Ni/Al Energetic Nanocomposites and the Solid Flame Phenomenon

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ABSTRACT: Reactive nanocomposites (RNCs), which are comprised of stochastically layered metals, were fabricated using short-term high-energy ball milling of nickel and aluminum powders. By varying the milling conditions, the internal nanostructure of the RNCs can be controlled. Utilizing the slice and view methodology by use of a dual beam scanning electron/ion microscope, 3D reconstruction of the RNC particles was accomplished and their nanostructures were quantitatively and statistically analyzed. The reactivity, including ignition and combustion parameters, as well as microstructure of the combustion wave, for different RNCs was analyzed using high-speed infrared imaging and high-speed micro video recording. The direct relationships between the 3D structural characteristics and reactivity parameters have been determined. A comparison with existing theoretical models allows us to conclude that, for specially designed RNCs, the reaction can be initiated and self-propagates solely due to solid-state mechanisms, i.e., in the solid flame mode. In addition, a novel nano quasi-homogeneous reaction regime was discovered. It was directly demonstrated that, by understanding the fundamental quantitative relationship between the structure and properties of RNCs, unprecedented control over the reaction can be achieved.

INTRODUCTION

Methods of energy storage that are safe, possess high energy density, and can be rapidly converted to usable forms are of global importance. Conventional renewable forms of energy, including solar, hydroelectric, wind power, and hydrogen, are useful and viable when available, but are intermittent or not typically located near areas of high-energy consumption, such as cities, or present significant safety and transportation issues. Throughout history, exothermic reactions that generate significant energy have been widely used, typically in the form of hydrocarbons. However, recently, substantial attention has been focused on reactive nanocomposites (RNCs), because of their high energy density (Table 1) coupled with high reactivity. These energetic nanocomposites have many uses, including as solid fuels, secondary energy carriers, for thermophotovoltaic wave harvesting, thermo-chemical energy storage, and also as explosives, propellants, and pyrotechnics. In addition to energy applications, RNCs can be used for synthesis of advanced materials. Combustion synthesis (CS) is a nontraditional green materials fabrication approach that saves energy and produces highly crystalline, low impurity products that are incredibly difficult or impossible to synthesize otherwise. CS has been shown to be valuable for the production of many classes of materials, including metals and alloys, cermet, ceramics and complex oxides, and biological materials. These materials have wide-reaching applications including as photocatalysts and photoactive materials, phosphors and biological phosphors, drug delivery materials, battery and energy materials, among numerous other advanced functional materials and uses. The CS approach has been shown to be environmentally friendly, completely removing the need to use toxic solvents or expensive purification steps. It is well recognized that in order to fully utilize RNCs for the above applications their reactivity, including reaction mechanism, ignition, and combustion characteristics, must be fundamentally understood to be able to control the energy release process. High-energy ball milling (HEBM) has seen widespread use in the preparation of amorphous compounds, composite materials, and other advanced materials. Recently, short-term HEBM has been used for fabrication of RNCs. This process involves

Table 1. Energy Density Comparison of Common Fuels

<table>
<thead>
<tr>
<th>type of fuel</th>
<th>energy density (MJ/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen (700 bar)</td>
<td>5.6</td>
</tr>
<tr>
<td>gasoline</td>
<td>34.2</td>
</tr>
<tr>
<td>ethanol</td>
<td>20.9</td>
</tr>
<tr>
<td>lithium-ion battery</td>
<td>0.9–2.6</td>
</tr>
<tr>
<td>thermites (Al, Fe, Cu, Bi)</td>
<td>15–21</td>
</tr>
<tr>
<td>gasless reactive systems (Ni/Al, Ta/C, Ti/C)</td>
<td>7.1–15.2</td>
</tr>
</tbody>
</table>

"The energy density is calculated per unit volume of fuel only."
energetic, repeated mechanical impact, which imparts significant plastic deformation, while fracturing and cold-welding the reactants. These particles contain all of the reactants in individual, typically pore-free, reaction cells, without any product formation induced during milling. This preparation method introduces oxide-free contact between the reactants, which leads to a significant enhancement of the reactivity, including a decrease in the self-ignition temperature and an increase of energy release rate.\textsuperscript{41,42} These changes, while observed before, are not well understood and all hypotheses have a qualitative basis.

