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Chapter 10

Kinetics of Heterogeneous Self-Propagating High-Temperature Reactions

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Additional information is available at the end of the chapter

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Abstract

In this chapter, we present an overview of experimental techniques utilized and kinetic data collected for exothermic self-sustained noncatalytic heterogeneous reactions. The data focuses on five primary experimental techniques: electrothermal explosion, differential thermal analysis, electrothermography, combustion velocity/temperature analyses, and several advanced in situ diagnostics, including time-resolved X-ray diffraction.

Keywords: self-propagating high-temperature synthesis (SHS), electrothermal explosion, electrothermography, combustion synthesis, mechanical activation, high-energy ball milling, intermetallics, thermites

1. Introduction

Self-propagating high-temperature synthesis (SHS) is a technological approach for fabrication of materials, which involves self-sustained noncatalytic reactions [1–3]. Currently, there exist three major types of SHS systems: (i) gasless; (ii) with gasification of initially solid precursors; (iii) gas-solid. Within gasless systems, there are three major types of chemical reactions that occur: metal-metal, producing intermetallic (e.g., NiAl, NiTi), metal-nonmetal, leading to synthesis of borides, carbides and silicides (e.g., TiB_2, TaC, $MoSi_2$); nonmetal-nonmetal, producing ceramics (e.g., B_4C, SiC). In the gasification reactions, one of the precursors is volatile, including such elements as S, Se, P, As, Sb. Finally, the gas-solid systems include reactions between metals or nonmetals with different gases, such as nitrogen, oxygen, hydrogen, CO, and CO_2 leading to formation of nitrides, oxides, hydrides and etc. These lists are by no means exhaustive, as different research groups are continually exploring the limits of SHS reactions with different systems, reactants, and conditions. In order to obtain materials with desired

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microstructures, and thus properties, one has to precisely control the synthesis conditions during SHS. These conditions are primarily defined by the kinetics of the chemical reactions taking place in the combustion wave.

In order to study and understand the kinetics of SHS reactions, it is important to examine the fundamentals of kinetics and how they relate to SHS itself. Let us start with general definitions. Thus, assuming that the concentrations of any initial reagent, c_i, and the product are uniformly distributed throughout the entire volume (homogeneous or quasi homogeneous cases), the chemical reaction rate can be expressed by the following equation:

$$W_i = \frac{dC_i}{dt} \text{ or } W_i = \frac{d\eta_i}{dt} \tag{1}$$

where W_i is the reaction rate for the i^{th} reagent or product, $\eta_i = (c^0{}_i - c_i)/c_0$ is the degree of conversion for the i^{th} reagent, $c^0{}_i$ is the initial concentration of the i^{th} reagent, and t is time.

In the nineteenth century, C.M. Guldberg with P. Waage and N.N. Beketov independently formulated the law of mass action. This essentially states that the chemical reaction rates at a given point are proportional to the concentration (mass) of the reactants raised to a proportional exponent. Thus, for an elementary chemical reaction between two reagents A and B of the following form:

$$v_1 A + v_2 B \rightarrow \mathrm{C}, \tag{2}$$

where v_1, v_2 are stoichiometric coefficients.

For this reaction, the law of mass action can be written in the form of a kinetic equation:

$$W = k c_A^{v_1} c_B^{v_2}, \tag{3}$$

where k is the reaction rate constant.

Along with the reactant concentration, the temperature affects the rate of the chemical reaction in a noncatalytic homogeneous reaction. However, the mechanisms of these processes are often unknown or too complicated. This is because the reactions occur in multiple steps, each of which has unique reaction rates. In order to describe the chemical kinetics, a single-step approximation is typically used. This states that the rate of the processes in the condensed state is generally a function of the temperature and degree of conversion:

$$\frac{d\eta}{dt} = F(T, \eta) \tag{4}$$

The single-step approximation employs the assumption that the function in Eq. (4) can be expressed as a product of two separable functions that are independent of each other; the first, $K(T)$, depends solely on the temperature, T, and the second, $\Phi(\eta)$, depends solely on the degree of conversion, η:

$$\frac{d\eta}{dt} = K(T)\Phi(\eta) \tag{5}$$

The temperature function $K(T)$ is generally considered to be the rate constant, while the conversion function $\Phi(\eta)$ is generally considered represent the process mechanism. It is assumed that the reaction mechanism is solely dependent on the conversion, and not the temperature. Eq. (3) resembles a single-step kinetic equation, even though it represents the kinetics of a complex condensed-phase process. The single-step kinetic approximation results in the substitution of a generally complex set of kinetic equations with the sole single-step kinetic equation. Eq. (5) represents a mathematical formulation of the single-step kinetic approximation. With few exceptions, the temperature function is exclusively expressed by the Arrhenius equation:

$$K(T) = A\exp\left(-E_a/RT\right) \tag{6}$$

where A and E_a are considered to be the pre-exponential factor and the activation energy, respectively, T is the absolute temperature, and R is the gas constant.

As our knowledge about the atomic and molecular structure of matter increased, coupled with the development of quantum mechanics, new directions in chemical kinetics have emerged. These directions are typically related to the interactions of individual atoms and molecules, which are more fundamental studies. The set of elementary events is called the reaction mechanism. Fundamental studies on the reaction mechanisms allow us to formulate physical explanations to the kinetic parameters (A, E_a, etc.), which were originally introduced as empirical constants. For example, the activation energy E_a is an energy barrier that must be overcome by molecules in the reaction mixture to reach an interatomic distance where they can from a chemical bond. From Eq. (5), it is clear that, if the concentration of substances or the temperature in the given system varies from point to point. Thus, it is impossible to introduce a common reaction rate for the entire system. In order to get closer to these ideal conditions, in classical kinetic experiments we must continuously mix the reagents and maintain a constant temperature by use of a thermostat.

In the case of heterogeneous reactions involving a condensed phase, where the reactants are not mixed on the molecular level, there is an additional parameter, which controls the rate of interaction, i.e., the contact surface area (S) between the reagents [2]. In this case, the rate of the chemical reactions can be represented as follows:

$$\frac{d\eta}{dt} = A \cdot S \cdot \Phi(\eta)\exp\left(-E_a/RT\right) \tag{7}$$

The presence of condensed phases complicates the reaction; this phase requires that transport plays a role in the reaction. Thus, in general, the kinetics of such reactions are determined both by the intrinsic rate of the chemical reaction and by mass transport (e.g., diffusion). The transport phenomena are essential for replenishing the reactants that were consumed in the reaction zone [4]. Describing the reaction rate is further complicated when the temperature of the reacting environment is changing with time. In this case, along with the processes of mass

transfer and chemical reactions, it is necessary to consider the specifics of heat transfer mechanisms [5]. Typically, the activation parameters are obtained after experiments considering the dependences of time vs. temperature (for isothermal measurements), temperature vs. heating rate (for integral and incremental methods with linear heating rates), or from reaction rate vs. temperature. Considering the above limitations and complications, only the effective or apparent activation energy can truly be considered, as it includes both the intrinsic kinetics as well as processes of heat and mass transport.

