressure has a significant influence on the rates of atomic mixing and alloying reactions.

## 1. INTRODUCTION

Reactive materials (RMs) hold the promise of delivering greater lethality in future weapons systems by serving structural and energetic functions with tailored mechanical and energetic properties. However, to achieve the full promise, we need to identify and understand the fundamental physical and chemical processes that control the energy release of RMs during dynamic loading. For example, we need to quantify physical properties such as diffusion rates in order to guide the development of RMs with tailored behavior. Measuring some of these properties can be very challenging, particularly in extreme loading environments, but a science-based modeling capability to predict such properties will provide a means for overcoming measurement limitations. Of particular importance in the design process is the accurate modeling of the dynamic response of an RM to rapid thermal or shock loading, since they are the key components that affect the performance of an RM in a weapons application. One of the most widely studied RM systems is a nickel-aluminum mixture. Studies indicate that when such a system is used as a projectile, the energy release occurs in stages, with the first stage immediately following impact. The energy release is due to an alloying reaction between the aluminum and nickel. The second stage energy release is the combustion of the alloyed metal particles in the air. Times scales for the various processes range from microscale to hundreds of milliseconds. Clearly such an event is a multi-scale phenomenon, and can only be accurately portrayed using a hierarchy of models and simulations based on fundamental physical principles. We are working toward instituting a multiscale modeling framework that can be used as a robust and reliable modeling and simulation tool in the design and development process of RMs.

The most detailed fundamental characterization of the chemical and physical behavior of RMs subjected to rapid thermal or shock loading is obtained through atomistic simulations. This information can then be transitioned to the meso- and continuum scale models that have been or are being developed for RMs. Such a transfer will reduce the limitations in predictive capabilities at larger scales that are due to insufficient knowledge of the details of the various chemical and physical processes under conditions of extreme mechanical, thermal and chemical gradients within a reacting RM. By capturing and incorporating the proper chemical and physical descriptions of the dynamic behavior at the smaller scales and transitioning this information to larger scale models, more accurate analyses or predictions of complex phenomena associated with material response can be performed. This information, in turn, can be used to design RMs with specific performance for various weapons that will maximize their performance. Incorporating a fundamental knowledge of material behavior under extreme conditions into the design and development of RMs will substantially reduce the time and fiscal

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expenditures associated with their development and testing.

In this work, we present our efforts to identify the role pressure plays in atomic mixing and reaction of a layered Ni-Al system. This is the first in a series of studies to characterize and identify elementary processes such as atomic mixing and melting under rapid thermal loading, a phenomenon that will result from either rapid mechanical loading or rapid thermal initiation. We initiated this study after an exploratory microcanonical molecular dynamics (NVE-MD) simulation of a Ni/Al layered system was performed, in which the system was initially equilibrated to 1200K, 1 atm. The exothermic alloying reactions occurring at the interface produced a continuous overall heating and pressure rise in the material to a point in time at which the alloying reactions stopped. At the point of the quenching of the reactions, the system pressure was extremely high, suggesting that pressure plays a significant role in the reaction rate for this system. Since RMs will be subjected to extreme pressures in military applications, it is important to understand the dependence on the atomic mixing and alloying with pressure.

The model material used to explore these processes is a system similar to that used in an earlier NVE-MD simulation [Zhao et al., 2007] of a Ni/Al bilayer whose initial temperature was 1500 K. In that study, the temporal behaviors of the system temperature and pressure were monitored, and showed very interesting features, particularly in the pressure profiles (with very similar features to those shown in Fig. 1(a), in our attempted reproduction of the Zhao et al. results).

The results of Zhao et al. [2007] showed that the system pressure for the first ~ 75 ps of the simulation is constant (~11 GPa), after which it rises to a maximum which coincides with the time the Al layer melts. Shortly thereafter, the Ni layer melts as heat continues to evolve with the continuous atomic mixing/alloying. The pressure drops and converges to a final value of ~11.3 GPa (in the Zhao et al. study) after alloying and intermixing reaches completion. In order to study the effect of pressure on the overall process, we will repeat the same calculation, except the equations of motion will be coupled with a barostat, thus generating a trajectory in the isoenthalpic ensemble (NPH). In this way, we can explore the temporal behavior of this system at a fixed pressure (in this case, 1 atm). We will also perform the simulation at in which the initial bilayer is at a lower temperature (1100 K), to examine the effect of initial temperature of the system on initiation and propagation of the alloying reactions.

