Thermal Explosion in Al−Ni System: Influence of Mechanical Activation

Jeremiah D. E. White,[†] Robert V. Reeves,[‡] Steven F. Son,[‡] and Alexander S. Mukasyan*[,†]

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, and School of Mechanical Engineering, School of Aeronautics & Astronautics (Courtesy), Purdue University, West Lafayette, Indiana 47907

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The influence of short-term (5−15 min) highly energetic ball milling on the ignition characteristics of a gasless heterogeneous Ni−Al reactive system has been investigated. By using Al−Ni clad particles (30−40 μm diameter Al spheres coated by a 3−3.5 μm layer of Ni, that corresponds to a 1:1 Ni/Al atomic ratio), it was shown that such mechanical treatment leads to a significant decrease in the self-ignition temperature of the system. For example, after 15 min of ball milling, the ignition temperature appears to be ~600 K, well below the eutectic (913 K) in the considered binary system, which is the ignition temperature for the initial clad particles. Thus, it was demonstrated that the thermal explosion process for mechanically treated reactive media can be solely defined by solid-state reactions. Additionally, thermal analysis measurements revealed that mechanical activation results in a substantial decrease in the effective activation energy (from 84 to 28 kcal/mol) of interaction between Al and Ni. This effect, that is, mechanical activation of chemical reaction, is connected to a substantial increase of contact area between reactive particles and fresh interphase boundaries formed in an inert atmosphere during ball milling. It is also important that by varying the time of mechanical activation one can precisely control the ignition temperature in high-density energetic heterogeneous systems.

Introduction

The ignition mechanism and ability to control the initiation and combustion processes in advanced heterogeneous high-density energetic mixtures (HDEM) is of particular interest because of a variety of potential applications, including chemical energy storage and microscale energetic systems, and materials synthesis, as well as propellants in rocket, air-breathing and other energetic formulations.[1−3] In this work, HDEMs of metal-based compositions are in specific focus. The ignition (or so-called thermal explosion, TE) characteristics of such systems have been extensively investigated during the last 10 years both in inert[4−6] and in reactive atmosphere.[7−10] Several important issues have been addressed, including (a) how does the ignition temperature depend on the experimental conditions (heating rate, heat losses, etc.); (b) what type of phase interaction (e.g., solid−solid or the formation of liquid phases) controls the process; and (c) how does the initial reactant medium microstructure influence TE parameters. For example, it has been demonstrated that, in the Ni−Al system, the preheating rate (ω_h) influences the ignition delay time (τ_d) and ignition temperature (T_{ig}); that is, higher ω_h leads to shorter τ_d and lower T_{ig}. In general, it has been concluded that as a rule the TE mechanism in heterogeneous gasless reaction mixtures is different from explosions in conventional homogeneous reaction systems. Indeed, for homogeneous systems, the relation between rates of chemical reaction and heat losses defines the ignition temperature, T_{ig}.[4] However, in gasless heterogeneous systems, the ignition temperature is typically related to specific features of the system phase diagram. For example, the eutectic melting point (or mp of the least refractory reagent), at which a significant increase in reactant contact area occurs, typically determines the system ignition temperature.[4−7] This conclusion presents challenges to control the ignition characteristics for such gasless HDEMs. The major question is can one decrease the ignition temperature of such systems below the eutectic melting point. In other words, can solid-state chemical reaction lead to thermal explosion in such systems? Up until recently, the answer was no.

One of the approaches used to control reactivity in metal mixtures is so-called mechanical alloying.[11] This method was used to influence the ignition and combustion characteristics of metal mixtures in argon[11−13] and oxygen (air).[8−10] The idea is to change the compositions of metal and fuel particles, by using long-term highly energetic ball milling, to form metastable metal-based compounds, for example, a supersaturated solid solution that includes a base metal (e.g., Al) as a solvent and another component (e.g., Mg, Fe, etc.) as a solute. For such nonequilibrium phases, the rate of reaction at the onset of combustion should be very rapid and not affected by the relatively slow diffusion and heat transfer processes that control conventional equilibrium phase transitions. Indeed, it was proven that long-term (6−10 h) mechanical alloying leads to the formation of such nonequilibrium phases with much lower ignition temperatures in oxygen and air.[9,10]

For the last two decades, our groups have been involved in the investigation of the mechanism of combustion wave propagation in heterogeneous highly energetic systems, such as metal−metal (e.g., Ni−Al), metal−nonmetal (e.g., Mo−Si), metal−gas (e.g.Ti−N_2) and their combinations.[14−16] On the basis of numerous studies using advanced dynamic techniques, it was concluded that rapid reaction propagation in gasless heterogeneous systems is primarily defined by the conditions at the boundary (contact surfaces) between reagents. For example, the contact heat conductivity of the heterogeneous reactive skeleton typically defines the rate of heat release.[2]

The combination of the above-mentioned concepts (i.e., the influence of highly energetic ball milling and the importance

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* Corresponding author. Phone: +1 574 631-9825. Fax: +1 574 631-8366. E-mail: amoukasi@nd.edu.