Gasless RNCs are a subset of reactive nanocomposites, where the entire reaction occurs in the condensed state, either in the liquid or solid phase. It is important that in order to release energy, these systems do not require a gas phase oxidizer (thus can be accomplished in vacuum, inert gas, under water, and even in liquid nitrogen), and no gas phase products are formed during the reactions; that is, they are green energy sources. There are a wide variety of gasless reactive systems that span energy densities and material properties, including brittle—brittle (Si+C), brittle—ductile (Ti+C; Ta+C), or ductile—ductile (Ni+Al) components.\textsuperscript{10,43,44}

The Ni/Al system has widely been used as a model for gasless RNCs because of its relatively low ignition temperature and resistance to oxidation. Previous work has shown that there is a significant effect of the Ni/Al RNC microstructure and particle size on the ignition and combustion characteristics. For example, the ignition temperature can be controlled and decreased to below 500 K.\textsuperscript{45,46,51} The microstructure affects the chemical reaction kinetics, resulting in a significant decrease (2–3 times) of the effective activation energy.\textsuperscript{44} The initiation energy required to mechanically stimulate the Ni–Al reaction can be drastically (100 times) diminished by fabrication of RNCs with a desired inner structure.\textsuperscript{45} A wide variety of both experimental and computational studies have been conducted to elucidate the reaction mechanism.\textsuperscript{46–51} However, none of these studies have provided a quantitative relationship between the observed properties and the RNC’s microstructure.

In this work, the reactivity of Ni/Al RNCs has been studied in direct relationship with their internal structure. By varying the HEBM conditions, nanocomposites with increasingly fine lamellar structures were produced. The internal nanostructure of these RNCs was studied by a combination of a scanning electron microscope (SEM) and a focused ion beam (FIB), which utilized the slice and view method, followed by the application of advanced 3D reconstruction techniques. The ignition and reaction parameters were measured by using a variety of advanced methods including high-speed infrared imaging (HSIRI) and high-speed micro video recording (HSMVR). Finally, the quantitative relationships between the structural features and the measured ignition and combustion parameters were determined, to identify the reaction mechanism. Thus, a major goal of this work is to shift the approach of investigation toward quantitative relations between structural and reactive characteristics of high-energy density materials, which allows precise control of the energy release process.

\section*{EXPERIMENTAL SECTION}

\textbf{Fabrication of the Reactive Ni/Al Nanocomposite Particles.} Nickel (Alfa Aesar, 3 to 7 \(\mu\)m) and aluminum (Alfa Aesar, 7 to 15 \(\mu\)m) powders were used as precursors. Reactive Ni/Al composite particles were fabricated through HEBM, which was performed by a PM100 (Retsch, Germany) planetary ball mill in a 250 mL steel jar with 10 mm balls of the same material. The jar was filled with 99.999\% pure argon. The ball to powder ratio was 5:1. A rotational speed of 650 rpm was used, with the sun wheel speed being 1300 rpm. For each treatment, 35 g of an equi-atomic (1:1) mixture of Ni + Al along with 20 mL of hexane was subjected to arrested reactive milling (ARM), or high energy wet grinding (WG), where the reactants undergo milling to produce RNCs, with no products produced during processing. WG was chosen because the resulting nanocomposite particles have a more uniform internal structure along with a smaller average particle size.\textsuperscript{47} The powders underwent milling for a total duration of 10, 20, 30, or 40 min, which involved 5 min periods of milling, followed by 60 min of cooling. The produced RNCs were thoroughly sieved for 48 h, and particles in the size ranges 10 to 20 \(\mu\)m and 53 to 125 \(\mu\)m were selected for further investigation.

\textbf{Material Characterization.} HEBM of Ni and Al powders leads to the formation of essentially pore-free composite particles, which involves both Ni and Al phases. A Nanolab 600 Helios Dual SEM/FIB (FEI, USA) was used for obtaining cross-sectional images through the volume of these mechanically induced structures. The slice and view (S&V, FEI) software package was used to collect sets of \(\sim\)500 images per particle with \(\sim\)10 \(\mu\)m width, \(\sim\)10 \(\mu\)m depth, and \(\sim\)5 nm pixel resolution. These images were taken in series after ion beam milling 10 nm in between each frame, resulting in an analyzed volume of \(\sim\)500 \(\mu\)m\(^3\) per particle.

3D reconstruction was accomplished with the AvizoFire (FEI) software package. Briefly, the images were aligned into an image stack using a least-squares algorithm, shear corrected, and then contrast normalized. The reactants were isolated by use of contrast thresholding, by choosing the minimum of overlapping grayscale values for the nickel and aluminum phases. In order to quantitatively analyze the image stacks, a 3D chamfer distance map, where the distance of each voxel of one phase is measured from the nearest voxel of the opposite phase, was used in conjunction with a distance-ordered thinner, which isolates the skeleton of the structure with conditions of homotopy, thinness, and medialness.\textsuperscript{52} Using these two sets of 3D data, the complete volume of each particle was analyzed. This procedure is described in detail with visualization of each processing step elsewhere.\textsuperscript{53} For this type of analysis, a number of quantitative features can be measured, including interphase contact surface area, thickness of the metallic layers, tortuosity, and porosity. At least five particles from each milling time were sectioned and their structural parameters were analyzed.