## 2. COMPUTATIONAL DETAILS

The Ni/Al bilayer used in all simulations is composed of 47628 Ni and 15552 Al atoms arranged in a 103 Å x 82 Å x 89 Å filament, with the Ni/Al interface normal to the [111] direction, as described in Zhao et al. [2007]. The potential energy function used in the simulations is the same as that used by Zhao et al. [2007] and was developed by Mishin et al. [2002] for *B*2-NiAl. This potential follows the embedded-atom method (EAM) formalism and was parameterized using both experimental properties and *ab initio* data. The potential accurately reproduces the basic lattice properties of *B*2-NiAl, planar faults, and point-defect characteristics. It also reproduces the energetics and stability of all other structures included in the fit. The FCC lattice constants used to generate the bilayer are 3.464 Å for Ni and 4.0785 Å for Al and were determined from NPT-MD simulations of both bulk Ni and Al at 298 K, 1 atm.

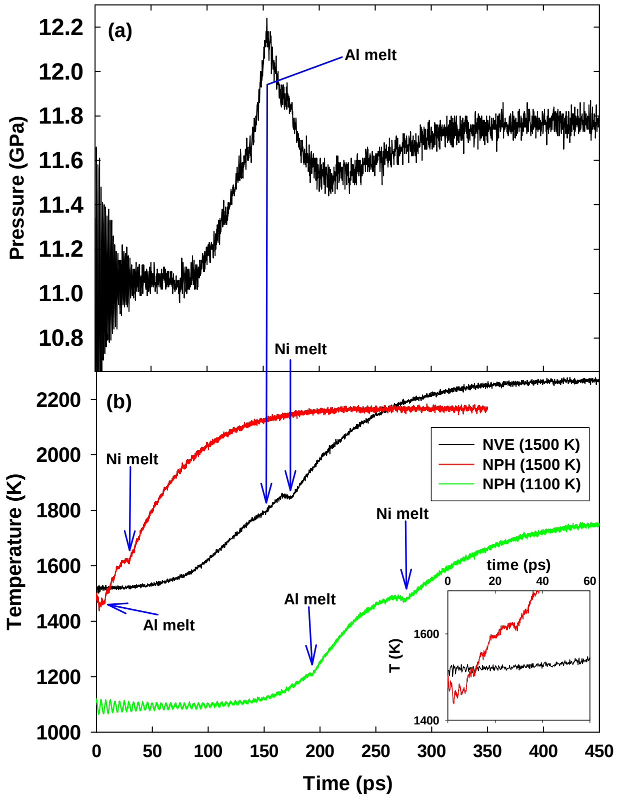

Figure 1. Temporal profiles of (a) system pressure and (b) system temperature for NVE-MD simulation in which initial Ni/Al bilayer is at 1500 K. The red line in Fig. 1(b) denotes the system temperature from NPH-MD simulations under the same initial conditions. The inset in Fig. 1(b) is an enlargement of these system temperature profiles between 0 and 60 ps. The green line in Fig. 1(b) denotes the system temperature from NPH-MD simulations for a bilayer with initial temperature of 1100 K.

Few details of the initial conditions used by Zhao et al in their NVE-MD simulations were given, other than the system was assigned an initial temperature of 1500 K. Thus, we arbitrarily chose to initiate the trajectory from an unrelaxed model in which all atoms are in the FCC lattice sites. Atomic velocities were randomly assigned to correspond to an initial temperature of 1500 K, and a short NVE-MD trajectory was run in which the atomic velocities were scaled at every 0.0072 ps to maintain an instantaneous system temperature of 1500 K. We were unable to perform an extended equilibration without alloying reaction at the interface occurring; thus, after a short period (after which the system was not completely equilibrated), we began a "production" NVE-MD simulation for a duration 450 ps to compare with the Zhao et al. results [see Fig. 1(a)].