2. Techniques for studying SHS kinetics

The task of accurately determining kinetics becomes even more complicated when accounting for the extremely high temperatures of SHS processes (>1800 K) and rapid heating rates (10^3–10^5 K/s). Such parameters are essentially impossible to achieve using conventional approaches for measurement of kinetics parameters. While standard nonisothermal TGA/DTA-based approaches [6] are still used to evaluate the kinetics of SHS reactions, several unique methods such as electrothermal explosion (ETE) [7] and electrothermography (ET) [8] were specifically developed to fit the experimental conditions of SHS reactions. Moreover, recently a variety of advanced in situ diagnostics, including time-resolved X-ray diffraction (TRXRD) [9], high-speed X-ray phase-contrast imaging [10], and high speed transmission electron microscopy (HSTEM) [11] were modified to obtain the kinetics of phase transformations during SHS reactions.

3. Electrothermal explosion

The ETE method was developed in 1977 to study the rapid, high-temperature kinetics that occur in SHS systems [7]. It relies on rapid, uniform preheating of the sample until adiabatic thermal explosion occurs. A representation of a typical ETE setup is shown in **Figure 1**. Briefly, the sample is clamped between two metallic electrodes with sufficient clamping pressure to ensure adequate contact. The power is then initiated, leading to preheating of the sample until a set T_{off} point. After initiation, the resulting time-temperature profiles are simultaneously collected across a number of high-speed photodiodes. In the commonly used ETA-100 system (Aloft, Inc., Berkley, CA), there are 16 photodiodes present, with 1 mm in between them; this corresponds to 0.5 mm spatial resolution. The photodiodes have a temporal resolution of 10^{-5} s and are accurate within 900–3000 K. Once the sample is heated to the selected T_{off} point, the equipment heating is halted, with the consequent rate of self-heating determined solely by the chemical reaction rate. Due to the experimental conditions, i.e., the rapid initial preheating, the reaction occurs in the adiabatic mode. Once thermal ignition occurs, analysis of the time-temperature profile enables extraction of the kinetic parameters (see details in [12]). This technique can be used to study the kinetics at temperatures much higher than can be achieved in other experiments. However, it is often limited in the systems that can be studied due to the stringent heating conditions caused by Joule preheating.

ETE has been used for different gasless SHS systems. These studies have provided valuable kinetic data in extremely high-temperature ranges that are essentially inaccessible by other

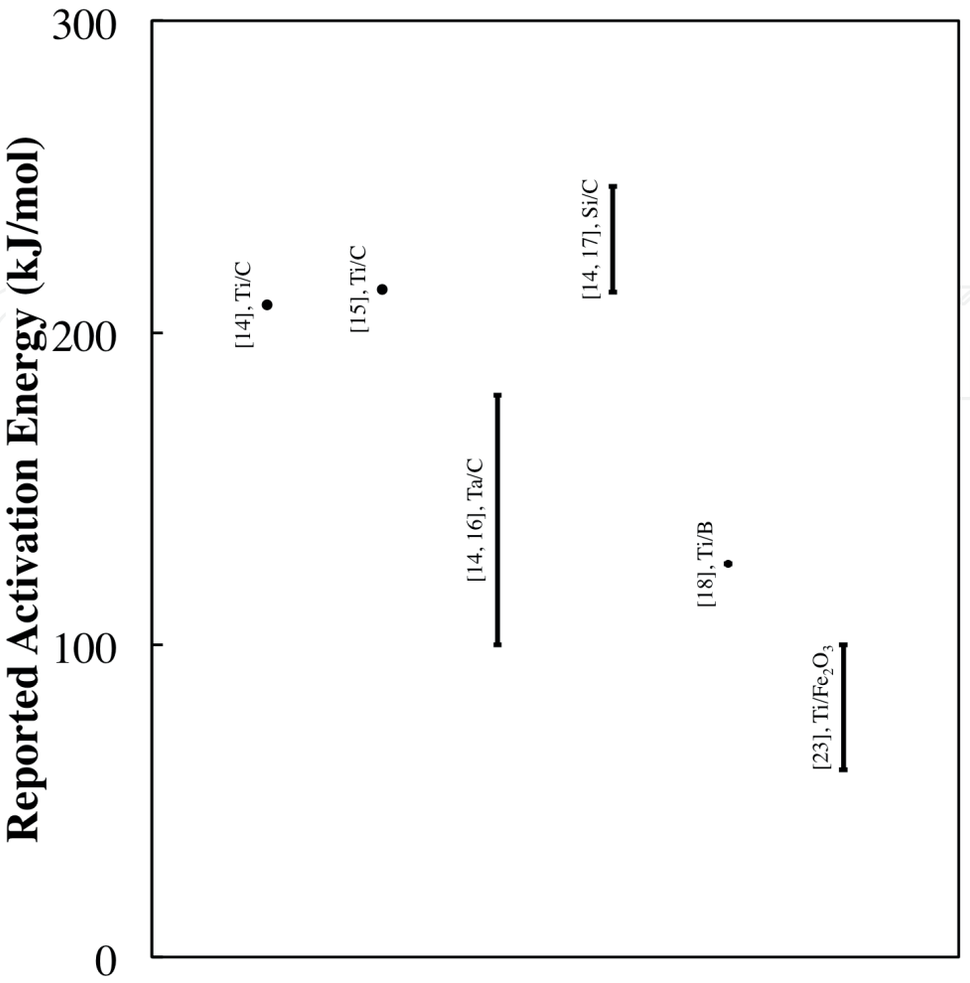


Figure 1. Summary of data collected using the electrothermal explosion technique.

methods. For carbides, the Ti/C system has been studied [13–15], with additional studies in the Ta/C [14, 16] and Si/C [14, 17] mixtures. The Ti/B system was also investigated [18]. The majority of ETE work being focused on the Ni/Al system [12, 19–21]. The Ti/Fe_2O_3 system is the only thermite system investigated by ETE [22]. In addition to the experimental studies, a number of theoretical models have been developed to better understand the ETE process [23–26]. **Figure 1** shows that ranges of reported activation energies for the above mentioned gasless systems, including both intermetallics and thermites obtained by ETE. It can be seen that the results are reproducible, confirming the reliability of the ETE approach. Additionally, the technique allows for a more complete understanding of systems that have multiple steps that rapidly occur in the high-temperature regime, which gives insight into the combustion process [2].

4. Differential thermal analysis/differential scanning calorimetry

This technique has been extensively used in many fields, including: polymer science, biochemistry, and materials science. In order to utilize these methods, a sample is heated at a constant rate until the maximum set temperature is reached. Throughout the experiment, the heat release characteristics of the sample are measured against an inert reference standard.

For typical systems, the points of differing heat release characteristics can be due to phase transitions, crystallization, or reactions; however, this section will only focus on SHS-reaction kinetics. In order to determine the reaction kinetics, the experiment is conducted multiple times with different heating rates. The classical method for determining the reaction kinetics, specifically the activation energy, is by use of the Kissinger method [27], however, many alternative methods for data analysis have been suggested and are widely utilized [28–34]. The 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 2**).

