

Article

A Novel Understanding of the Thermal Reaction Behavior and Mechanism of Ni/Al Energetic Structural Materials

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Abstract: Ni/Al energetic structural materials have attracted much attention due to their high energy release, but understanding their thermal reaction behavior and mechanism in order to guide their practical application is still a challenge. We reported a novel understanding of the thermal reaction behavior and mechanism of Ni/Al energetic structural materials in the inert atmosphere. The reaction kinetic model of Ni/Al energetic structural materials with Ni:Al molar ratios was obtained. The effect of the Ni:Al molar ratios on their thermal reactions was discussed based on the products of a Ni/Al thermal reaction. Moreover, depending on the melting point of Al, the thermal reaction stages were divided into two stages: the hard contact stage and soft contact stage. The liquid Al was adsorbed on the surface of Ni with high contact areas, leading in an aggravated thermal reaction of Ni/Al.

Keywords: Ni/Al energetic structural materials; thermal reaction; reaction kinetic model; two reaction stages; reaction mechanism



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1. Introduction

All-metal energetic structural materials, such as Al/Ti, Al/Zr, Ni/Al, and so on, have received more and more attention due to their good strength and energy-releasing properties [1–5]. Among them, Ni/Al was considered as a promising material for further application in the defense industry, such as in the fields of fragments and shaped charges, because of its higher energy density (1507.7 J/g at the equal molar ratio), higher strength properties, and faster energy-releasing capacities. Its energy release, which originates from an intermetallic reaction, has received much attention in recent decades. However, its reaction behavior and mechanism have not been explained clearly, which has limited its application.

Currently, for Ni/Al energetic structural materials, a lot of works mainly focused on its macroscopic reaction. For example, Vandersall and Thadhani [6] reported that the shock response of Ni/Al energetic structural material was divided into two categories: shock-assisted chemical reaction and shock-induced chemical reaction. Song and Thadhani [7] proposed the thermodynamic calculation model for the shock reaction, based on the effects of the reaction energy release and the formation of products on the equation of state. Bennett and Horie [8] improved the thermodynamic reaction model to reduce the errors and ambiguities of existing Hugoniot calculations. Zhang et al. [9] also built the thermal chemical model of shock-induced chemical reaction. The reaction efficiency was evaluated by combining shock kinetics and chemical reaction kinetics. These works could be used to describe the macroscopic response of the Ni/Al energetic structural material. However, they did not illustrate the microscopic reaction mechanism in detail.

Essentially, the energy release of all-metal energetic structural materials depends on the chemical reaction process [10–12]. The critical parameters of the chemical reaction are determined through the impact-induced energy release test instead of the direct measurement [13]. This method strongly depends on the shock compression theory with the chemical reaction. Due to some assumption, it is difficult to widely use the reaction model for another type of energy release tests.

Generally, the thermal analysis test, referring to the differential scanning calorimeter, has been widely used to understand the chemical reaction of energetic materials [14,15]. To directly determine the activation energy and the pre-exponential factor in the chemical reaction equation of energetic materials, the Kissinger method [16], Flynn–Wall–Ozawa method [17], and Satava–Sestak method [18] were used. Moreover, for a complex chemical reaction, the classical differential methods and kinetic integration methods were built to analyze the thermal decomposition mechanism function and kinetic parameters [19,20]. These works showed a good analysis result, and further revealed that classical thermal analysis methods could be used to analyze the reaction kinetic parameters of energetic structural materials.