Initial conditions for the NPH simulations were generated after a series of NPT-MD equilibration trajectories to raise the system temperature gradually. First, the same Ni/Al bilayer used for the previously described NVE-MD simulation was equilibrated using NPT-MD simulations at T=298 K, P = 1 atm. Upon completion of this trajectory, the final state was used in a subsequent short NPT-MD simulation (15 ps, 1 atm) with a target temperature of T=800 K. No reaction occurred at the interface by the end of this second trajectory. This procedure was repeated choosing a target temperature of 1100 K, and the system configuration at the end of the equilibration trajectory was used for initial conditions of the "production" NPH-MD simulation at T=1100K. Again, reactions at the interface had not yet begun at the end of the equilibration trajectory at 1100 K. We attempted to ramp the temperature up to 1500 K using the aforementioned procedure, and equilibrate to P=1atm; however, reaction at the interface began almost immediately. Thus, in order to study the system at 1500 K, 1 atm, we were forced to use an incompletely equilibrated system configuration for which only a few equilibration steps were taken to provide the proper system temperature and an approximately relaxed system pressure. Although not fully equilibrated this initial state was sufficiently relaxed that the imposed pressure (1 atm) was quickly reached.

## 3. RESULTS AND DISCUSSION

**3.1 NVE-MD, T=1500 K.** The behavior of the pressure as a function of time during this trajectory is shown in Fig. 1(a) and can be directly compared with Fig. 5 of Zhao et al. [2007]. The corresponding system temperature is shown in Fig. 1(b). The features of the pressure profile are very similar to those of Zhao et al. [2007], except they are shifted in time by ~ 20 ps, and the pressure profile is consistently higher by 0.3 GPa for the duration of the trajectory. Zhao et al. [2007] did not provide a system temperature profile in their study; however, they provided a figure that described the temporal behavior of the Al layer only. Unfortunately, Zhao et al. [2007] did not define what the Al layer is, and we were unable to determine whether it is a fixed spatial range or whether it was the portion of the material composed only of Al atoms. Regardless, we were unable to reproduce that figure. In Fig. 1(b), however, we see that the system temperature begins to increase at about 75 ps, and there is a very slight dip at ~160 ps, which corresponds to the peak pressure of the system during this trajectory (Fig. 1a). This is the point at which Al melts, and corresponds to a system temperature of ~ 1800 K. After a short time and small temperature increase, the temperature profile shows yet another "dip", which corresponds to the point at which Ni melts in this simulation.

**3.2 NPH-MD, T=1500 K.** The temporal behavior of the system temperature in this trajectory is also shown in Fig. 1(b) for comparison with the results of the NVE-MD trajectory. In the NPH-MD simulation, pressure is continually relieved as the system temperature rises due to the coupling of the equations of motion with a barostat that requires the system to maintain an imposed pressure (in this case, 1 atm). The profiles are dramatically different. The temperature of the NPH-MD simulation immediately drops during the first few ps of the trajectory integration (see inset), which corresponds to the almost immediate melting of the Al layer at a temperature of ~ 1500 K. The system temperature then steadily increases until ~ 30 ps, at which time there is another slight dip in temperature before the temperature continually rises and levels off to 2164 K, ~ 100 K lower than that of the NVE-MD simulations. This second dip corresponds to the melting of the Ni layer, at a temperature of ~ 1600 K. Both melting temperatures are substantially lower than those in the system constrained to a constant volume (i.e. high pressure). The NPH-MD temperature profiles indicate that the alloying reactions and mixing have reached completion by 200 ps, well before that of the NVE-MD simulations.

A comparison of the snapshots from the NPH-MD and NVE-MD trajectories show no visual differences in the materials during the transition from bilayer to fully-mixed material; it appears the most significant impact of the pressure is on the rates of alloying, mixing and melting.