The DTA/DSC based methods are the most widely used for gasless SHS systems, with multiple studies into intermetallics, specifically the Ni/Al [35–43], Ti/Al [44–46], Co/Al [47], Al/Ru [48], Nb/Al [49], and Mg/Al [50] systems, in addition to other binary solid-solid compositions, i.e., the Si/C [51], Mo/Si [52], Zr/B [53], Fe/Se [54]. More complicated ternary systems were also investigated [54–61]. In general, a wide variety of factors can influence the measured kinetics, including variations in reactant microstructure, heating rates, among other factors. Although there are a number of studies into the same systems, it would be valuable for systematic work to be conducted where these factors are studied in depth across different systems to see what

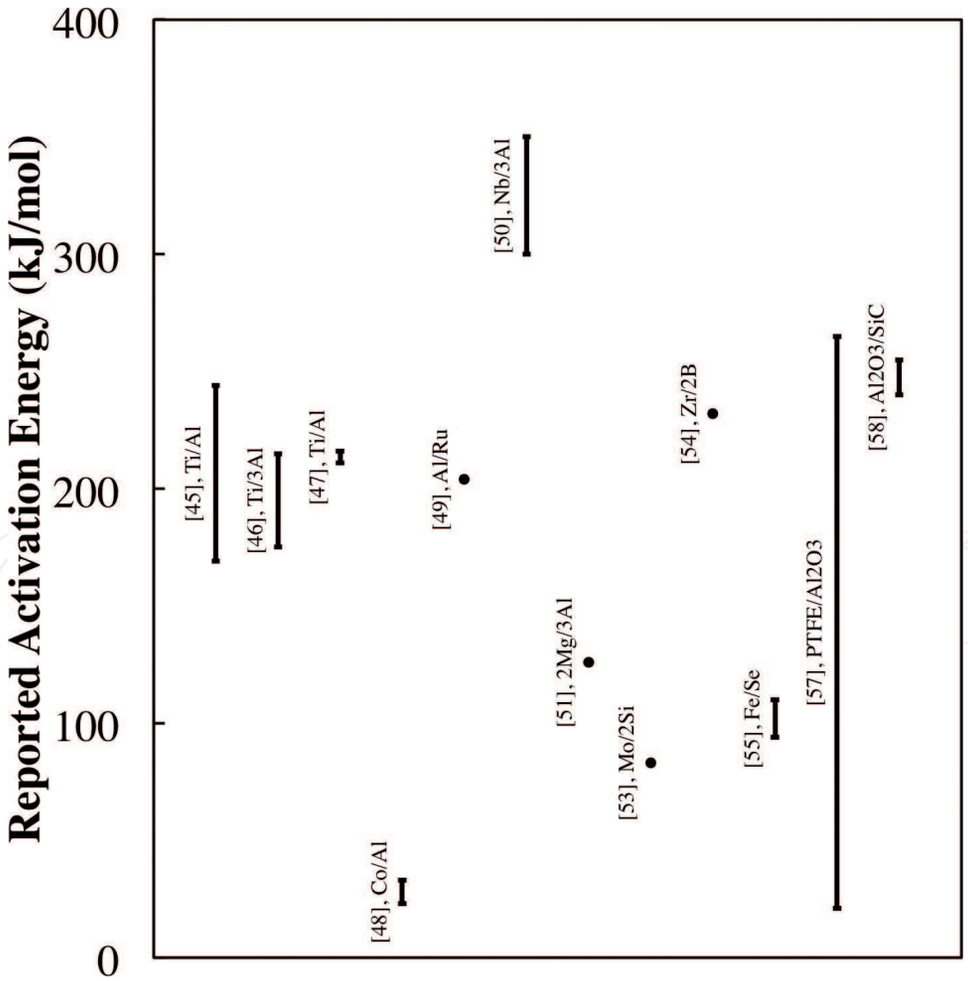


Figure 2. Summary of data collected using isothermal kinetic analysis methods.

general conclusions can be drawn. Additionally, because the experimental conditions, typically specifically heating rate and temperature ranges, are not the same as in traditional SHS, it is unclear whether the determined values can be directly compared or if there is some systemic difference that is occurring.

Figure 2 illustrates the ranges of the obtained values of activation energies for a variety of gasless exothermic reactions measured by DTA method. It can be seen that the determined values are dependent on the experimental conditions utilized, including variations in reactant microstructure, heating rates, among other factors. This issue is discussed in detail below. It would be valuable for systematic studies to be done where these factors are studied in depth across different systems. Additionally, while the activation energies reported using different DTA-based approaches does not appear to be significantly different, it is still important to understand why these differences are present and which methods of analysis are most suitable for these systems.

5. Combustion velocity/temperature analysis

There has been significant effort done to accurately correlate experimental combustion parameters, such as combustion wave velocity and temperature, with the kinetics parameters. Two major approaches have been developed to determine the activation energy by measuring the layer-by-layer combustion front combustion velocity. The first was suggested in 1977 by Merzhanov for 1D propagation [62]. The derived equation takes the form:

$$v^2 = \frac{\lambda}{(-\Delta H_r)\rho}\frac{RT_c^2}{E}\frac{k_0 \exp\left(-\frac{E}{RTc}\right)}{f(\eta_s)} \tag{8}$$

where $f(\eta_s)$ is the selected kinetic law. This technique is most commonly used by adding diluent to the sample. This affects the combustion velocity and temperature; the change in both of these values is measured then compared, leading to the kinetic relationship being understood.

The other major approach to determining the kinetics based on the velocity was developed by Boddington et al. [63]. The relationship takes the form:

$$\frac{\partial \eta}{\partial t} = \frac{\left[\frac{T-T_0}{t_d - t_r} + \frac{\partial T}{\partial t} - \left(\frac{\alpha}{v^2}\right)\left(\frac{\partial^2 T}{\partial t^2}\right)\right]}{\tau_{ad}} \tag{9}$$

where t_d and $t_{r,}$ are the decay and rise times, with τ_{ad} being the temperature rise under adiabatic conditions. More complete derivations of these two models can be found in the original articles [62–64]. Additionally, a more complete understanding of these models, including their relative merits, has been examined in a number of prior works [65–68]. In order to properly use these techniques, relatively simple equipment is required. Typically, sets of thermocouples are used to measure combustion wave propagation velocities, but there are many alternatives, such as IR or high-speed cameras, to measure the propagation velocity.

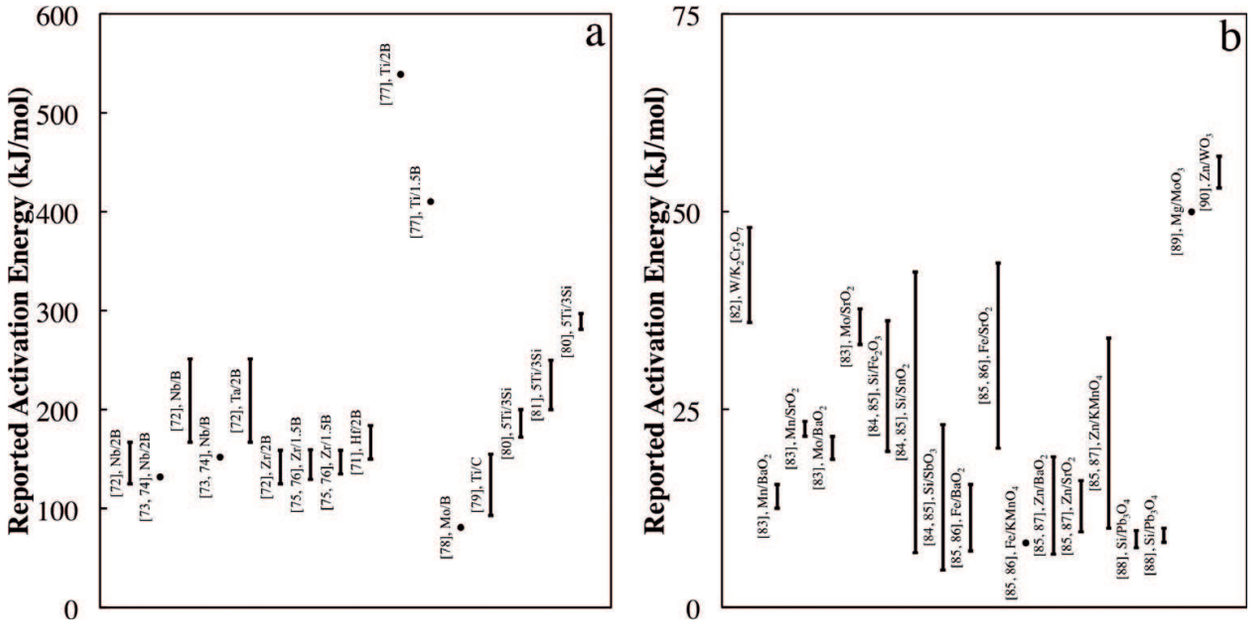


Figure 3. Summary of data collected using layer velocity analysis approached for (a) binary elemental and (b) thermite systems.