[†] University of Notre Dame.

[‡] Purdue University.

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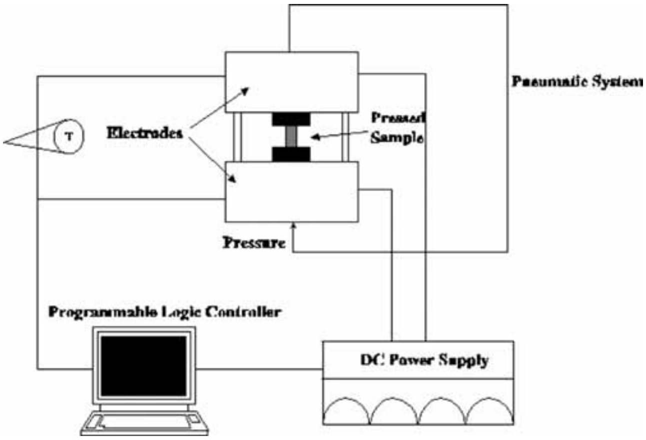


Figure 1. Electro-thermal explosion (ETE) experimental scheme.

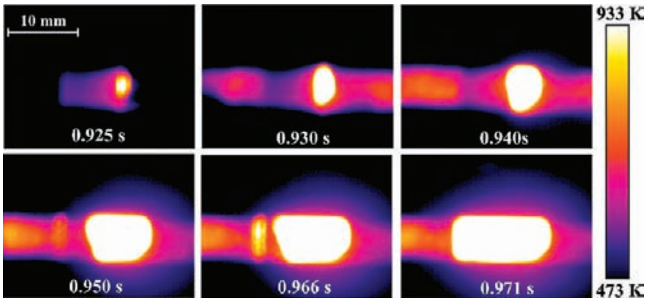


Figure 2. Sequence of frames of the TE process recorded by high-speed IR camera.

of the contact boundaries between reagents for system reactivity) allows one to formulate the following hypotheses, which were tested in this work. First, short-term (<20 min) high-energy ball milling should result in a change of reactant contact surface area, without formation of any new phases. Second, this increase in reactant contact surface area may lead to an acceleration of phase interactions in metal-based HDEMs, for example, a decrease in the ignition temperature below the melting point of the least refractory element (or eutectic). Thus, solid-state reactions will define the ignition process. Moreover, this approach should allow precise control of the ignition temperature because by changing the time of ball milling one can accurately control the specific contact surface area between reactants. This type of highly energetic ball milling, which leads to the acceleration of chemical reaction without the formation of any new phases in the reactive media, will hereafter be referred to as mechanical activation (MA), in contrast to mechanical alloying mentioned above.

Experimental Section

Experiments were conducted with, so-called, Al−Ni clad particles (Federal Technology Group, Bozeman, MT), that is, 30−40 μm diameter Al particles coated by a 3−3.5 μm layer of Ni, which corresponds to a 1:1 Al/Ni atomic ratio. A PM100 single-station planetary ball mill (Retsch GmbH, Germany) was used for high-energy milling of the powder. The rotational speed of the mill is adjustable from 100 to 650 rpm. A special locking device and jar lid allows one to evacuate the vial and perform grinding operations in an inert atmosphere (e.g., argon). The mass charge ratio between milling media (3 mm steel balls) and powder was 2:1. The durations of treatment investigated were 2, 5, 10, and 15 min. When it was required, initial and ball milled powders were cold pressed with uniaxial pressure into cylinders (typically $\text{Ø} = 10$ mm × $h = 7$ mm) or thin plates (2 cm × 2 cm × 2 mm) with relative densities, ρ, in the range of 75 to 85% of the maximum theoretical value.

An SDT-2960 (TA Instruments, New Castle, DE) was used to conduct simultaneous DTA−TGA analysis on the powders under the following conditions: argon gas flow at 80 cc/min, heating rates 5, 10, and 50 K/min in the temperature range 300−1000 K. The scheme of the experimental setup for investigation of thermal explosion of investigated HDEMs is shown in Figure 1. Pressed samples were placed between two electrodes. Then, electrical current was passed through the sample, causing heat to build up because of the electrical resistance of the material. The temperature rapidly (seconds) raises to the ignition temperature and the reaction initiates. A high-speed infrared thermal imaging system (SC6000; FLIR Systems, Boston, MA) was used to monitor the temperature−time history of the process. With FLIR's ThermaCAM Researcher software, thermal images and videos can be captured in frame sizes ranging from 64 × 8 to 640 × 512 over several different temperature ranges which include temperatures as high as 2000 °C. Depending on the frame size and temperature range of investigation, frame rates upward of 15 000 fps are achievable. The SC6000 is capable of using 50 or 100 mm lenses or a 4× microscope objective (scale resolution ~5 μm). A typical series of frames obtained by IR camera during ignition of an Al−Ni sample is presented in Figure 2 and discussed below.