**3.3 NPH-MD, T=1100 K.** NPH-MD simulations at this lower temperature produced a different system temperature profile than the NPH-MD simulations at T=1500 K, as seen in Fig. 1(b), and provided a profile that was similar to the NVE-MD simulations at 1500 K. In this trajectory, the system temperature fluctuates about 1100 K up to 100 ps, after which time the temperature steadily rises to ~1200 K at 190 ps [see inset of Fig. 2(a)], which is the point at which the Al layer melts. A small dip in the system temperature occurs at ~ 275 ps, the point at which the Ni layer melts (~ 1480 K). The temperature then continually increases for the next 150 ps before leveling off to a final value of 1764 K.

Although we are showing system temperature profiles for the three trajectories, the material does not necessarily have a uniform temperature distribution throughout the material. To explore the temperature distribution in the material as it undergoes alloying, we will examine first the temporal profiles of layers of the material during the NPH-MD simulation in which the initial temperature is 1100 K. We partitioned the bilayer into 12 sections, for which temperature within each section was determined. Figure 2 shows the temporal profiles for each section of the material for the duration of the trajectory.

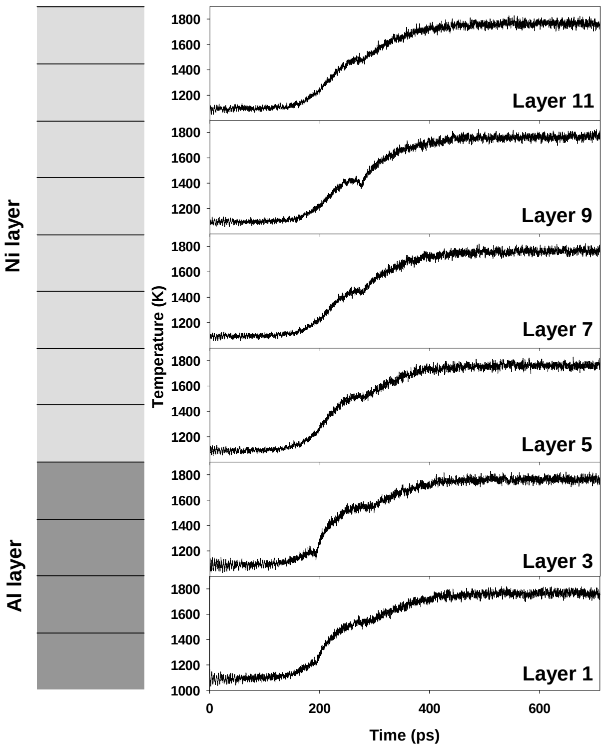

Figure 2. Temperature as a function of time at partitions of the layered material. The left-most schematic depicts the overall Ni/Al bilayer and the 12 partitions within which temperature of the material was averaged. The corresponding temperature profiles of the material are at the right of the schematic.

For convenience, the left-most shaded area in Fig. 2 is a schematic of the initial Al/Ni bilayer, illustrating the partitioning of the system to explore local temperature throughout the trajectory. For the most part, the overall features of the layers track those of the system temperature, with small differences corresponding to the features associated with melting. For example, layers 3 and 9 correspond to the central regions of the Al and Ni layers, respectively; these show the sharpest "dips" in the temperature profiles that are associated with their respective melting points.

Snapshots of the bilayer at 232, 275 and 710 ps during this trajectory are shown in Fig. 3. Under each snapshot is the corresponding temperature contour of the material relative to the instantaneous system temperature. It is clear that at 232 ps, the aluminum layer is disordered, and the melted Al layer is much hotter than the Ni layer, indicating that mixing into the melted Al is occurring rapidly.