Because of the relative simplicity in using these techniques, they have found widespread use within SHS reactions. These layer velocity approaches have been used to describe the kinetics in the Ni/Al system [69, 70], in boride systems, including Nb/B [71–73], Ta/B [71], Zr/B [71, 74, 75], Hf/B [71], Ti/B [76], Mo/B [77], along with other binary systems such as Ti/C [78], Ti/Si [79, 80], thermites [81–89] and more complex ternary systems [78, 90–93].

The results obtained are presented in **Figure 3**. It can be seen that there are a wide variety of systems analyzed. It worth noting that these data were obtained through direct analysis of the combustion parameters, which were obtained at extremely high temperatures and rapid heating rates, which are difficult to accomplish by other kinetics methods. However, it is important to remember that the quasi-homogeneous approximation is utilized for this layer-by-layer combustion front combustion velocity based method, which should be applied with caution [68]. Finally, because this method can be easily used for any type of system, a comparison between thermite and non-thermite type reactions can be analyzed. Comparing **Figure 3a** and **b**, it is obvious that the activation energies for thermites is significantly lower than non-thermite type reactions. This is interesting and is likely related to the specific reaction mechanism that occurs in thermites, compared to non-thermites.

6. Electrothermography

Electrothermography is a technique that utilizes metal wires in either a gaseous or clad environment [8]. The wire is resistively heated rapidly to the desired temperature, with the electric power being adjusted to compensate for the heat release due to the chemical reaction. The obtained data allows for extraction of the rate of heat generation during the reaction under

conditions similar to those in SHS wave. Additionally, because the wires are thin, the sample is quenched essentially as soon as the power is turned off. After the wire is cooled, cross-sections of the wire are collected and the width of the product films is measured, which allows for information on the kinetics of phase formation. This, when done at multiple temperatures and times, gives a more complete picture of the reaction mechanism.

The electrothermography technique has been widely used to study gas-solid reactions. This is because the wires can be exposed to any sort of gaseous environment and also because of the equipment itself; the wires can be heated with any heating rate, mirroring those found in conventional SHS reactions. Because of this, a number of experiments were conducted in nitrogen environments. In specific, the Ta/N [94], Ti/N [95–98], Nb/N [98, 99], and Zr/N [8] systems have been studies. However, the technique has also be used to study carbides, including the Ti/C [100], Zr/C [100], W/C [101], Nb/C [102], along with other systems, including Mo/Si [103–106], W/Si [107, 108], Ni/Al [109], and Ni/Ti [109].

Figure 4 shows the values of the activation energies obtained by this method in gas-solid systems. It can be seen that some reactions have limited steps relating to the gas pressure, while others are relatively independent, suggesting that there are different mechanisms for the

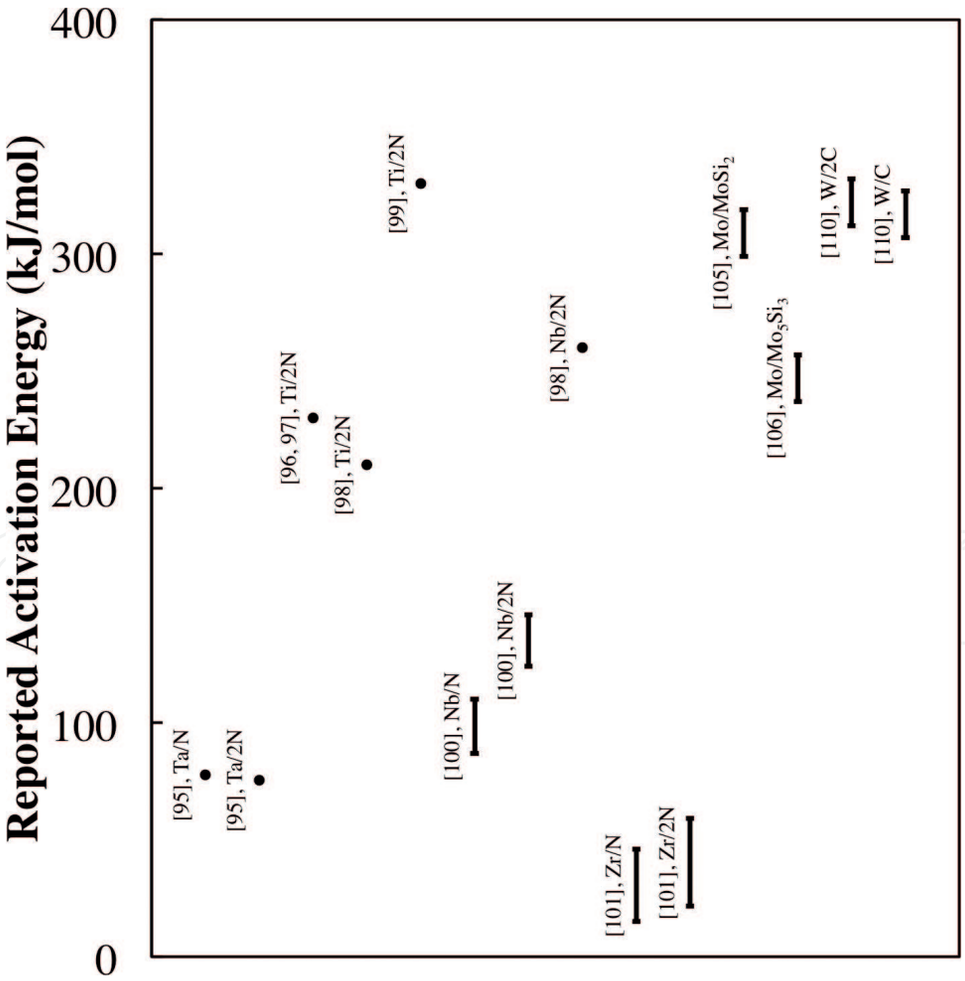


Figure 4. Summary of data obtained using the electrothermography approach.

two classes of reactions. This is also true for the gasless systems investigated. This method provides a window into determining the mechanism and, due to the nature of the experiment, allows for control over the experimental conditions to the degree that individual steps in the reaction can be isolated.

7. Modern in situ high-speed high-resolution methods

There currently exist a number of techniques to study in situ reactions on the time and length scales that occur during SHS reactions; these techniques are incredibly valuable to determine the reaction mechanisms. The most widespread technique is time-resolved X-ray diffraction (TRXRD), and is used to determine the phases that are present during the reaction. It allows for information on the phases present at every stage of the reaction, depending on the time resolution. The lower the time resolution, the more information that can be attained. Depending on the specific setup, whether synchrotron or laboratory-scale based, time resolutions ranging from 10^{-6} to 10^{-2} s are reasonable, with the absolute limit being continually improved with improved synchrotron and detector technology. There has been significant work done with SHS systems due to their solid nature, which is simple to use in TRXRD systems. It is possible to measure solid solution formations, intermediate phases, any melting processes, and the general reaction progress. Through these data it should be possible to extract kinetic data on all reaction stages based on the growth rates of the peaks for the new phase formation coupled with the decomposition of peaks from the previous phase, however, there are currently no established models illustrating this.