Finally, the microstructure and phase composition of the powders before and after milling were examined by different material science techniques, including field emission scanning electron microscopy (EVO 50 Series; Zeiss, Peabody, MA), energy-dispersive spectroscopy (INCAx-sight model 7636; Oxford Instruments, Concord, MA), and X-ray diffraction (Scintag X1 advanced diffraction system; Scintag Inc. USA, Cupertino, CA).

Results and Discussion

DTA Analysis. Let us first consider DTA results obtained using a relatively fast heating rate of 50 K/min under argon flow on the initial clad particles. Figure 3a represents the typical DTA curve for these conditions. It can be seen that essentially no chemical activity is observed up to $T \sim 913$ K at which a very sharp exothermic peak is detected. It is important to note that 913 K (640 °C) is exactly equal to the eutectic melting point in the Al−Ni system (see phase diagram in Figure 3b). Also, this temperature was previously shown to be an ignition temperature (T_{ig}) for samples pressed from Al−Ni clad particles that were externally preheated in a furnace under an argon atmosphere.[4] Thus, DTA results confirmed that, in contrast to homogeneous systems, the characteristic temperature T_{ig} for such heterogeneous reaction mixtures is defined by its phase diagram.

The DTA data obtained for reaction mixtures with different mechanical activation time (t_{MA}), specifically $t_{\text{MA}} = 2$, 5, and 15 min, are presented in Figure 4. It can be seen (Figure 4a,b) that while, for powders with $t_{\text{MA}} = 2$ and 5 min, the maximum exothermic peak is still at ~913 K, some amount of energy was also released at lower temperatures (e.g., starting at $T \sim 700$ K for 5 min of ball milling). However, after longer times, that is, 15 min (Figure 4c), of MA, the degree of conversion at temperatures below the eutectic is very large, and only a small peak was observed at $T > 913$ K. It means that, for the reactive media formed after a relatively short duration of ball milling, almost all interaction takes place through solid-state reactions. Note that, in general, several (at least three) peaks can be outlined on the DTA curve, which may indicate that several

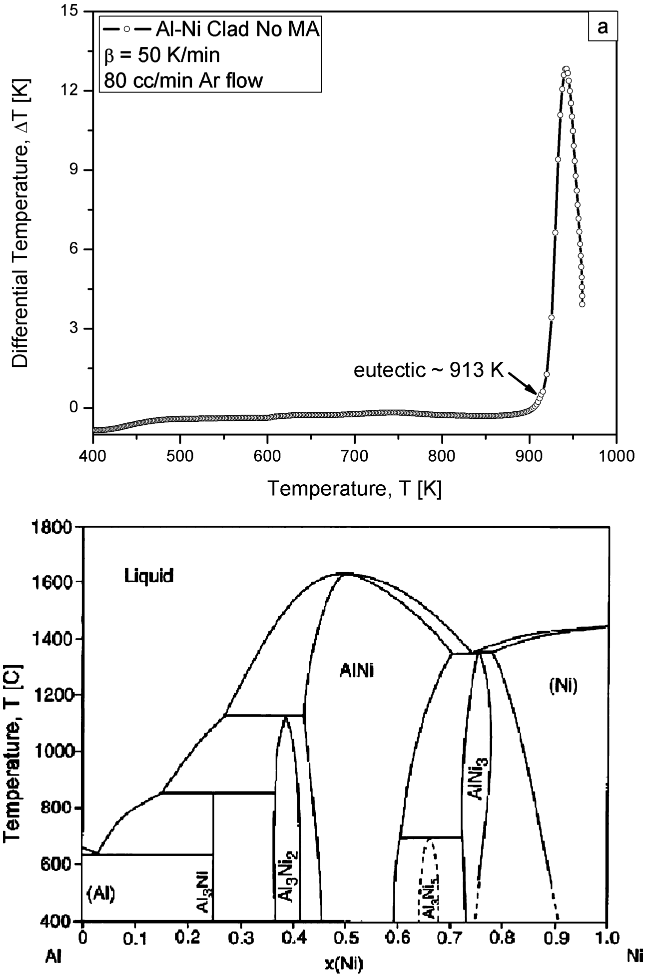


Figure 3. (a) Typical DTA curve for Al−Ni clad particles; (b) Ni−Al phase diagram.