\textbf{Reaction Characterization.} For complete reaction characterization, a number of different size and time-scales have to be investigated.\textsuperscript{11,54} Macro-scale parameters such as ignition temperature (\(T_\text{ig}\)) and ignition delay time (\(\tau_\text{d}\)) were studied with compacted disks. The average combustion propagation velocity across cold-pressed long cylinders was also investigated. Finally, the microstructure of the reaction wave, including instantaneous combustion velocity and hesitation time, was analyzed by use of HSMVR.

\textbf{Ignition Parameters.} The Ni/Al composite powders were cold-pressed into disks of 5 mm diameter and 0.5 mm height to 70\% theoretical maximum density (TMD). For each characteristic milling time, ten samples were analyzed. The disk was placed onto a hot plate preheated to 540 \(^\circ\)C and observed using a high-speed infrared thermal imaging system (SC6000, FLIR Systems, MA, USA) at 1325 fps. Using FLIR’s ExaminIR software, thermal images and videos can be captured over several different temperature ranges up to 2300 K. Depending on the frame...
size and temperature range of the investigation, frame rates upward of 15000 fps are achievable. Typical time—temperature plots are shown in Figure 1. For each of these experiments, the temperature was measured on the spot where ignition first occurred. \( T_{ig} \) was defined as the point where the temperature diverged from linear into exponential growth, corresponding to the increased time—temperature derivative, and \( \tau_d \) was likewise determined to be the time where exponential growth began, from the first frame that the disk reached the thermally uniform temperature until ignition occurred. Visual depictions of \( T_{ig} \) and \( \tau_d \) are shown in Figure 1.

**Macro-Combustion Characteristics.** For the average combustion velocity studies, the powders were cold-pressed into 70% TMD cylinders of 5 mm diameter and 15 mm height. For each characteristic milling time, five samples were analyzed. The sample was ignited with a resistively heated tungsten filament and imaged using the IR camera with a filming rate of 600 fps. The use of a high-speed IR camera obtains temperature distributions on the sample surface during the heating process, as shown in Figure 2, making it convenient for monitoring ignition and combustion wave propagation processes. The combustion propagation velocity was measured by following the reaction front over time. For each cylinder, the average velocity was determined by measuring the front positions in 20 frame increments, in the middle portion (10 mm) of the sample height.

**Microstructure of the Combustion Wave.** Micro combustion characteristics were studied by a HSMVR system (Phantom Miro eX2, Vision Research Inc., NJ, U.S.A.) with attached microscope lenses (K1 CentriMax, NTX Tube, MX5; Infinity Photo-Optical, CO, U.S.A.) operating at 64 × 64 pixel resolution, with a spatial resolution of 10 \( \mu \)m/pixel and temporal resolution of 21.25 \( \mu \)s/frame. Depending on the frame size of investigation, frame rates above 100000 fps are attainable. The total recording time was 8.73 s for the utilized capture rate of 47058 fps. The images were processed and analyzed to yield quantitative characteristics of the reaction wave structure, including local curvature of the brightness map, hesitation duration, and instantaneous velocity. As visualized in Figure 3, the combustion front location was determined by calculating the point in each column with the greatest change in intensity as defined by

\[
x_i = \left( \frac{\Delta I}{\Delta x} \right)_{\text{max}}
\]

where \( I \) is the intensity of each individual pixel and \( x \) is the vertical pixel location. The combustion front location was tracked while the entire combustion front was visible across all 64 columns. Using a one-dimensional analysis method, the position with respect to time (Figure 4) was analyzed to determine the distribution of interparticle ignition hesitation times (\( t_h \) is the frame to frame change in position \( \leq 0 \)), as well as the distribution of instantaneous velocities (\( U_{\text{inst}} \) is the frame to frame change in position \( > 0 \)). The intraparticle reaction time (\( t_r \)) is calculated by

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**Figure 1.** Example time—temperature ignition profiles from high speed IR imaging.

**Figure 2.** Set of frames obtained through FLIR recording of the combustion wave propagation in the Ni/Al system.

**Figure 3.** Set of video frames from the combustion experiments. The combustion front location, as determined by maximum gradient with respect to pixel intensity, is shown.
\[ t_r = \frac{\Delta x_{\text{avg}}}{U_{\text{inst}}} \]

where \( \Delta x_{\text{avg}} \) is the length of the average propagation step observed in the HSMVR experiments. This method of analysis is shown in Figure 4, depicting a position vs time graph from which \( t_h \) and \( t_r \) can be calculated.