There have been a wide variety of experiments conducted on SHS systems by a number of different groups. For intermetallic systems, groups have studied the Ni–Al [9, 110–116], Fe–Al [111, 117–121], Nb–Al [122–124], and numerous other systems [110, 125–127]. Additionally, many groups have examined other SHS based systems, such as carbides, including Ti–C [110, 128, 129], Ta–C [129, 130], and other carbides and cermets [129, 131–134], nitrides [135, 136], oxides [137–139], silicides, including Fe–Si [140, 141], Mo–Si [119, 123, 142, 143] and Ti–Si [144, 145], among a variety of other systems [113, 129, 146–155].

In addition to TRXRD, there is a variety of other, less common, but still very useful techniques available. For example, high-speed X-ray phase-contrast imaging [10] utilizes a synchrotron source coupled with the fact that different phases absorb X-rays differently to determine which phase transformations occur during reaction, essentially high-speed X-ray phase contrast imaging. This technique was illustrated on the W-Si system at the Advanced Proton Source in Argonne National Laboratory. This method allowed for direct imaging of irreversible reactions in the W-Si reactive system at frame rates up to 36,000 frames per second with a 4-μs exposure time and spatial resolution of 10 μm. Another advanced technique is high-speed transmission electron microscopy (HSTEM) [11], which utilizes all abilities of conventional TEM, but at nanosecond time scales. This allows for direct observation of both the structural changes and crystal structure during the reaction with unprecedented resolution, as shown in **Figure 5**. Specifically, a high-time resolution dynamic transmission electron microscopy (DTEM) was developed in Lawrence Livermore National Laboratory (USA) and captures the material

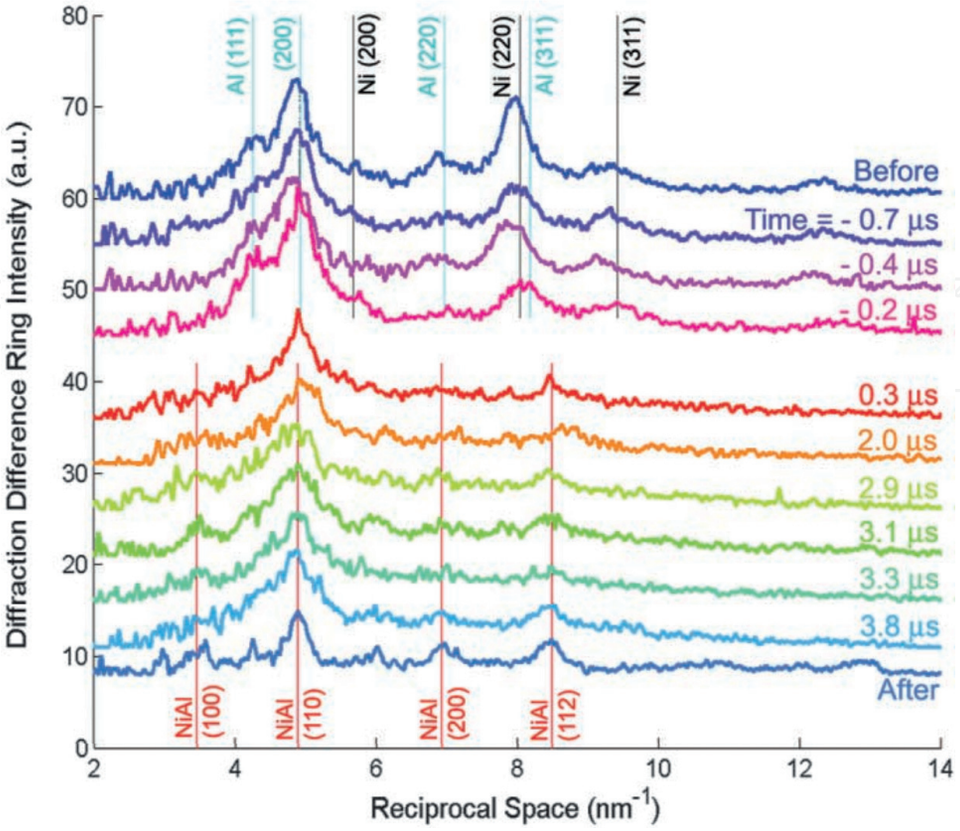


Figure 5. Dynamic single-shot diffraction with 15-ns time resolution of regions before, during, and after the exothermic mixing reaction front has passed. The times indicated at right are in relation to the reaction front, set at t = 0 s. The crystal structure clearly changes from separate fcc Al/Ni and Ni/V layers to an intermetallic B2 structure NiAl phase within 300 ns after the arrival of the hot reaction front; a.u., arbitrary units. Adapted from Kim et al. [11].

dynamics with nanosecond time resolution. The current DTEM performance shows a spatial resolution less than 10 nm for single-shot imaging, using 15 ns electron pulses. The solid-state reactions in NiAl reactive multilayer films, the martensitic transformations in nanocrystalline Ti, and the catalytic growth of Si nanowires were studied by DTEM [156].

The above unique diagnostics, which are used to determine phase and structural transformations in situ, are incredibly valuable. Used alone, they provide information on the reaction progress and mechanism; however, there are two significant paths that would make these techniques more valuable. When coupled with current methods for determination of kinetics, the understanding of the reaction mechanisms in all systems will be improved. Furthermore, there is no current way to extract kinetic parameters from some techniques (TRXRD, DTEM, etc.); it would be valuable to develop reliable approaches for these techniques.

8. Structure-kinetics relationship of SHS systems

There have been a number of studies shown that indicated that the structure of materials plays a role in the kinetics; multiple groups using a wide variety of techniques and approaches have confirmed this conclusion. For example, it was shown that by changing the internal structure

of the reactive composite by using high-energy ball milling (HEBM) in the same binary system, one can significantly change the measured effective activation energy [20]. There are two approaches to quantifying this effect; the first is by rigorous quantification of the already existing structures, and the second is by use of more simple, so-called model microstructures, typically manifested in reactive nanofoils with periodically fabricated layers of reactants.