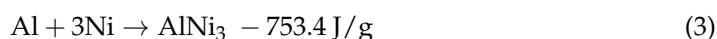
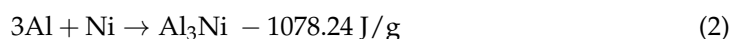
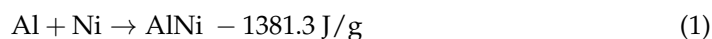
A few works on dynamic thermal analysis refer to the basic thermal reaction parameters of all-metal energetic structural materials. It was found that a simple analysis strategy was not used to match the whole thermal reaction process of Al-based energetic structural materials, especially for Ni/Al. According to the Ni–Al binary phase diagram, the Ni–Al eutectic temperature is higher than the melting point of Al. During the thermal reaction process, the state change of Al from solid to a liquid state occurred in a thermal reaction. Resulting from the state change of Al in the Al-based energetic structural materials, the existing reaction model mismatches the kinetic result of thermal reaction. The traditional analysis strategy only considers the solid-solid reaction in the thermal process, but ignores the influence of the state change of Al on the thermal reaction between Al and Ni. This causes the misunderstanding of the thermal reaction process. Therefore, it is urgent and important to study the thermal reaction behavior and mechanism of Ni/Al energetic structural materials depending on the state change of Al.

Herein, we studied the thermal reaction behavior and mechanism of Ni/Al energetic structural materials with the state of Al at two different reaction stages, depending on the melting point of Al. By fitting the differential scanning calorimeter (DSC) curves of Ni/Al energetic structural materials with different Ni:Al molar ratios, the hard contact stage and soft contact stage were distinguished. Their reaction kinetic models were obtained and the thermal reaction parameters, referring to activation energy E , pre-exponential factors (A), and reaction function (f), were calibrated at different reaction stages. Reaction products of Ni/Al thermal reaction was used to analyze the effect of the Ni:Al molar ratios on their thermal reaction. Furthermore, the thermal reaction mechanism of Ni/Al energetic structural material was provided, based on two different reaction stages. This work offered a new way to understand thermal reaction behavior and mechanism of Ni/Al energetic structural materials under the different temperature stages.

2. Experimental

2.1. Materials

Different Ni and Al molar ratios will lead to different chemical reactions. Theoretically, when the molar ratio of Ni and Al is 1:1, 1:3, and 3:1, the corresponding apparent reaction is shown in the Equations (1)–(3), respectively [21].



Three types of samples Ni/Al with different molar ratios were prepared. The molar ratio was set Ni/Al = 1:1, Ni/Al = 1:3, and Ni/Al = 3:1, respectively. The components Ni and Al with the particle size of 20 μm , and 25 μm , respectively, were used. Powders Ni and Al were purchased from Shanghai ST-Nano Sci & Tech., Co., Ltd., Shanghai, China. Alcohol was provided by Chengdu Kelong Chem., Tech., Co., Ltd., Chengdu, China.

The components Ni and Al were mixed with the different molar ratios. Then, the mixed powders were prepared by the milling technique for 5 h in the alcoholic environment. Finally, the powder was obtained with drying treatments.

2.2. Thermal Analysis and Characterization

The thermal reaction behavior of the mixed powder samples was recorded in an argon atmosphere by a STA449F3 differential scanning calorimeter (Netzsch, Bavaria, Germany). The mass of each sample tested was 20 mg. The test conditions were alumina crucible with cover, 20 mL/min of protective gas, and 60 mL/min of purging gas. The DSC curves with the range from the room temperature to 1200 K were collected to study their thermal reaction processes under the different heating rates (5 K/min, 10 K/min, 15 K/min, and 20 K/min).

The structure of the reaction products from the thermal reaction of Ni/Al samples were characterized by X-ray diffraction (XRD). XRD patterns from 5–90 degrees were carried out via a D8 Advances XRD apparatus with the voltage of 40 kV and the current of 40 mA.

Generally, the chemical reaction kinetics equation is used to quantify the reaction behavior. According to the DSC test, the parameters of the equation can be obtained [22]. Assume that the reaction of Ni/Al samples follows the Equations (4) and (5), which builds the relation between the reaction degree and the temperature. Actually, the two equations are equivalent as the differential and integral forms of non-isothermal systems for calculating the thermodynamic parameters.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{(-\frac{E}{RT})} f(\alpha) \quad (4)$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \left(\frac{A}{\beta} \right) e^{-\frac{E}{RT}} dT \quad (5)$$

where α is the reaction degree, T is the absolute temperature with the unit K, A is the pre-exponential factor with the unit min^{-1} , β is the heating rate with the unit K/min, E is the apparent activation energy with the unit J/mol, R is the universal gas constant 8.31 J/(mol·K), and $f(\alpha)$ is the reaction function. According to the DSC curve, the reaction degree α means the ratio of the area enclosed by the curve at some temperature to the whole area enclosed by the whole DSC curve.