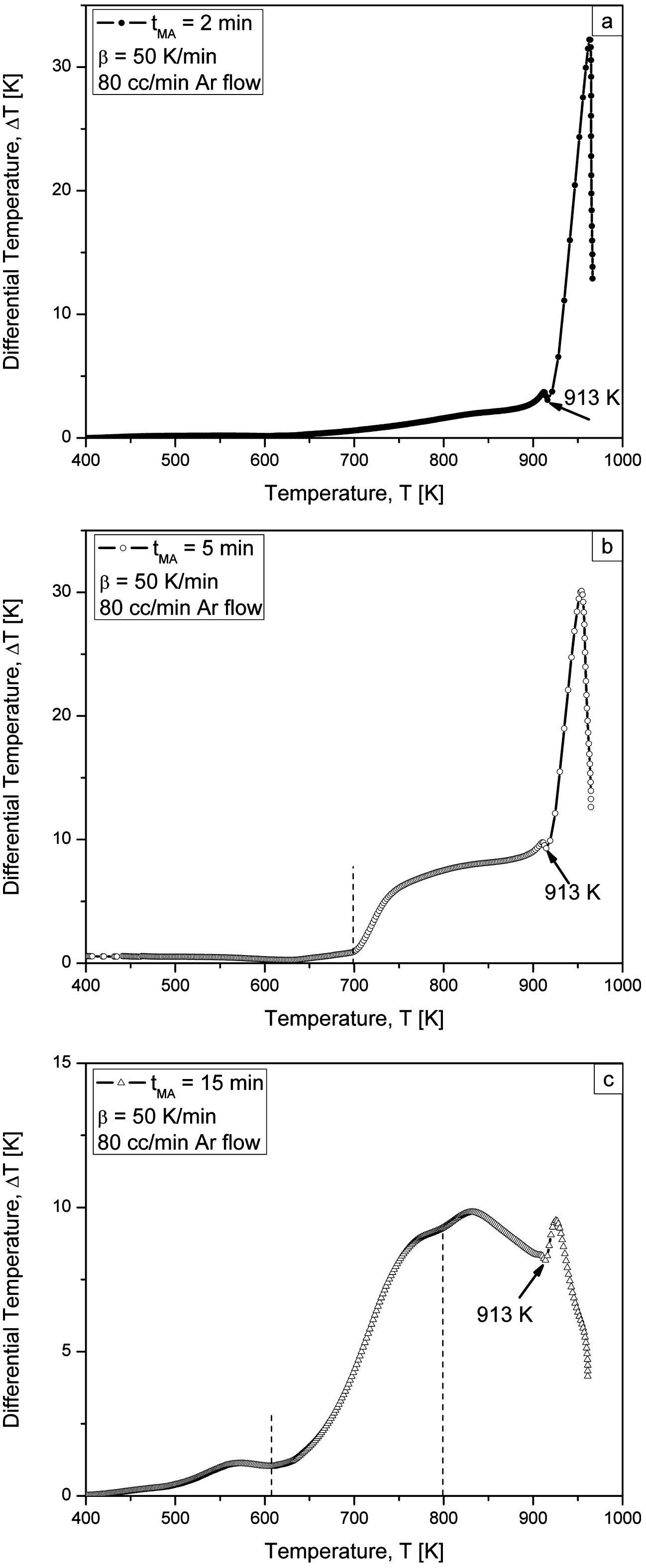


Figure 4. DTA curves for clad particles with different durations of mechanical activation: (a) 2 min, (b) 5 min, and (c) 15 min.

chemical reactions contribute to the process. Before we provide some explanation for the obtained results, let us also discuss data from TE experiments for samples formed from the considered reaction mixtures, including those after high-energy ball milling.

Electro-Thermal Explosion. As explained earlier in this work, the so-called electro-thermal explosion (ETE) approach[17] was used to study the ignition phenomenon in the considered system. The idea is to utilize Joule sample preheating by passing high electric current (200−600 amps) through the reaction media. Note that the very fast heating rates (200−300 K/s) that can be achieved by ETE (see Figure 2) allow one to neglect heat losses, thus realizing the adiabatic explosion mode. Also, there is no experimental evidence that such short Joule preheating may influence the kinetics of chemical interaction in the investigated systems. Use of a high-speed IR camera allows one to obtain unique data of the sample temperature map during the heating process, making the ETE approach very convenient for such studies.