Shuck et al. utilized two techniques for quantitative determination of HEBM-produced materials [5, 157]. The first technique, X-ray Nanotomography, works by passing high brilliance X-rays through the sample and collecting the transmitted X-rays. In order to convert this 2D projection into three dimensions, the sample is rotated and the same quality of X-rays is passed through again and the projections at different angles are collected; this collection of images can be combined, leading to a 3D map of the internal sample. The second technique, focused ion beam (FIB) sectioning, uses a FIB to serially section the HEBM-produced particles. The series of images were first shear corrected, contrast normalized, and then aligned using a least-squares method, with the reconstructions shown in **Figure 6**. After structure analysis, Shuck and

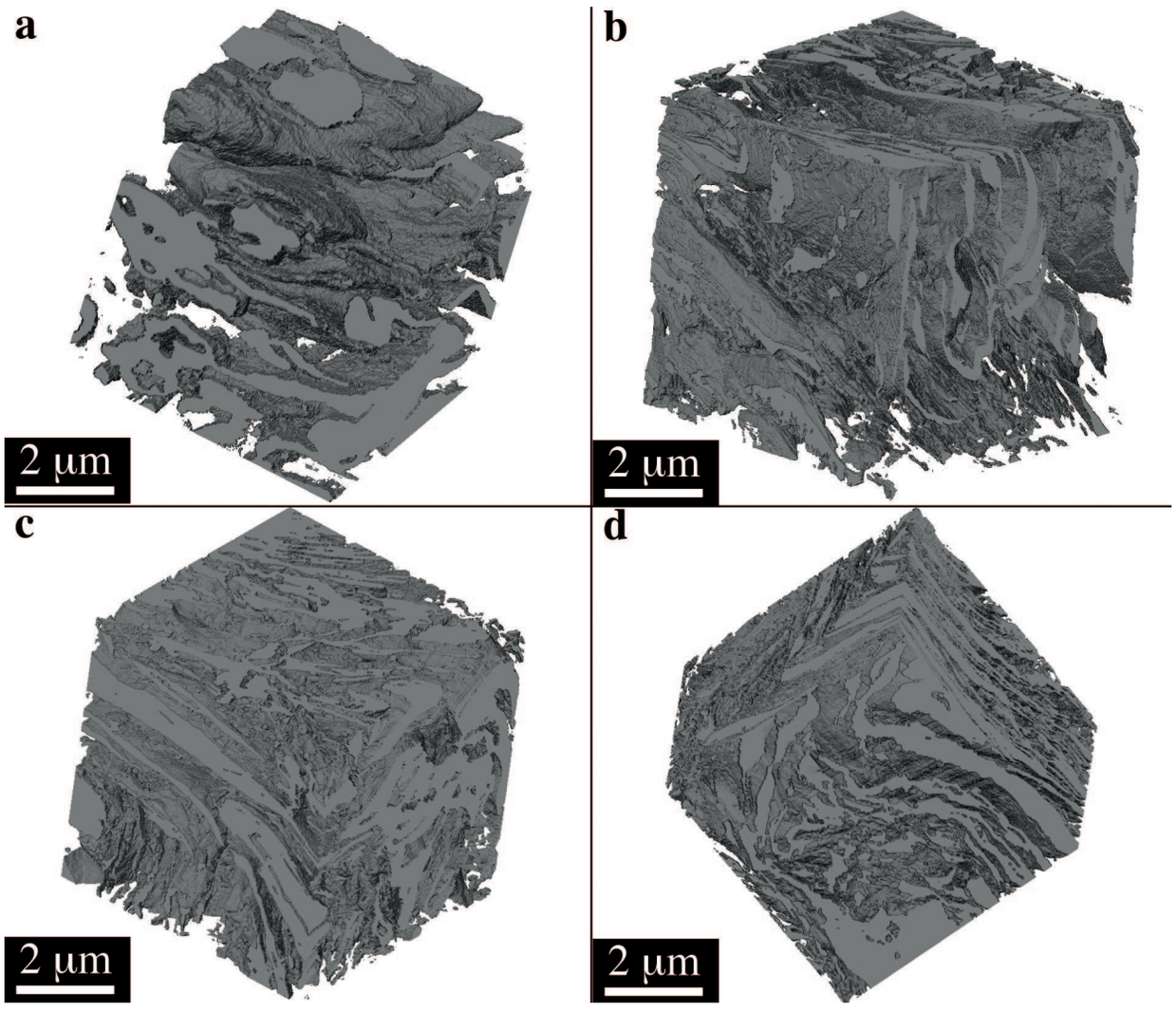


Figure 6. Reconstructed internal volumes of the nanocomposites for different time (min) of WG: (a) 10, (b) 20, (c) 30, and (d) 40 (Ni is the gray phase, and Al is the void-space). Adapted from Shuck et al. [5].

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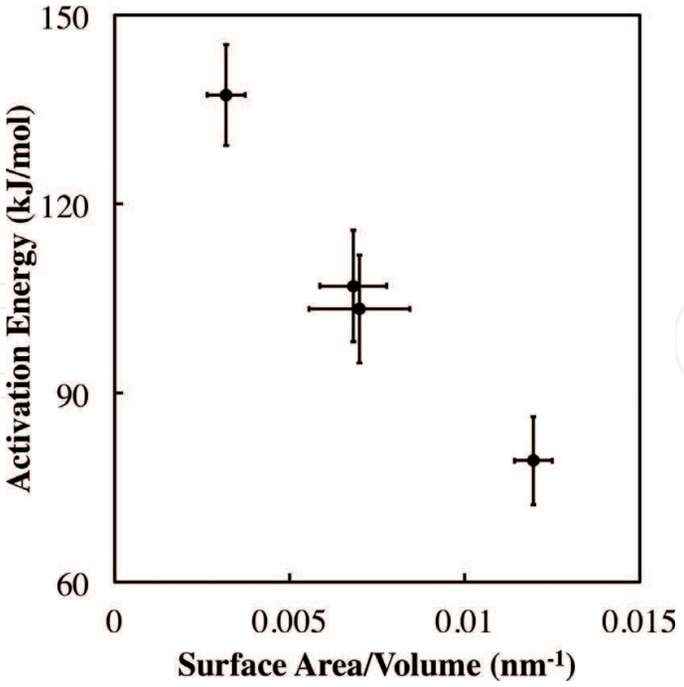


Figure 7. Dependence of effective activation energy of the reaction as a function specific contact surface area between Ni and Al phases. Adapted from Shuck and Mukasyan [20].

Mukasyan [20] further studied these effects on the kinetics in the Ni–Al system using the ETE approach. They showed, by use of the above 3D reconstruction techniques, that it is possible to control the activation energy by modification of the contact surface area between the reactants. Effectively, they lowered the effective activation energy from 79 to 137 kJ/mol, which corresponded to a change in the contact surface area/volume ratio between 0.0120 and 0.0032 nm^{-1}, respectively; this relationship is shown in **Figure 7**. Additionally, it was suggested that, for SHS systems, the apparent activation energy is affected primarily by the contributions between the diffusion and intrinsic reaction activation energies. Additionally, they offered an explanation for the relationship, relating to the difference in contribution between the diffusive activation energies (volume, grain-boundary, and surface) in conjunction with the intrinsic activation energy. This suggests that the measured and reported activation energies presented in literature are effective, or apparent, activation energies that depend highly on the structure and experimental conditions.

9. Modification of the reaction mechanism depending on the experimental conditions

In a very early study on the reaction mechanisms, Philpot et al. examined the effect of varying factors on the reaction rate [35]. In one study, they systematically varied the aluminum concentration, the heating rate, and the nickel particle size. Briefly, they showed that, depending on the applied heating rate, two different mechanisms could be initiated. The first, when using slower heating rates, was related to the melting of the aluminum metal, followed by spreading over the nickel particles. For their studies, they saw two definite peaks relating to the reaction.