### RESULTS

3D-Structure of the Composite Ni/Al Particles. Typical backscattered SEM images of the cross sections of Ni/Al RNC particles (Ni-lighter phase; Al-darker phase; pores are black) obtained by different milling times are shown in Figure 5. It can be qualitatively seen that increased milling time leads to finer internal structures. It is worth noting that internal porosity of the particles is low.

After 10 min of milling (Figure 5a), there are relatively thick layers of both Ni and Al, likely where entire particles were cold-welded into the composite. As milling time is increased to 20 min, fewer large chunks of Ni are present, with a large portion instead being characterized by thin tortuous layers. At 30 min of milling, nearly all of the large Ni chunks are absent. It can be seen that the features are much thinner, and the internal particle volume is more homogeneous. After 40 min of milling, there are essentially no large chunks left; instead the internal structure is comprised of thin tortuous lamellae, intimately mixed and stochastically oriented. It is worth noting that, with this increased homogeneity within the individual particles, no reaction has occurred, which was confirmed by both XRD and TEM analysis.

It is well recognized that such qualitative analysis of the arbitrary selected cross-section does not provide sufficient data for understanding the internal structure of the whole particle. As is described in the Experimental Section, the slice and view (S&V) method was used to obtain such information. The 3D reconstructed internal nanostructure of the particles based on treatment of S&V data (see ref 53 for additional details) are shown in Figure 6. The images represent the volume of the Ni phase for each milling time, with Al filling the intervening void-space. Such 3D-reconstructions, allow us to precisely understand the internal structure of the composite particles. It is more important that they permit quantitative analysis of a variety of structural characteristics by use of a chamfer distance map coupled with a distance-ordered thinner. In order to quantitatively obtain information about the nanostructural characteristics of the RNCs, 3D skeletonization using a distance-ordered thinning algorithm was utilized (see details in ref 53). This method is often described as an “onion peeling” approach, because it strips the outer boundary layers and then iteratively checks to ensure that the algorithmic criteria is met.
before removing another layer. This algorithm thins the foreground objects, while preserving the topology, resulting in thin homotopic skeletons. 3D chamfer distance maps were used to determine the distance of each voxel to the nearest voxel of opposite composition. Finally, the skeleton is multiplied by the distance map, which provides the thickness for each segment (Ni or Al phases) of the structure.

The results of the volume-weighted distribution for the thicknesses of the Al and Ni layers are shown in Figure 7. It can be seen that the layer thickness of the Al phase continually decreases with increasing WG time. Initial \( \sim 10 \mu m \) Al particles, after 10 min of milling, are transformed into the bulk of each composite particle, both relatively thin \( \sim 1.5 \mu m \) lamellas and relatively large \( \sim 3 \mu m \) chunks (see Figures 5 and 6), which explains the bimodel distribution of phase size. An increase of WG time leads to unimodal distributions with corresponding decrease of average lamella thickness to less than 500 nm after 40 min of WG (Figure 7a).

The nickel distributions, however, do not follow a similar monotonic trend. After 10 min of milling, the distribution maximum exceeds the average size of initial Ni particles. This means that relatively large \( \sim 10 \mu m \) chunks of the Ni phase are formed due to cold-welding of relatively low ductile Ni. After an additional 10 min of WG (total 20 min), there is a significant

Figure 6. Reconstructed internal volumes of the nanocomposites for different time (min) of WG: (a) 10, (b) 20, (c) 30, and (d) 40 (Ni is as gray phase, and Al is void-space).

Figure 7. Quantitative diffusive layer thicknesses of (a) aluminum and (b) nickel. The distributions are shown for the four different milling times.
reduction of the large areas with a corresponding increase in the number of lamellas with thickness less than 5 μm. A unimodal distribution is observed for the thickness of the Ni layers after 30 min of WG with average size of ~1 μm. As milling is continued, the Ni 40 min distribution remains similar to the 30 min case. There is slight broadening of the distribution, likely due to additional cold-welding of the Ni layers. The quantitative results of Figure 7 are summarized in Table 2.