First of all, it is important to note that, even if the preheating of the sample occurs in a uniform fashion, that is, temperature differences between points on the sample surface do not exceed 2% of the average temperature, using high-speed IR (~1000 frames/sec) micro-recording allows one to resolve the exact point of thermal explosion. The virtual combustion wave then rapidly (with velocity ~0.5 m/s) "propagates" along the sample (see Figure 2). It is interesting that, in the case of the self-propagating reaction regime, the velocity of the real combustion wave in this system is ~10 times lower as compared with that in the case of TE. Such behavior for gasless heterogeneous systems was theoretically predicted in another work[18] and was for the first time observed using an IR camera for the Ni−Al system later.[15] It appears that TE in heterogeneous reactive media indeed has a stochastic wave-type nature, which is related to the stochastic distribution of the thermal conductivity properties on the micro-level.[2]

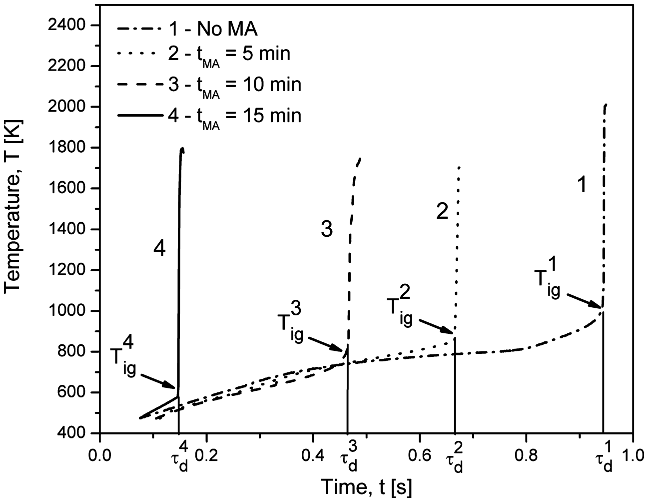


Figure 5. Typical TE curves for systems with different times of energetic ball milling.

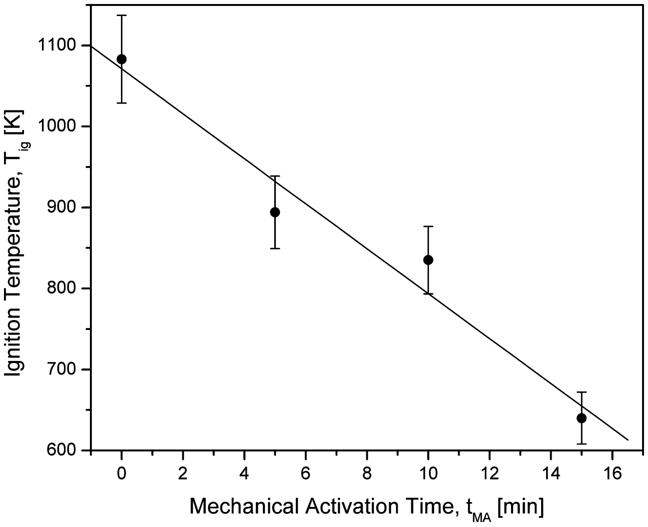


Figure 6. Dependence of Tig as a function of energetic ball milling time.

By taking into account the above specifics of TE in gasless heterogeneous systems, the initial TE spot was identified, and the temperature−time history of this spot was recorded. Figure 5 shows typical temperature−time dependencies obtained on samples pressed from different powders, that is, sample 1 from initial particles and samples 2−4 from powders after 5, 10, 15 min of mechanical activation correspondingly. First, it can be concluded that indeed samples (samples 2−4) pressed from powders which were treated with high-energy ball milling have shorter ignition-delay times ($\tau^4_{\mathrm{d}} < \tau^3_{\mathrm{d}} < \tau^2_{\mathrm{d}} < \tau^1_{\mathrm{d}}$) and lower ignition temperatures ($T^4_{\mathrm{ig}} < T^3_{\mathrm{ig}} < T^2_{\mathrm{ig}} < T^1_{\mathrm{ig}}$) as compared with the baseline (sample 1) Al−Ni clad system. Second, indeed T_{ig} after only 5 min of mechanical activation is lower than the eutectic temperature in the Al−Ni system. These observations are in good agreement with the DTA results discussed above. Third, and perhaps most importantly, it appears that an increase of treatment time leads to a monotonic decrease of ignition temperature (see also Figure 6). The latter allows one to precisely control T_{ig} in such HDEM systems. It is worth noting that the activated material maintains its reactivity after exposure to air for several weeks. In fact, the powders after activation were exposed to air with no further special consideration to inert handling.

