Molecular dynamics simulations of the reaction mechanism in Ni/Al reactive intermetallics

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ABSTRACT

We present an atomistic level description of the reaction mechanisms in thermally ignited samples of reactive core/shell Ni/Al wires. The combination of very long simulation times (up to 0.1 µs) and very reactive core/shell nanostructures enables ignition at unprecedentedly low temperatures for molecular dynamics simulations. Samples ignited at low temperatures (900 K or less) follow a multi-stage reaction process involving solid-phase diffusion and the formation of the B2 NiAl phase, while samples ignited at higher temperatures, follow a direct reaction path with accelerated diffusion of Ni into molten Al, leading to a completely molten final state. Interestingly, NiAl nucleates and grows under a significant concentration gradient, which may explain the absence of other phases like $AlNi_3$. The formation of the B2 intermetallic slows atomic diffusion and consequently the reaction rates.

1. Introduction

Intermetallic reactive composites (IRCs) are a class of materials that can undergo exothermic reactions under mechanical or thermal insult. These materials are fast burning [1] and reach high combustion temperatures [2] without significant volume expansion or the formation of gaseous products. Such characteristics make IRCs promising candidates for applications where strong, localized sources of heat are required. They find applications as environmentally friendly primers [3], as nanoscale energy sources for bio-agent defeat and medical treatment [4], in thermal batteries [5] and in soldering or brazing [6]. Recent work has shown it is possible to engineer the performance of these materials by tailoring the nanostructure, either through the process of arrested milling [7,8] or through thin film deposition [9,10]. Such processing techniques lead to the formation of a finely dispersed laminated microstructure of Ni and Al, which shows increased sensitivity to thermal and mechanical initiation [8–10]. One of the long-standing, open scientific questions in this field is the reaction mechanism and its influence on reaction kinetics. This remains poorly understood, even for the most widely studied Ni/Al system. Such an understanding is vital for the macroscopic modeling and targeted design of IRCs.

Experimental determination of reaction mechanisms in nanostructured reactive composites is challenging due to the characteristic length (nanometers) and time scales (nanoseconds) involved. In particular for the Ni/Al system, speculation persists about mechanism of intermetallic formation during ignition and self-propagation. While in situ studies [11–13] have begun to shed light on the sequence of reactions during self-propagation of these formation reactions, the temporal and spatial resolutions attainable experimentally are still insufficient to capture the initial sequence of reactions. In particular, we lack a clear understanding of the process of nucleation and growth of the intermetallic phases in regions where Ni and Al have intermixed. Information regarding the microstructural evolution during self-propagation has also been obtained indirectly using rapid quenching experiments and ex situ cross-section transmission electronic microscopy [14–16].

Complementing experimental efforts, molecular dynamics (MD) simulations have provided insight into the atomistic mechanisms driving the reaction progress [17]. MD simulations have the advantage over other simulation techniques in that they explicitly capture the complex interplay between phase transformations, chemical mixing, thermal transport and mechanics [18–20] occurring under extreme conditions of temperature and pressure [21,4,22], with no input parameters save for the interatomic potential that describes the interactions between atoms. MD studies of the reaction mechanism under adiabatic conditions in samples ignited at elevated temperatures (1200 K and higher) [22–24] found a two-stage reaction where a period of Ni diffusing into

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molten Al is followed by the melting of Ni, leading to a final molten mixture of Ni + Al. All prior adiabatic simulations failed to observe the formation of intermetallics during reaction. Artificially maintaining a constant temperature during reaction in atomistic simulations has resulted in the formation of the B2 (NiAl intermetallic) [25–27]. The nucleation of B2, which followed the amorphization of the Al-rich side, was seen to adversely affect the effective diffusion rates [27]. However, the isothermal nature of these simulations do not allow for the study of the interplay between fast reaction kinetics and the formation of the intermetallic phases. Atomistic modeling of thermal ignition at lower temperatures (less than the melting point of Al), where the reaction progression could be expected to result in the formation of intermetallics, has remained computationally prohibitive.

In this work, we use long time (up to 0.1 μs), million atom simulations that lie at the limit of current computational capability [28] to describe the reaction process following thermal ignition of samples at temperatures as low as 650 K. We find that samples ignited at high temperatures follow reaction paths consistent with prior MD work [23] without the formation of intermetallics. However, samples ignited at 900 K or lower, show the heterogeneous nucleation of B2 NiAl *during* the exothermic intermixing process, providing the first atomic-level picture of the complex reactions during atomic intermixing and phase formation. Interestingly, B2 NiAl nucleates and grows under significant concentration gradients, which may be precluding the formation of the other intermetallic phases.

The remainder of the paper is organized as follows: Section 2 describes the simulation details. Section 3 describes the effect of phase formation on the overall reaction kinetics. Section 4 describes the characteristics of the nucleation and growth of the intermetallic phase. Finally, we discuss our conclusions in Section 5.