Considering the results of thermal analysis based on multiple heating rates are more accurate [23], the Ozawa method is used in the current work to determine the parameters in Equation (5). Firstly, define $u = \frac{E}{RT}$, the equation can be rewritten as

$$\int_0^T e^{-\frac{E}{RT}} dT = \int_{-\infty}^u -\frac{E}{R} \frac{e^{-u}}{u^2} du \quad (6)$$

Substitute Equation (6) into Equation (5), and define $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ and $P(u) = \int_{-\infty}^u -\frac{e^{-u}}{u^2} du$. Then, Equation (5) can be rewritten as

$$g(\alpha) = \frac{AE}{\beta R} P(u) \quad (7)$$

The Doyle approximation [24] is used to estimate $P(u)$,

$$\lg P(u) = 2.315 - 0.4567u \quad (8)$$

Take the logarithm of Equation (4) combined with Equation (5), and Equation (6) can be rewritten

$$\lg \beta = \left[\lg \frac{AE}{Rg(\alpha)} - 2.315 \right] - 0.4567 \frac{E}{RT_\alpha} \quad (9)$$

In order to obtain the parameters in the equation, the least square method is used to fit the straight line as Equation (9), where $\frac{1}{T_\alpha}$ is the abscissa and $\lg \beta$ is the ordinate. Four DSC curves, under different heating rate conditions, can determine four data points to be fitted. The apparent activation energy can be obtained according to the slope of the fitting line.

It should be stressed that in order to obtain E , α must be chosen to be 1. In addition, the pre-exponential factor A and the reaction function f are coupled in the vertical intercept.

Further, in order to determine the reaction function f , the master curve method will be used [25–27]. Firstly, to calculate $P(u)$, the reaction degree value α is chosen from 0.1–0.9, and the corresponding temperature T_α is obtained based on the DSC curve. Next, to calculate $g(\alpha)$, the form of $f(\alpha)$ need to be chosen. Generally, the reaction function has different forms, such as the n th-order reaction model, Avrami–Erofeev reaction model, and so on, and it depends on the type of materials. In the current work, the Avrami–Erofeev reaction function was chosen based on the reaction characteristics of Ni/Al energetic structural materials. It can be written as Equation (10), where n is the parameter related to the reaction mechanism.

$$f = n(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{n-1}{n}} \quad (10)$$

Based on Equation (7), the parameter of the reaction function is determined by using the master curve method. Considering the two-stage reaction, taking α_c as the transition point, Equation (7) can be rewritten as,

$$g(\alpha_c) = \frac{AE}{\beta R} P(u_c) \quad (11)$$

Divide Equation (7) by Equation (11),

$$P(u)/P(u_c) = g(\alpha)/g(\alpha_c) \quad (12)$$

According to the Equation (9), choose an appropriate Avrami–Erofeev reaction function parameter n and reaction degree α until the two reaction curves ($P(u)/P(u_c) - T_\alpha$ and $g(\alpha)/g(\alpha_c) - T_\alpha$) have the highest correlation, and so the best reaction function f could be determined. Generally, $P(u)/P(u_c) - T_\alpha$ should be called the test reaction curve, and $g(\alpha)/g(\alpha_c) - T_\alpha$ should be called the standard reaction curve. The processing is conducted for the different heating rate conditions.

3. Results and Discussion

3.1. DSC Analysis

Figure 1 shows the morphology of the Ni/Al energetic structural material mixed powders with different molar ratios of 1:1, 1:3, and 3:1. It can be seen that by the mixed and ball milling technique, the Ni and Al particles were randomly dispersed, where the bright particle was Ni and the dark particle was Al.