<table>
<thead>
<tr>
<th>milling time, min</th>
<th>Al layer thickness (nm)</th>
<th>Ni layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1700</td>
<td>5800</td>
</tr>
<tr>
<td>20</td>
<td>960</td>
<td>2600</td>
</tr>
<tr>
<td>30</td>
<td>720</td>
<td>1180</td>
</tr>
<tr>
<td>40</td>
<td>430</td>
<td>1200</td>
</tr>
</tbody>
</table>

For Al, the thickness appears to continually decrease with increased milling time. The Ni layer thickness plateaus between 30 and 40 min of milling, with the layer size staying essentially constant. During the same period, however, the Al layer thickness decreases in average thickness by almost 300 nm. The difference in milling behavior between the metals is likely due to the difference in ductility. Because Al is a softer and a more ductile material, milling preferentially deforms it. This can be explicitly seen in the 10 min milling case; the precursor aluminum was twice the size as nickel, yet after only 10 min of milling, the average aluminum thickness is four times less than nickel. An additional way to consider the difference in layer thickness trends is through strain hardening and general hardness. Both Ni and Al experience different strain hardening properties. At this point in the milling, it may be more mechanically favorable to deform the Al layers, rather than the Ni layers. For the following plotted relationships, the average thickness and contact surface area will be compared against the measured ignition and combustion parameters.

**Ignition Characteristics.** As described in the Experimental Section, the ignition delay time and ignition temperature were determined by analysis of the preheated sample temperature maps, which were tracked over time by the high-speed IR video system. From Figure 8a,b, the change in \( T_{ig} \) and \( t_c \) can be qualitatively understood, as milling time is increased; both \( t_c \) and \( T_{ig} \) gradually decrease. It is worth noting that in the conventional Ni–Al system, \( T_{ig} \) is at the eutectic point (921 K) or higher. It can be seen that after 10 min of milling the ignition temperature is well (100 K) below the Al melting point (933 K) and the \( T_{ig} \) continually decreases, with increased milling time. After 40 min of HEBM, ignition occurs at 676 K, or almost 300 K below the melting point of Al. Likewise, \( t_c \) decreases significantly with increased milling time. After 10 min of milling it takes 8.5 s until the sample ignites. This value sharply decreases with milling time, e.g., being 3.1, 2.7, and 2.2 s for the samples obtained after 20, 30, and 40 min of WG respectively. Note that with the utilized experimental setup, with maximum temperature of 813 K, the ignition delay time values could not be compared with the conventional Ni–Al system, since this temperature is lower than the eutectic point (921 K) in the Ni–Al system.

However, it is clear that milling time is a technological parameter, which may vary from one milling machine to another. In order to understand the physics of the observed phenomena, the dependences of the ignition parameters versus structural parameters of the system must be obtained. These dependences are presented in Figure 8c–h. Three structural parameters were selected; the Al and Ni layer thickness, as well as surface to volume ratio, which characterizes the contact surface area between the reactants in the bulk of the composite particle. It can be seen that both ignition characteristics change monotonically as a function of thickness of Al layers. This result will be discussed in detail below.

**Macro-Combustion Characteristics.** The relationships between the combustion propagation velocity as a function of milling time, as well as different structural parameters, are shown in Figure 9. The average macroscopic combustion velocity \( U_{avg} \) increases with increasing milling time. For the 40 min milling case, \( U_{avg} \) is 0.225 m/s. This is almost twice the 10 min case, which has a macro combustion velocity of 0.127 m/s. Again the change of \( U_{avg} \) is monotonically correlated with the change of Al layer thickness, as well as a function of contact surface area, while the dependence of \( U_{avg} \) against the average Ni layer thickness is not so obvious.

Typical temperature–time profiles obtained by IR high-speed thermal vision system are shown in Figure 10. It can be seen that, while the rate of temperature change in the initial stage of reaction increases with increase of milling time, the maximum combustion temperature remains essentially constant (see Figure 10).

**Microstructure of the Combustion Wave.** To better understand the combustion mechanism, it is important to examine the micro combustion characteristics. As it was found in previous work, and described in the Experimental Section, the reaction front, which looks stationary and steady on the time scale of 0.1 s and length scale of 1 mm, propagates fundamentally unsteadily on 1 ms time and micron length scales. The periods of rapid front movement are successive (consecutive) with the periods of its hesitation. Thus, one can measure the values of the hesitation time (\( t_h \)) as well as instantaneous combustion \( (U_{inst}) \) velocity, which are important characteristics of the combustion process. Based on the measured \( U_{inst} \) and knowing the average propagation step size, one may calculate the reaction time (\( t_c \)), which corresponds to the combustion of a single composite particle.

Using HSMVR, it was shown that \( t_h \) decreases with layer thickness of both metals. The dependence of hesitation time vs Al layer thickness is shown in Figure 11a. It can be seen that at Al layer thickness ~2 μm (10 min of WG), the \( t_h \) is about 220 μs. This value decreases continually, to a minimum of 50 μs for 400 nm layer thickness (40 min WG).