2. Simulation details

2.1. Model nanostructure

The model nanostructure we have chosen consists of Al clad Ni wires with a Ni core diameter of 12 nm and an Al shell thickness of 1.5 nm. The wire is oriented with the [0 0 1] crystallographic direction along its length (Z direction). The number of Ni and Al unit cells along the length of the wire are chosen so as to minimize the interfacial strain. The wire was created by combining 230 unit cells of Ni and 200 unit cells of Al along its length, leading to a strain mismatch of 0.05%. This structure contains 310,400 Al atoms and 841,110 Ni atoms, giving a Ni : Al ratio of ~2.72. The wire is 81 nm long, with periodic boundary conditions along the Z direction, while we use open boundary conditions in the transverse directions. Fig. 1 shows the as-built structure.

2.2. Thermal ignition and atomic interactions

To create a well-equilibrated sample, the structure is first relaxed using energy minimization, followed by a thermalization at 300 K. The pressure along the length of the wire is kept at 0.01 atm. Nosé-Hoover thermostat and barostat are used for the equilibration with coupling constants of 0.01 and 0.1 ps, respectively. To simulate the thermal ignition of IRCs, the entire structure is rapidly heated to the desired ignition temperature (T_{ig}) in 20 ps, still using the NPT ensemble. The samples were then thermalized at T_{ig} for a further 10 ps at 0.01 atm. The chemical evolution of the reactive system is then followed under isobaric–isoenthalpic conditions (NPH ensemble) for the duration of the reaction. The coupling constant for the barostat is switched to 1.0 ps for the

NPH simulations, and a time step of 0.5 fs is used to integrate the equations of motion. We use the LAMMPS package [29,30] to perform all our simulations and use the embedded atom potential developed by Purja and Mishin [31] to describe the interatomic interactions. The potential was parameterized using the lattice constants and formation energies of several intermetallics including NiAl and Ni_3Al and accurately captures the melting temperatures of these intermetallics as well as those for Ni and Al.

To extract local averages of variables of interest, the sample is binned using a two-dimensional grid in the transverse directions (X–Y) with cell dimensions of 5×5 Å. Local temperatures within each bin (T_I) are calculated after subtracting the center of mass velocities (v_I^{cm}) as follows:

$$v_I^{cm} = M_I^{-1} \sum_{i \in I} m_i v_i$$

where I is the set of atoms in each bin and $M_I = \sum_{i \in I} m_i$ is the mass of atoms in the bin.

$$T_I = \frac{2}{3N_I k_B} \sum_{i \in I} \frac{1}{2} m_i |v_i - v_I^{cm}|^2$$

k_B is the Boltzmann constant, N_I is the number of atoms in bin I and m_i and v_i are the masses and velocities of the atoms.

3. Reaction kinetics and associated mechanisms

3.1. Thermal ignition and underlying atomic processes

Fig. 2(a) shows the temperature evolution during the adiabatic reaction process for the samples ignited at different temperatures. Samples ignited at 1000 K and above are completely reacted within 1.5 ns and show reaction characteristics similar to those reported previously for bulk laminated structures [23]. Fig. 2(b) shows an expanded view of the first 2 ns in Fig. 2(a). Reaction times for samples ignited at 900 K or lower are considerably longer, with a mere 350 K decrease in ignition temperature being sufficient to increase reaction times by two orders of magnitude. To obtain an effective, overall reaction time (τ) for each temperature we approximate the temperature evolution with time by an exponential:

$$T = (T_{ig} - T_{fin}) * e^{-\frac{t}{\tau}} + T_{fin}$$

where T_{ig} and T_{fin} are the ignition and final, adiabatic temperatures respectively. Following Ref. [23] the extracted characteristic times can be used to obtain an effective mass diffusion constant for the overall reaction; here we assume a diffusion distance equal to the radius of the wire (7.5 nm): $D_{eff} = \frac{x^2}{\tau}$. Fig. 2(c) shows an Arrhenius plot for the effective diffusion constant. We clearly see low and high temperature regimes that hint at different reaction mechanisms operating at high and low temperatures. The effective diffusion coefficients extracted at high temperatures are roughly consistent with prior MD simulations on periodic laminates [23]; see open squares and diamonds in Fig. 2(c). The kinetics at lower ignition temperatures are significantly slower, as indicated by reduced mass transport coefficients (Fig. 2(c)).

We now turn our attention to the atomistic processes responsible for the change in behavior at low temperatures. Fig. 3 shows snapshots of the wires during the reaction process for samples ignited between 650 and 1000 K. Atoms are colored by the local structure type using an adaptive common neighbor analysis in Ovito (a-CNA) [32,33]. fcc atoms (either Ni or Al) are colored green, while atoms with a local bcc configuration (representing the NiAl intermetallic phase) are colored blue. For clarity, atoms in the liquid or amorphous phase without a well-defined local crystal structure are made translucent orange. A very striking difference is observed in samples ignited at 900 K or lower from all prior