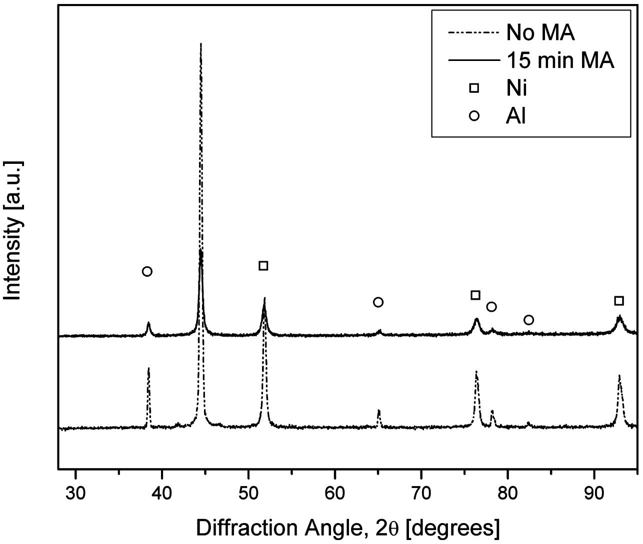


Figure 7. XRD patterns for initial and mechanically activated samples.

TABLE 1: Crystalline Size (Angstrom) of Different Phases in Reaction Mixture As a Function of Mechanical Activation Time

	time of mechanical activation, min				
phase	0	4	6	15	30
Al	405	409	387	276	229
Ni	238	190	173	166	164

HDEMs Microstructure. A couple of questions arise from the above results: (i) Why is there such a significant change in reaction characteristics in this HEDM system after short-term mechanical activation? (ii) How does MA influence the kinetics of chemical interaction between Al and Ni? To address these issues, let us consider microstructural changes that take place with Al−Ni clad particles during short-term highly energetic ball milling.

Figure 7 shows the XRD data on the phase composition of the initial Al−Ni clad particles and that after 15 min of MA. These data reveal that, within the accuracy limits of XRD analysis, no new phases were formed during short-term ball milling of clad particles under an inert atmosphere. All peaks observed after 15 min of MA nicely fit with those for initial particles, that is, indicating only Al and Ni phases. However, further analysis of the XRD data shows that a decrease of Al and Ni crystalline size occurred during MA (see Table 1). These calculations were performed using the Scherrer equation:

$$\beta_{hkl} = \frac{K\lambda}{L_{hkl}\cos\theta_{hkl}}$$

where β is the width of the peak at half-maximum intensity of a specific crystalline phase (hkl) in radians, K is a constant that varies but is approximately 0.9−1, λ is the wavelength of incident X-rays, θ is the center angle of the peak in radians, and L is the length of the crystallite (angstrom). Data was taken from XRD scans obtained with Cu/Kα X-rays (λ = 1.54059 Å), a 0.02° step size, and 0.5 s preset time. The peaks used for this analysis were (111) for Al, and (200) for Ni, as the (111) Ni peak overlaps with the (200) Al peak. It can be seen that this is one but not the key difference which high energy ball milling introduced to the reaction media.

The microstructures (backscattering images) of the initial and MA treated samples are presented in Figure 8. The initial

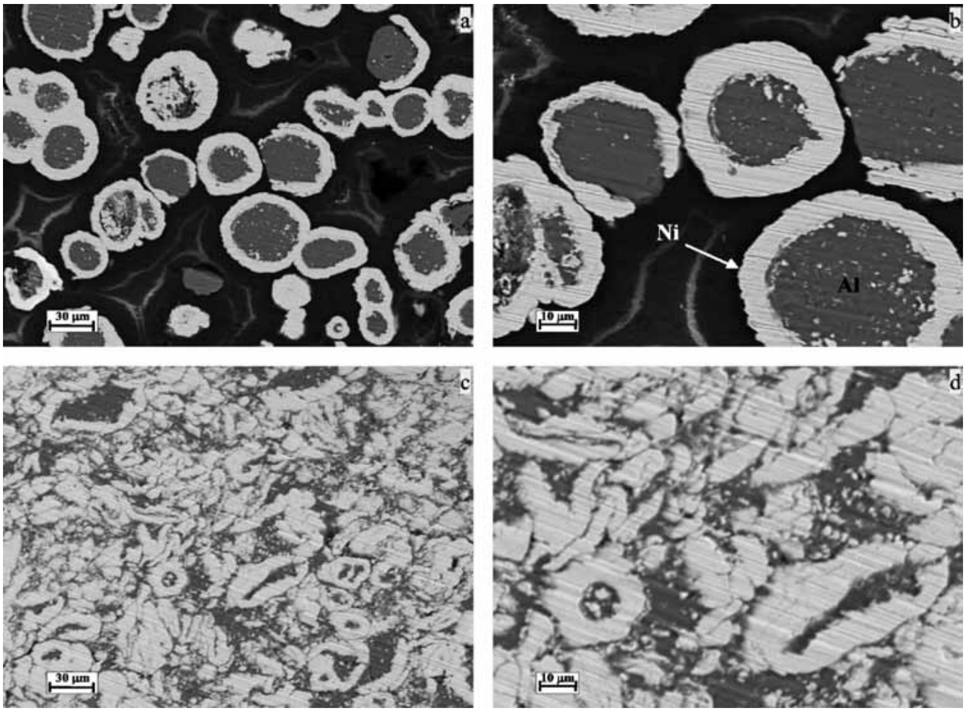


Figure 8. Typical microstructures of initial and mechanically activated samples.