The derived particle reaction times and measured instantaneous combustion velocity are shown in Figure 11b,c. In Figure 11b, the intraparticle reaction time remains essentially constant as the layer thickness decreases, with the reaction time ranging from 33 to 40 μs. A comparison of Figures 9b and 11c shows that the average instantaneous velocity is 1 order of magnitude higher than the average macroscopic combustion velocity. It is worth noting that the instantaneous velocity follows the opposite trend as the average macroscopic velocity. \( U_{inst} \) decreases as the layer sizes decrease, from 1.25 to 0.84 m/s for the 10 and 40 min cases, respectively.

**DISCUSSION**

Controlling the ignition parameters, such as ignition temperature and ignition delay time, is a key element in designing high energy density materials. It was demonstrated that HEBM is an effective approach to control these parameters. As seen in Figure 7a,b, the diffusive layer thickness for both metals decreases with increasing
milling time, which leads to the corresponding decrease of $T_{ig}$ (Figure 8). However, the ignition temperature appears to correlate better to the Al layer thickness than to Ni. To understand this result we must discuss the reaction mechanism of
the Ni–Al system. It was previously shown that the reaction in the Ni–Al system occurs first through Ni dissolving into the Al lattice.\textsuperscript{42,50,51} As the Al layers get thinner, two major effects should be accounted for. First, the thinner the Al lamellae are, the shorter the Ni diffusive distance is required to be to reach a critical degree of conversion, which is sufficient for self-ignition under the investigated conditions. Additionally, as the layers are reduced in size, there is an increase of surface contact area between the reactants (Figure 7). In turn, this effect leads to an increase of the surface diffusion contribution to the overall mass transport process. Because surface diffusion is much faster than volume diffusion, the overall diffusion rate increases significantly.\textsuperscript{59} The latter statement sheds light on the well-known result that HEBM affects the effective activation energy of the reaction.\textsuperscript{44} It is clear that, with an increased contribution from surface diffusion, which has a lower activation energy than volume diffusion, a lower effective activation energy is expected for the overall combustion reaction. The following equation, derived from Semenov theory,\textsuperscript{60} shows the relationship between the effective activation energy and ignition temperature:

\[
E_{\text{eff}} = \frac{RT_0^2}{T_{\text{ig}} - T_0} \quad \text{and} \quad T_{\text{ig}} = \frac{E_{\text{eff}}}{2R} \left[ 1 + \sqrt{1 - \frac{4RT_0}{E_{\text{eff}}}} \right]
\]

where \(T_0\) is the ambient temperature. The Arrhenius number \(\text{Ar} = RT_0/E\) is typically small for a thermal explosion. In our case, \(T_0 < 800\) K and effective activation energy ranges from 40–210 kJ/mol,\textsuperscript{44} then \(\text{Ar} \approx 0.05\). Thus, with high accuracy, we can estimate \(T_{\text{ig}}\) as

\[
T_{\text{ig}} \approx T_0 + \frac{RT_0^2}{E_{\text{eff}}}
\]

Thus, on the one hand, the reduction of the effective kinetic activation energy, which is manifested in the increase of surface diffusion, results in a decrease of \(T_{\text{ig}}\) under the same heat loss conditions \((T_0)\). On the other hand, the experimental observation that \(T_{\text{ig}}\) decreases with milling time suggests that \(E_{\text{eff}}\) should also gradually decrease. This hypothesis was verified and confirmed in our recent work.\textsuperscript{61} It is worth noting that \(T_{\text{ig}}\) for the conventional Ni + Al powder mixture remains essentially constant in the vicinity of the Al melting point and thus cannot be controlled.\textsuperscript{58}

The relationship between the ignition delay time and the structural properties is shown in Figure 8. It can be seen that \(\tau_d\) decreases with increasing milling time. It is more important that for the ignition delay time, the Al and Ni thickness \((\Delta)\) both correlate well and, for either, the relationship between the \(\tau_d\) and
Δ is consistent with an exponential function. The following relationship exists between the $\tau_d$ and activation energy ($E_a$) in a homogeneous reaction media:

$$
\tau_d \propto \frac{k_B R T^2}{E_a} e^{E_a/RT_c}
$$

which illustrates that the self-ignition delay time depends on the activation energy exponentially. Because the initial temperature was kept constant in all of our experiments, it again implies that the effective kinetics, i.e. $E_{\text{eff}}$, must be changing to account for the observed relation of the ignition delay times. However, it is also likely that the pre-exponential factor must depend on the structural parameters, e.g., surface contact area. In order to determine which value contributes, additional studies are required.