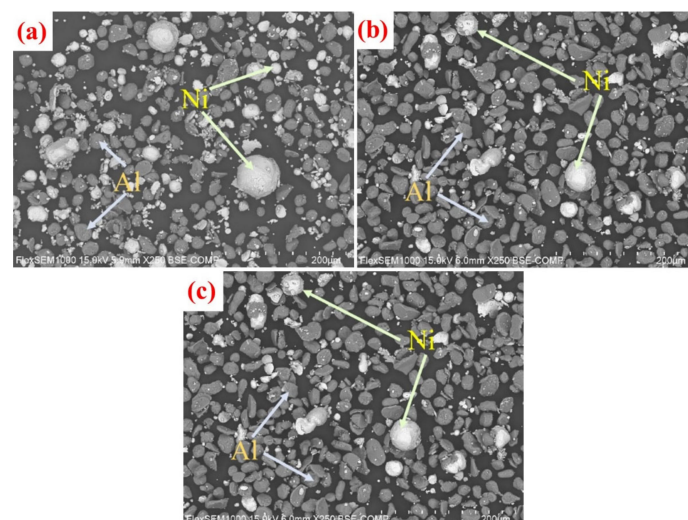


Figure 1. SEM images of (a) Ni/Al = 1:1, (b) Ni/Al = 1:3, and (c) Ni/Al = 3:1.

The DSC curves of Ni/Al energetic structural materials with the molar ratios 1:1, 1:3, and 3:1 at different heating rates are shown in Figure 2. For Ni/Al = 1:1, only one exothermic peak occurred during the thermal reaction process from room temperature to 1200 K, which were located at the range from ~870 K to ~950 K. In the DSC curves of Ni/Al = 1:3, two peaks, referring to an exothermic peak at ~900 K and endothermic peak at ~1150 K, appeared in Figure 2b. The exothermic peak represented the thermal reaction of Ni/Al, which was consistent with that of Ni/Al = 1:1 in Figure 2a. The endothermic peak was attributed to the melting process of NiAl₃, which was further discussed in XRD results. In addition, the DSC curves of Ni/Al = 3:1 are shown in Figure 2c. The thermal reaction processes between Ni and Al were seen at the exothermic peak.

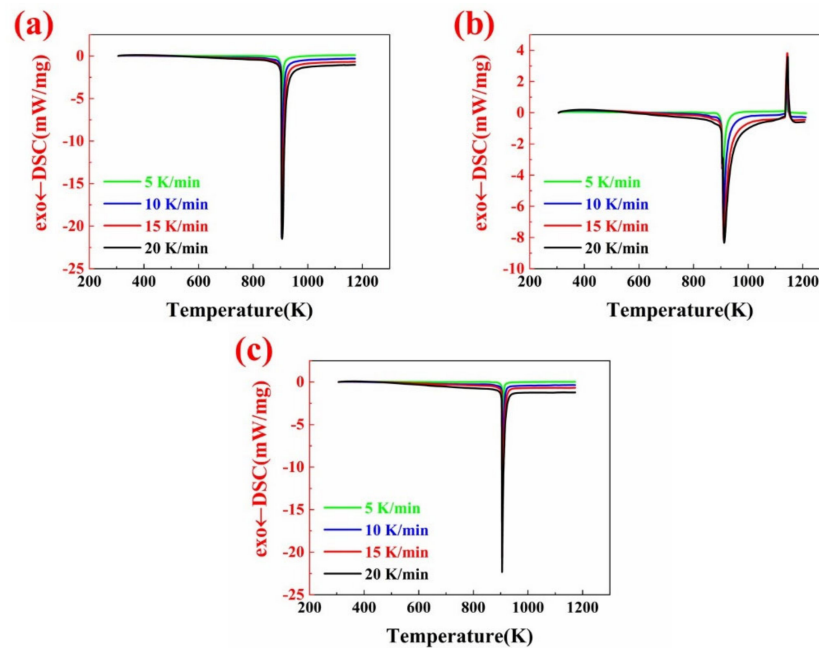


Figure 2. DSC curves of Ni/Al energetic structural materials: (a) Ni/Al = 1:1, (b) Ni/Al = 1:3, and (c) Ni/Al = 3:1.