particles have a spherical shape ~35 µm in diameter with ~3.5 µm coating (light phase) of Ni, which approximately corresponds to 1:1 mol ratio. After relatively short-term (compared with 5−10 h in previous works[8−10]) high-energy ball milling, while almost no changes occur with the material crystalline structure, a vast modification of the media microstructure takes place (see Figure 8). Note that in contrast to previous work[10] no process control agents (PCA) were used during MA in this study. For this reason, owing to cold welding, the size of the particle increases with increasing MA time, reaching about 300 µm after 15 min of treatment. Close inspection of the microstructure of the media after MA shows that the thickness of the Ni layers ($\Delta \sim 3$ µm) did not change much, while a significant decrease of scale for the Al phase occurred (from $r_o \sim 40$ µm to $r_o \geq 2$ µm). It is more important that after MA not only has the spherical geometry completely vanished, but also the magnitude of the contact surface area between Al (gray phase) and Ni (light phase) significantly (~2.5 times) increases. It is also important that because MA was conducted under inert atmosphere (argon) "fresh" Al−Ni boundaries do not have any oxide films formed in between, which was proven by additional TEM analysis.

Thus, it can be concluded that formation of small crystallites with possibly a large amount of defects and a significant increase in contact surface area with fresh surfaces formed under inert conditions define the influence of MA on the reactive heterogeneous media.

Kinetics of Chemical Reaction. Because the DTA data and TE results are in good agreement, one can use the DTA approach to define the influence of MA on kinetics of chemical reaction in the investigated HDEM system. For example, the Kissinger method has been used in literature to determine the activation energy of solid-state reactions.[19] Typically, these reactions can be described by an equation:

$$\frac{dx}{dt} = A(1 - x)^n e^{-E_a/RT}$$

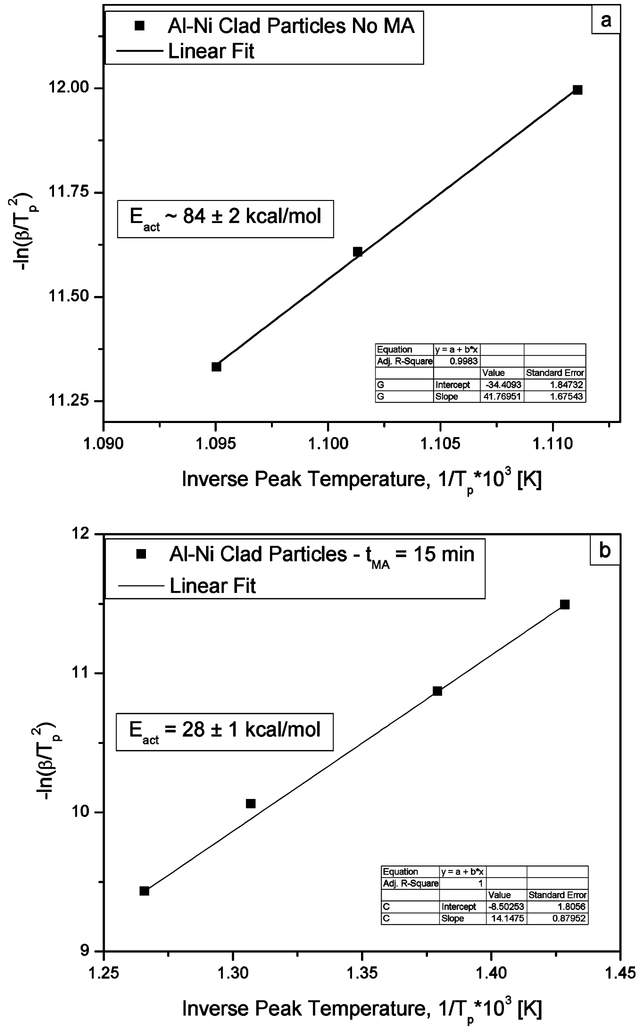
where dx/dt is the rate, A is the frequency factor, x is the fraction reacted, n is the empirical reaction order, E_a is the activation energy, and T is the temperature in Kelvin. If the reaction is accompanied by a rise in temperature, the reaction rate, dx/dt, will rise to a maximum value and return to zero once one of the reactants is depleted. This maximum occurs when the time derivative of the reaction rate is zero. Through differentiation and setting the result equal to zero, the Kissinger equation is obtained:

$$\frac{E_a\beta}{RT_p^2} = An(1 - x)_p^{n-1} e^{-E_a/RT_p}$$

where β is the heating rate, which is expressed as $\beta = \mathrm{d}T/\mathrm{d}t$, and T_p is the temperature at which the maximum rate occurs. Taking the logarithm of the above equation, one obtains

$$-\ln\left(\frac{\beta}{T_p^2}\right) = -\ln\left(\frac{AR}{E_a}\right) + \left(\frac{E_a}{R}\right)\left(\frac{1}{T_p}\right)$$