Now let us consider the observed dependences of average combustion velocity (Figure 9) and temperature (Figure 10). Theoretical models have previously been derived for macroscopic combustion kinetics with regards to the geometry and microstructure of the sample. These models result in different fractional inverse relationships $U_{\text{avg}} \approx 1/\Delta^x$ between the macroscopic combustion propagation velocity ($U_{\text{avg}}$) and the layer thickness ($\Delta$), with the $x$ value depending on the specific assumptions of the model, including diffusion through a product layer or melting and spreading of the reactants. For the diffusion-based models, the $x$ values vary based on the assumptions of linear, cubic, or exponential kinetic dependencies. One such case that aligns with the observed results is of the solution with zeroth order kinetics, which results in an $x$ value of exactly 0.5. For models that assume melting and spreading of the reactant there are differences in assuming that either only one material melts or both. However, for both cases, i.e., product formation occurs on the surface of the more refractory material or through interdiffusion of the liquids, the $x$ value is 1.

As noted above, due to the reaction in the Ni–Al system it is logical to assume that the Al layer thickness is the defining structural feature of the combustion velocity (Figure 9a). Fitting the corresponding experimental data with $1/\Delta^x$ function shows that the best fit is obtained with $x = 0.5$. This agreement between the measured experimental data and solid-diffusion models implies that solely solid-state reactions are responsible for the combustion wave propagation in RNC Ni/Al particles. While it is now well recognized that solid-state mass transport controls the ignition process in Ni/Al RNCs, we for the first time demonstrate that the combustion wave propagation is also defined by solid-state reaction. It means that the recently discussed solid flame phenomenon may also occur in the Ni–Al system, which involves a reagent (Al) with a melting point (912 K) below the adiabatic combustion temperature (1911 K).

For deeper understanding of combustion in a heterogeneous media, the application of the micro combustion parameters must be discussed. While on the macro level, with time resolution on the order of 100 ms, a reaction front appears to propagate relatively steadily, on the micro level with recording speed higher than $10^3$ fps, we have observed that the process consists of hesitation stages (essentially zero instantaneous velocity) and rapid propagation stages (instantaneous velocities much higher than the average macroscopic combustion velocity). To quantitatively analyze the phenomenon three parameters were introduced, $t_h$ and $t_s$, as well as $U_{\text{avg}}$. First, as seen in Figure 11a, it is logical that the average hesitation time decreases with decreasing Al layer thickness ($\Delta$). This effect is more easily understood by considering the ignition temperature. RNCs of similar size, regardless of the milling conditions or structural parameters, have the same amount of energy stored within. Once they react, they release an identical amount of energy and will reach the same temperature (see Figure 10). Because of this, particles that have a lower $T_{\text{ig}}$ require less interparticle heat transfer time prior to self-ignition.

Dependences of the instantaneous velocity and, as a result characteristic reaction time (Figure 11 b,c) do not seem as straightforward. It appears counterintuitive that the reaction time increases as the structure becomes increasingly fine. This unexpected effect can be explained assuming that the reaction of each particle occurs in the thermal explosion (TE) mode, instead of in the self-propagating mode. In this case, the virtual combustion front propagation occurs, which was described before but is now applied at the level of individual particles. Due to the stochastic heterogeneous nature of the nanocomposite particles, different spatial regions of the sample have temperature variance, leading to nonuniformity of the chemical reaction rate and therefore heat release along individual particles. In this mode, the ignition condition will be achieved in some local spot and then TE may rapidly spread throughout the whole particle. It is important to note that all other spots of the particle up to the moment of TE are assumed to be preheated to a temperature within a few degrees of the ignition value. For an external viewer, the spreading of high temperature regions appears similar to the propagation of a conventional combustion wave. However, the reactions at each point of the medium proceed essentially independently of the heat released in other.
parts of the sample. In this case, the characteristic reaction time is defined primarily by the interparticle heat transfer, which at constant TMD and composition, is not influenced by the internal microstructure of the particle.

In order to better understand how the micro- and macro-combustion velocities are related, the following, described in previous work, relationship between average combustion velocity and microstructure of the combustion wave is utilized:

\[ U_{avg} = \frac{\Delta x_{avg}}{(t_i + t_h)} \]

where \( \Delta x_{avg} \) is the length of the average propagation step. This assumes that the average combustion velocity is solely composed of either hesitation or reaction across the particle. The measured average combustion velocity, from IR experiments, and calculated average combustion velocity, from HSMVR, is shown in Table 3.