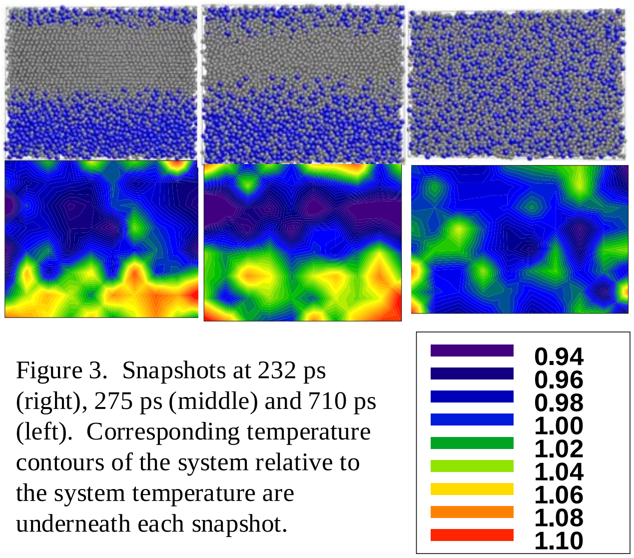

Figure 3. Snapshots at 232 ps (right), 275 ps (middle) and 710 ps (left). Corresponding temperature contours of the system relative to the system temperature are underneath each snapshot.

At 275 ps, the Ni region of the bilayer has a semblance of order but the temperature contour shows that this area is colder than the rest of the system, again indicating that heat from the mixing reactions is being absorbed by the Ni crystal as it melts. The Ni portion is completely disordered at 280 ps. The snapshot corresponding to the end of the trajectory (710 ps) shows that the mixing is complete and the Ni and Al are distributed in a homogeneous fashion. These figures indicate that in this process, there are significant spatial and temperature inhomogeneities in the material that will lead to large, ever-changing concentration and thermal gradients.

The snapshots in Fig. 4 allow an examination of the initial mixing reactions at the interface. Each snapshot in Fig. (4) corresponds to three views of the same configuration; the left-most snapshot shows the bilayer and the middle and right-most views are the top and bottom of the simulation cell. Since periodic boundary conditions are imposed in the simulation, the top and bottom show both sides of the Ni/Al interface, respectively.

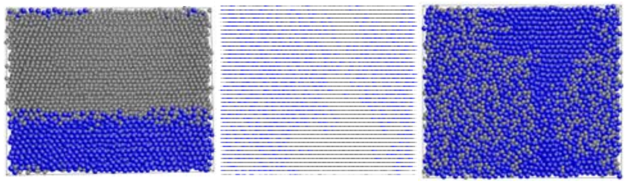

Figure 4. Snapshots of the system at 180 ps from three perspectives (see text). The middle and right-most frames show a perspective at the bilayer interface.

The snapshots correspond to the material at 180 ps, immediately preceding the time at which the Al melts (192 ps). The interface contains regions of both reacted and unreacted material. The interface at 192 ps has a larger degree of mixing; only a small portion of the Al layer remains unmixed at the interface. It is clear that uniform mixing at the interface does not occur, and is consistent with the inhomogenieties evident in the temperature contours of Fig. 3.

These inhomogeneities in local temperature and concentration gradients, coupled with an ever-increasing system temperature, will influence mass and thermal diffusion effects on the rate of reaction. Determining diffusion rates under these conditions poses quite a challenge. However, these effects are probably enhanced due to the small size of the bilayer and separation of the two interfaces. We expect that such rapid changes in temperature gradients for a bilayer having a significantly larger separation between reacting interfaces would probably not exhibit such rapid changes in the thermal gradients. We are continuing investigations to determine the influence on the layer thicknesses at various pressures on the reaction rates, in order to unravel and characterize the intricate relationship between pressure, temperature and system configuration.

## CONCLUSIONS

We have begun explorations into the dynamic behavior of a layered Ni-Al system subjected to rapid thermal loading; we have demonstrated that pressure strongly influences the reaction rate, but that the overall mechanism and material features during the atomic mixing and alloying process do not differ. This study has suggested further explorations into the effect on the reaction of the reactant space (i.e. the separation between interfaces in a layered system), as well as the dependence on temperature and pressure in the alloying reaction. Information generated such as this is crucial for proper inclusion in higher level scales to adequate capture the salient physics and chemistry of a complex, interdependent process.

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