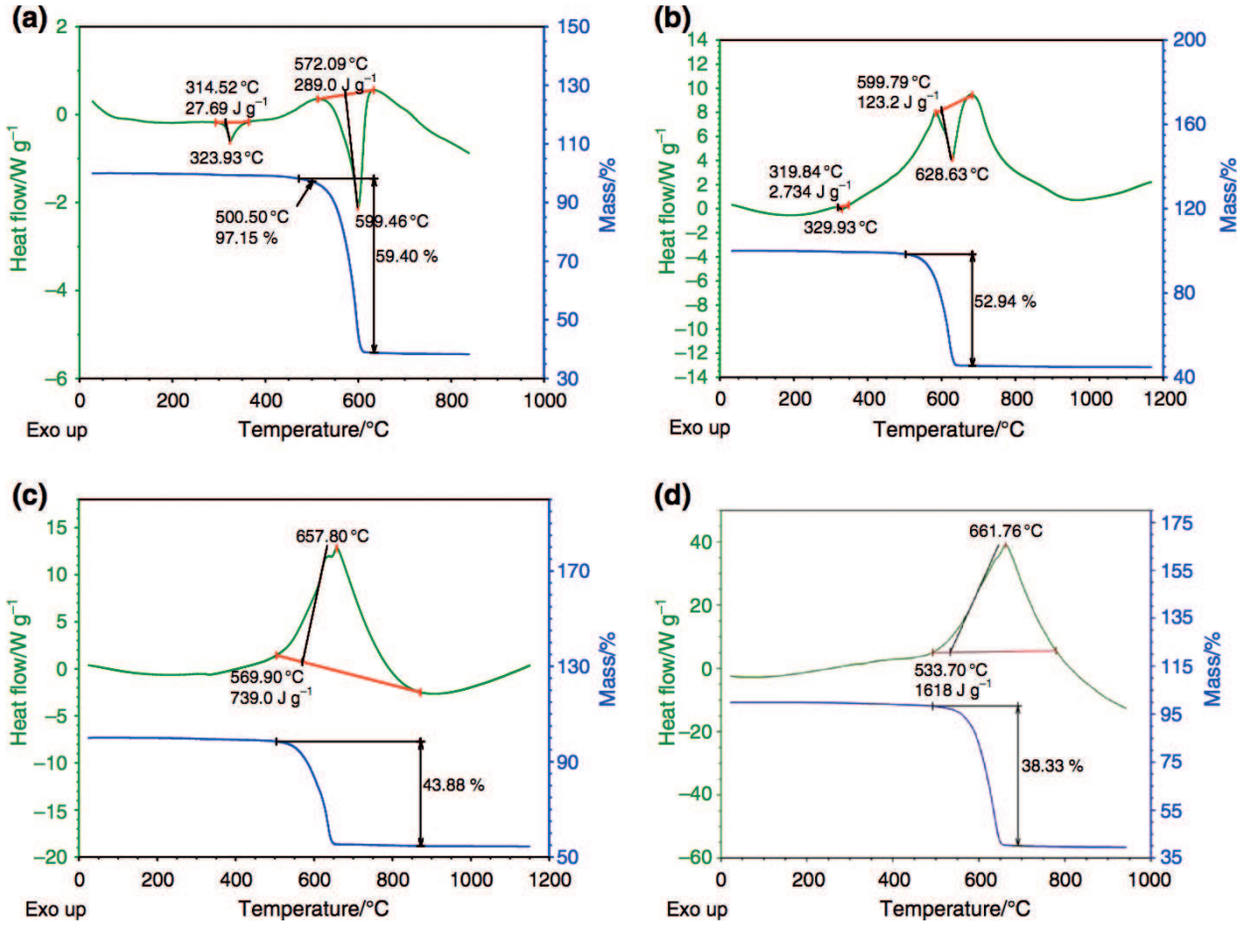


Figure 8. DTA-TG curves for the PTFE-Al_2O_3 system using heating rates of (a) 20, (b) 80, (c) 150, and (d) 160°C min^{-1} under an argon atmosphere. The additional lines are showing the changes in heat flow and mass percentage values. Adapted from Hobosyan et al. [56].

However, when they increased the heating rate, they instead only witnessed a single peak. This peak was related to the solid state transition to the final product. For transitional values between the two extremes, they found that there were relative contributions of both different mechanisms. This is an important observation which should be accounted when investigating the reaction kinetics in highly exothermic systems. Indeed, it shows that it is possible to control the reaction mechanism depending on the applied experimental conditions. This effect was confirmed by many researchers both for gasless and gas-solid systems [36, 56, 158–162] and is illustrated in **Figure 8**. Furthermore, depending on the reaction mechanism, it is possible to control both the final product phases and their microstructures, thus producing materials with tailored properties.

10. The Ni/Al system as a model for SHS kinetics

In the SHS community, the Ni/Al system has been widely used a model system. It was chosen because of its low ignition temperature, high oxidation resistance, and ease of processing. Because of this, all of the above mentioned techniques have been utilized to study kinetics in

this system. Thus it is possible to compare the data collected across a large number of experimental conditions to give more complete understanding of this gasless reaction. Although this system has been extensively studied for over 40 years now, a consensus has not emerged on the exact activation energy, as can be seen in **Figure 9**. The data again illustrate the effect that differing experimental conditions play, whether in the material structure, heating rates, or other experimental factors.

In 1987, Philpot et al. did preliminary studies on the Ni/Al system kinetics using the Kissinger approach [35]. They showed that there is an effect of heating rate, the nickel particle size, as well as an effect of a varying Al content, on the reaction mechanism in this system [35], this work is highlighted in more detail in an above section. Hunt et al. examined the effect of particle size on the apparent activation energy using a CO_2 laser to control the heating coupled with the DTA-based Kissinger approach. Using 800 nm size Ni particles coupled with 20 μm, 4 μm, 80 nm, and 40 nm Al particles, it was found that that these reactions had activation energies of: 103.5 ± 10.5, 97.3 ± 5, 21.2 ± 2.5, and 17.4 ± 2.85 kJ/mol, respectively [36]. They then increased the Ni size to 15 μm and measured with the four Al sizes, resulting in 162.5 ± 1.4, 131.2 ± 2.6, 103.6 ± 5.2, and 80.1 ± 6.3 kJ/mol, respectively [36]. This confirms that the initial reactant structure plays a significant impact on the kinetics. The size of either reactant significantly alters the effective kinetics. Kim et al. studied this reaction using nanolaminated composite micro-foils with different thickness ratios between Ni and Al at heating rates between 5 and 100 K/min. For 4:1 foils, they found that the formation of $NiAl_3$ occurred, followed by Ni_2Al_3, with activation energies of 142 and 106 kJ/mol, respectively [37].

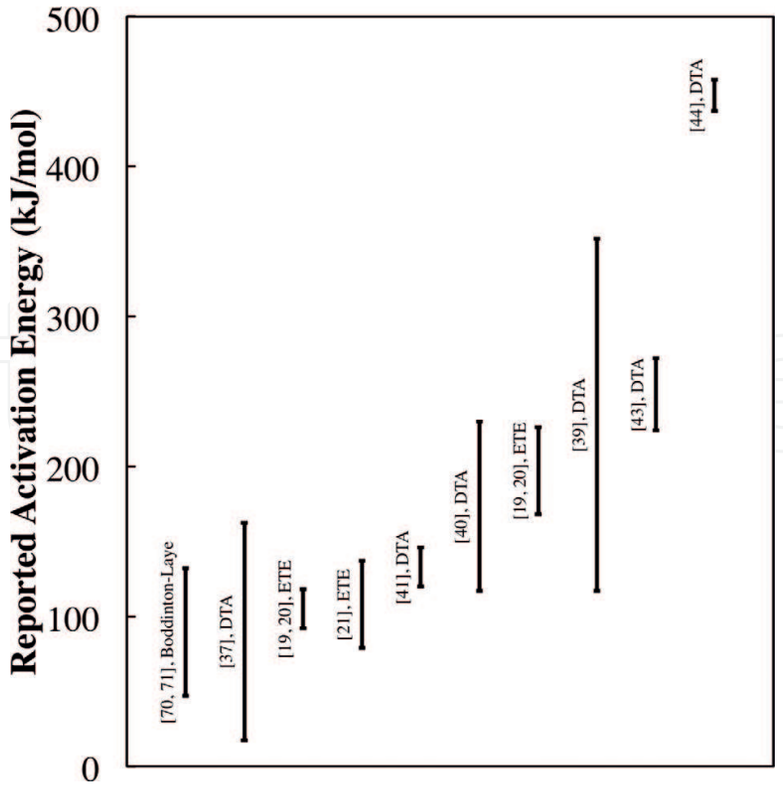


Figure 9. Summary of kinetic data collected for the Ni/Al system.