Thus, activation energy, E_a can be computed by plotting $\ln(\beta/T_p^2)$ as a function of $1/T_p$, where T_p is the peak temperature. Figure 9 shows such Arrhenius type dependencies plotted for initial and mechanically activated powders based on the DTA data obtained at different heating rates. While we expect that the obtained values of activation energy (E_a) are not intrinsic, they are probably effective at describing the combination of different processes. It is evident that MA leads to a significant decrease in E_a from 84 to 28 kcal/mol. The kinetics of interaction in Ni−Al system has been investigated previously.[20,21] Specifically, in ref 20, by using DTA, it was shown that reaction for a mixture of conventional Ni and Al powders starts at exactly the eutectic temperature. The same result was observed for nonactivated Al−Ni clad particles in this work. The activation energy for Ni dissolution in molten aluminum was defined[21]



Equation	y = a + b*x		
Adj. R-Square	0.9983		
		Value	Standard Error
G	Intercept	-34.4093	1.84732
G	Slope	41.76951	1.67543

Equation	y = a + b*x		
Adj. R-Square	1		
		Value	Standard Error
C	Intercept	-8.50253	1.8056
C	Slope	14.1475	0.87952

Figure 9. Kissinger analysis for chemical kinetics in (a) initial and (b) mechanically activated systems.

and appeared to be ∼40 kcal/mol. This value, while lower than the activation energy of chemical reaction for initial Al−Ni clad particles (∼80 kcal/mol), is much greater than E_a for the mechanically activated media (∼28 kcal/mol). Thus, highly energetic ball milling indeed accelerates the rate of solid-state reaction between Al and Ni. As stated above, this effect may be attributed to (i) the increase of contact surface area between the reactants, (ii) formation of "fresh" (oxygen free) boundaries, and (iii) decreasing the scale of heterogeneity of the reactant media in the bulk of the composite agglomerated particle formed during high-energy ball milling.

Concluding Remarks

It was demonstrated that a change of surface contact area between reactants, achieved through short-term (<15 min) energetic ball milling, significantly enhances the kinetics of solid-state reactions in metal−metal systems. Effective activation energy in the temperature range 450−800 K drops by close to a factor of 3 as a result of mechanical activation. It was clearly shown that thermal explosion for mechanically activated energetic mixtures occurs at temperatures well-below any melting points in the considered binary system. Thus, solid-state reactions are responsible for the observed TE phenomenon. The obtained data presents a new approach in "hunting" for experimental confirmation of the beautiful fundamental idea of "solid flame", predicted about 40 years ago.[22]

Also, let us outline that in previous publications[23,24] investigating the ignition characteristics in HDEM systems, a relatively short ball milling time (15−30 min) was also used. However, for the investigated reduction-type mixtures, this short duration was sufficient for self-ignition of the system. Thus, the idea of mechanical alloying prevailed in these previous works. In current work, the opposite concept was tested; that is, mechanical treatment should not lead to a change in the reactive mixture composition but only influence the conditions on the boundaries between the reactants.

Several issues still need to be addressed. First, it is important to know if mechanical activation changes the route of phase formation during TE. Second, it would be interesting to determine if the high temperature kinetics (>800 K) are different for the activated samples. Third, it is critical to know if the reaction initiation mechanism for thermal explosion by electrical preheating is different as compared with those for thermal and mechanical stimulation initiations.

Finally, it is recognized that the melting point of the elements may change when the size of the particles approaches a few nanometers. However, we are confident that this is not the case in this work. On one hand, the size of the Al and Ni grains after activation is on the order of 20−40 nm, which is still large enough for the considered effect. And, direct DTA analysis of Al and Ni particles of such size did not show any endothermic peaks, which may correspond to the melting process, at $T <$ 913 K. On the other hand, time-resolved X-ray diffraction analysis of the mechanically activated media during preheating did not show any liquid phase (noncrystalline) zone before self-ignition. Finally, the microstructure of a MA particle treated at $T <$ 913 K which caused full conversion to the AlNi phase did not show any features of melting; that is, it completely maintained its morphology. All of these issues are discussed in detail in another recent work.[25]

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