From the DSC curve in Figure 2, the starting reaction temperature T_s and the reaction end temperature T_e were collected. For the endothermic process of Ni/Al = 1:3 at ~1175 K, the start melting temperature T_{s1} and the end melting temperature T_{e1} were also shown. The value of the heat release H was determined by the integral heat flow over time on the DSC curve. The analysis data is listed in the Table 1.

Table 1. Thermal reaction parameters of Ni/Al samples.

Heating Rate (K/min).		5	10	15	20
Ni/Al = 1:1	T_s (K)	904.05	903.45	902.85	902.75
	T_e (K)	912.04	923.11	934.37	948.17
	H (J/g)	840.70	840.30	839.40	840.90
Ni/Al = 1:3	T_s (K)	905.35	905.45	906.25	906.75
	T_e (K)	925.42	943.02	965.92	977.31
	H (J/g)	764.00	762.40	765.40	764.00
	T_{s1} (K)	1127.05	1127.05	1126.15	1126.35
	T_{e1} (K)	1152.95	1158.05	1165.85	1170.05
Ni/Al = 3:1	T_s (K)	905.75	905.15	904.75	903.85
	T_e (K)	913.11	923.73	932.55	942.83
	H (J/g)	463.70	464.00	464.00	464.10

Based on the thermal reaction characteristics of the Ni/Al samples, it could be found that T_s had no obvious changes, but T_e had increased obviously, as the heating rate increased.

With a higher heating rate, the peak value of Ni/Al samples was higher, and the reaction was faster. As the typical DSC curves of Ni/Al = 1:1, T_e had increased from 912.04 K to 948.17 K. The case of Ni/Al = 3:1 had a similar observation, where T_e increased from 913.11 K to 942.83 K. However, as the typical DSC curves of Ni/Al = 1:3, T_e had increased from 925.42 K to 977.31 K. The heat release H with different molar ratios Ni/Al = 1:1, Ni/Al = 1:3, and Ni/Al = 3:1 were about 840 J/g, 764 J/g, and 464 J/g, respectively. For all cases, the heat release H was almost constant as the heating rate increased.

3.2. Reaction Products Analysis

In order to determine the composition of the thermal reaction products of Ni/Al samples, the residue after DSC testing was collected for XRD analysis. The phase structure of the residue is shown in Figure 3. For the sample Ni/Al = 1:1, the main reaction products were Al_3Ni_2 and AlNi , as shown in Figure 3a. As the Al contents increased, the thermal reaction products of Ni/Al = 1:3 become complicated (shown in Figure 3b), including different Ni/Al intermetallic compounds, such as Al_3Ni , Al_4Ni_3 , Al_3Ni_2 , Ni_5Al_3 , AlNi , and so on. As the Al contents decreased, the reaction products of Ni/Al = 3:1 (shown in Figure 3c) led to the XRD peaks of Al_4Ni_3 , AlNi_3 , Ni_5Al_3 , AlNi and Al_3Ni_2 . It could be found that the actual reaction products of Ni/Al powders with different molar ratios were different from the theoretical products, which indicated that the complex and incomplete reaction processes resulted in the diversity of products.