In order to more fully understand the relationship between structure and the kinetics, White et al. investigated the effect of mechanical activation (MA) on the Ni/Al system kinetics using the Kissinger approach. Two types of Ni/Al composites were used; Ni clad Al particles, as well as Ni/Al composite particles produced by high-energy ball milling (HEBM). The Ni clad Al particles were found to have an apparent activation energy of 352 ± 8 kJ/mol, while after MA the particles had much lower activation energy of 117 ± 4 kJ/mol [38]. Reeves et al. studied the thermal and impact reaction kinetics in the Ni/Al system for both MA and nano-sized reactants using the Kissinger approach. For the nano-mixture, the reactants were both ~80 nm in size and, for the MA particles, they underwent 15 minutes of HEBM. The nano-mixture exhibited a 230 ± 21 kJ/mol activation energy, while the MA mixture was calculated to be 117 ± 8 kJ/mol [39]. Manukyan et al. studied the Ni/Al system after MA and the effect of a coarse vs. nanolaminated nanostructure on the kinetics using the Kissinger approach. Using heating rates between 10 and 50 K/min, they found that the reaction proceeds in three steps, $NiAl_3$, Ni_2Al_3, and then finally NiAl. For the coarse microstructure, these peaks corresponded to 99 ± 4, 138 ± 13, and 120 ± 37 kJ/mol, while the nanolaminated microstructure corresponded to 93 ± 2.5, 145 ± 13, and 146 ± 14 kJ/mol, respectively [40]. This illustrated that the activation energies depend on the microstructure, even after MA.

Kuk et al. studied compression bonded Ni/Al nanofoils with and without a BN lubricant using the Kissinger approach. With the BN lubricant, it was found that the reaction proceeded in two steps, with the activation energies being 224 and 272 kJ/mol, respectively, resulting in the formation of Al_3Ni_2 [42]. Without the lubricant, the reaction proceeded in a single step with activation energy of 470 kJ/mol, this difference was attributed to the oxide layer between the reactants [42]. Maiti and Ghoroi studied the Ni/Al system using the Friedman, Ozawa, and Kissinger approach, yielding activation energies of 437.0, 448.4, and 457.6 kJ/mol, respectively [43].

Using the ETE approach, Shteinberg et al. and Mukasyan et al. confirmed that MA affects the activation energy in the Ni/Al system, as shown in **Figure 10** [12, 19]. Initially, they studied the kinetics of the Ni clad Al system (which was also studied in [38]), which showed two distinct steps. The first step was related to the melting of Al and subsequent cracking of the Ni layer, which had an activation energy of 197 ± 29 kJ/mol. The final step was the diffusion of Ni into Al, which was measured as 523 ± 84 kJ/mol. In the MA system, they found that only a single step occurred and was measured to be 105 ± 13 kJ/mol. Shuck and Mukasyan further studied the effects of MA on the kinetics in the Ni/Al system using the ETE approach [20]. Using 3D reconstruction techniques, they showed that the surface area contact between the reactions is directly related to the effective activation energy, which ranged from 79 to 137 kJ/mol, which corresponded to a change in the contact surface area/volume ratio between 0.0120 and 0.0032 nm^{-1}, respectively. This work is further highlighted in an above section. Finally, using the ETE approach, Filimonov et al. studied the effects of MA on the nonstoichiometric, 3Ni/Al system [21]. They utilized a criterion based on the minimum curvature of the heating rate logarithm, which resulted in an anomalously low measured activation energy of 9.5 ± 2 kJ/mol.

Marin-Ayral et al. studied the Ni/Al system under different gas pressures using the Boddington-Laye method. They showed that for pressures of 100, 320, and 500 MPa, the measured activation energies were 47, 59, and 132 kJ/mol, respectively [68, 69]. Vadchenko et al. studied the Ni/Al

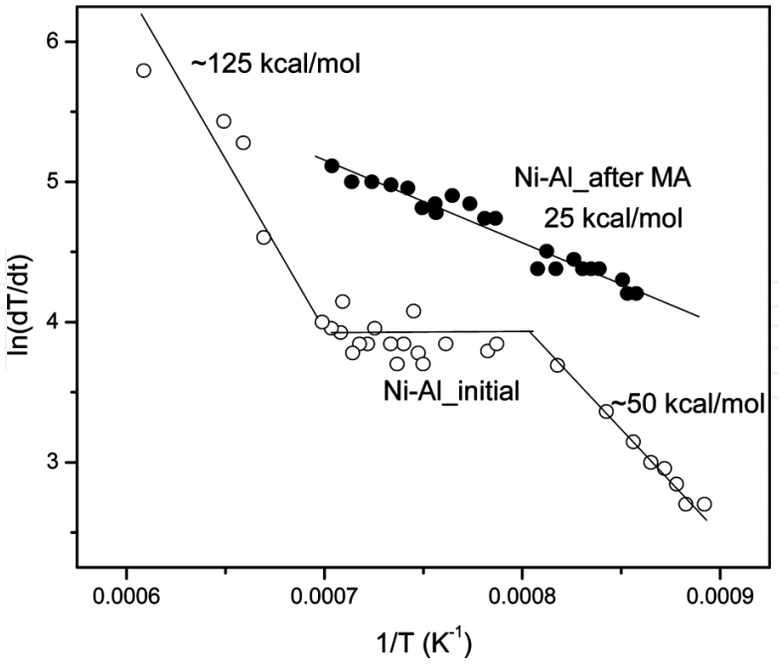


Figure 10. Arrhenius plots for reactions in Al clad by Ni systems before and after high energy ball milling. Adapted from Shteinberg et al. [12].

system using electrothermography. Their results showed that the reactions occur first through grain boundary diffusion, followed by diffusion of the solid metal into the liquid phase [109]. Finally, Mukasyan et al. examined the Ni/Al system using a combination of TRXRD and ETE, showing that the reaction mechanism itself changes based on the structure, this work is highlighted in an above section [116].

Thus we may conclude that although a wide variety of studies were conducted on the Ni/Al system with many different experimental and structural conditions, the reported values of activation energies vary drastically. Additionally, there would be great benefit to combining utilizing multiple methods simultaneously to bridge understanding between the different experimental techniques.

11. Future directions in SHS kinetics

More complete understanding on the kinetics of SHS reactions is vital for both fundamental science and also for practical or industrial reasons. To better understand the kinetics, combinations of techniques must be utilized, specifically coupling techniques that give information on the kinetics while simultaneously examining the phase transformations that are occurring. To further understand the reaction mechanisms, additional studies must be conducted on the relationship between the structure and the resulting kinetics. Additionally, work must be done to compare the different methods of studying kinetics and their interrelationships. In the limited cases where there is data available for the same system across different techniques,

there is a wide range of published kinetic data. It is imperative to continue to study SHS kinetics in a more systematic, fundamental fashion.

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