Table 3. Macro-Combustion Velocities Determined through Both IR Measurement and HSMVR Calculations

<table>
<thead>
<tr>
<th>milling time (min)</th>
<th>measured average combustion velocity (m/s)</th>
<th>calculated average combustion velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.127 ± 0.015</td>
<td>0.187 ± 0.033</td>
</tr>
<tr>
<td>20</td>
<td>0.129 ± 0.014</td>
<td>0.195 ± 0.035</td>
</tr>
<tr>
<td>30</td>
<td>0.152 ± 0.012</td>
<td>0.269 ± 0.039</td>
</tr>
<tr>
<td>40</td>
<td>0.225 ± 0.030</td>
<td>0.364 ± 0.078</td>
</tr>
</tbody>
</table>

The results of this analysis show reasonably close agreement between experimental and calculated \( U_{avg} \), suggesting that the model describes the combustion front propagation in the RNCs well. This allows us to directly use these constituent results to examine the fundamental reaction mechanism across single particles. To understand this phenomenon, we have to discuss known heterogeneous gasless combustion mechanisms in more detail.

Recall that there are two primary models that have been considered, a quasi-homogeneous type, where the reaction is limited by the kinetics, and the thermal-explosion type, which is limited by interparticle heat transfer. Previous studies of various heterogeneous gasless reactive systems (e.g., Ti–C, Ti–Si, Ni–Al) have revealed that the macroscopically steady-state planar combustion front has a microscopically nonsmooth surface and propagates with sudden jumps followed by periods of stagnation. Observations spurred the formulation of a new mechanism for combustion wave propagation in such systems. This discrete thermal explosion, or relay-race mechanism, has been described by microheterogeneous models and involves two stages: rapid burning across an elemental chemical cell followed by a delay stage during which the next cell is preheated to the ignition temperature. In the case where the intraparticle thermal relaxation time is less than the interparticle hesitation time, the reaction propagation is not limited by the reaction kinetics of the material, but rather by heat transfer from one particle to the next and is considered to be within the microheterogeneous regime. For this regime, the entire volume of the particle is uniformly preheated and reacts essentially simultaneously. In the reverse case, when the intraparticle thermal relaxation time is greater than the interparticle hesitation time, one can expect the occurrence of a previously unobserved regime, the nano quasi-homogeneous regime.

Another important conclusion can be made after comparing the characteristic intraparticle thermal relaxation time (\( t_{relax} \)) to the interparticle hesitation time. \( t_{relax} \) can be estimated as

\[ t_{relax} = \frac{d^2}{\alpha} \]

where \( d \) is the average particle diameter and \( \alpha \) is the thermal diffusivity. By comparing the ratio of \( t_{relax} \) and \( t_h \), we can determine which regime most accurately describes the combustion process. The ratio of the two characteristic times (Figure 12) is presented as a function of the aluminum layer thickness. It can be seen that that by decreasing \( \Delta \) it is possible to switch from the thermal explosion, or microheterogeneous regime, \( t_{relax} > t_h \) to a previously unobserved regime, the thermal ignition, or nano quasi-homogeneous regime \( t_{relax} < t_h \). For this system, if we interpolate between the 30 and 40 min milling times, we find that the boundary between these two regions occurs at \( \Delta = 680 \text{ nm} \).

Below this boundary, the chemical reaction occurs at a rate slower than the hesitation time. During the hesitation time between particle ignition, the next particle develops a temperature distribution across its volume. Once the edge of the unreacted particle closest to the reacted particle heats to the ignition temperature, the reaction will propagate across the next particle. This regime is essentially a nano quasi-homogeneous regime where steady combustion occurs in a smooth, steady propagation across the individual particle. This result again illustrates the effect of the microstructure on the combustion mechanism and possibility for precise control of energy release process.

CONCLUSION

Quantitatively examining the structure for HEBM-produced Ni/Al nanocomposites allows us to fundamentally understand the mechanism of self-sustained reactions in the heterogeneous high energy density media. It was shown that the ignition temperature highly correlates with the aluminum layer thickness. The relationship between the combustion propagation velocity and the Al thickness agrees with theoretical solid diffusion-reaction models, implying that no melting process occurs during the reaction. This means that, for Ni/Al nanocomposites, where the melting point of the precursors is below the adiabatic combustion...
temperature, the solid flame phenomenon (as recently discussed for Ta–C system)\(^1\)\(^2\) is also accomplished. Examining the micro combustion wave propagation characteristics, it was shown that the interparticle ignition hesitation time decreases from 220 to 50 μs, while the intraparticle reaction time remains essentially constant. This allows the reaction to be switched between the previously observed thermal microheterogeneous regime and the novel nano quasi-homogeneous regime. These fundamental relationships give insight into the reaction itself, including how one may specifically tailor these, and other similar systems, to the desired application, as well as provide important information for development of more accurate reaction models. Understanding how the sensitivity and reaction parameters are related to the microstructure gives unprecedented control over all aspects of the energy release process. This work represents a new paradigm in combustion and materials sciences, where rigorous quantitative studies are completed to fundamentally understand the underlying physics of such phenomena as self-sustained reactions in nanostructured high energy density media.

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