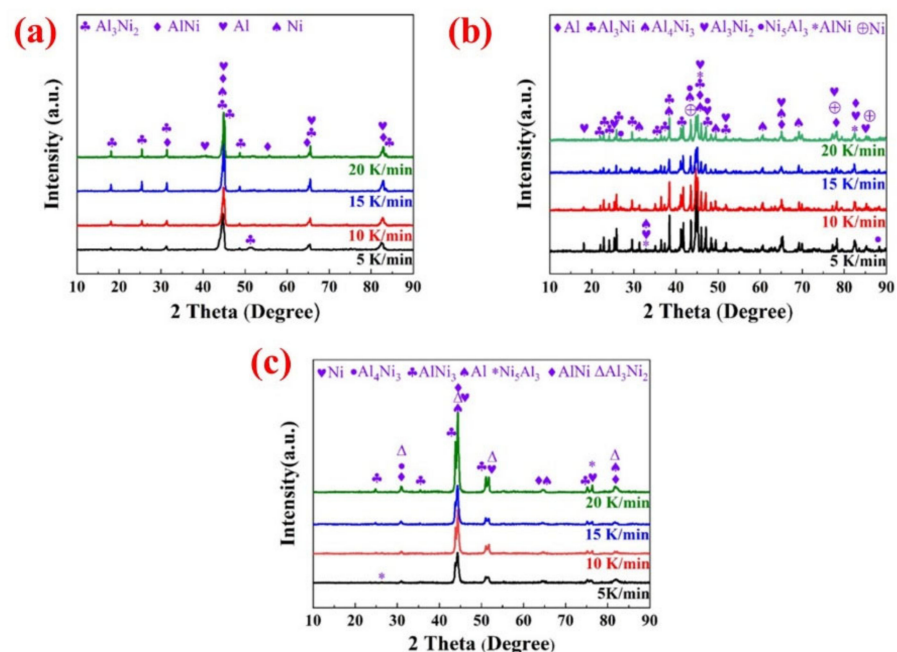


Figure 3. XRD results: (a) Ni/Al = 1:1, (b) Ni/Al = 1:3, and (c) Ni/Al = 3:1.

Generally speaking, when the heating temperature was lower than the Al melting point temperature, the reaction between Ni and Al took place in a solid–solid contact mode and the main product Al_3Ni was first formed [28]. When the heating temperature reached the temperature of the melting point of Al, Al and Al_3Ni would form a eutectic liquid phase. The liquid spread to the surface of Ni powders under the action of capillarity, which accelerated the liquid–solid contact with Ni particles. Ni would react with Al_3Ni in liquid phase to form Al_3Ni_2 . Further, the formation of Al_3Ni_2 layer gradually covered the Ni powder and separated Ni from the liquid phase. Moreover, the ongoing formation of Al_3Ni_2 could only depend on the diffusion of atoms. At the same time, Al_3Ni_2 would continue to dissolve into the liquid phase side, and gradually form an enrichment layer. When the Al_3Ni_2 layer increased to a certain thickness, Al_3Ni_2 and Ni would form AlNi [29]. When the sample was heated to the reverse peritectic reaction temperature around 1130 K,

the reverse peritectic reaction of Al_3Ni occurred, which corresponded to the endothermic process of $\text{Ni}/\text{Al} = 1:3$ in Figure 2b. Considering the low quantity of Al in $\text{Ni}/\text{Al} = 1:1$ and $\text{Ni}/\text{Al} = 3:1$, the product of Al_3Ni was low, which was not found by XRD. In the high content of Ni in $\text{Ni}/\text{Al} = 3:1$, AlNi_3 formed due to the diffusion reaction between AlNi and Ni [30].

3.3. The Reaction Kinetics Analysis

The kinetic parameters referring to the apparent activation energy E and the pre-exponential factor A were calculated by the Ozawa method described in the Section 2.2. The reaction function f was also obtained by the master curve method derived from the temperature integral described in the Section 2.2.

In order to calculate the apparent activation energy E , the end reaction temperature T_e under different heating rates were required. It should be explained that T_e corresponded to $\alpha = 1$. The temperature data of Ni/Al samples at four different heating rates of 5 K/min, 10 K/min, 15 K/min, and 20 K/min were listed in Table 1. According to the chemical reaction kinetics equations described in Section 2.2, T_e corresponding to β of each sample was taken out to calculate $\lg\beta$ and $1/T_e$. The scatter plot shows the abscissa $1/T_e$ and the ordinate $\lg\beta$. The apparent activation energy E was obtained by the least square fitting method. The results of the linear fitting and apparent activation energy E are shown in Figure 4.

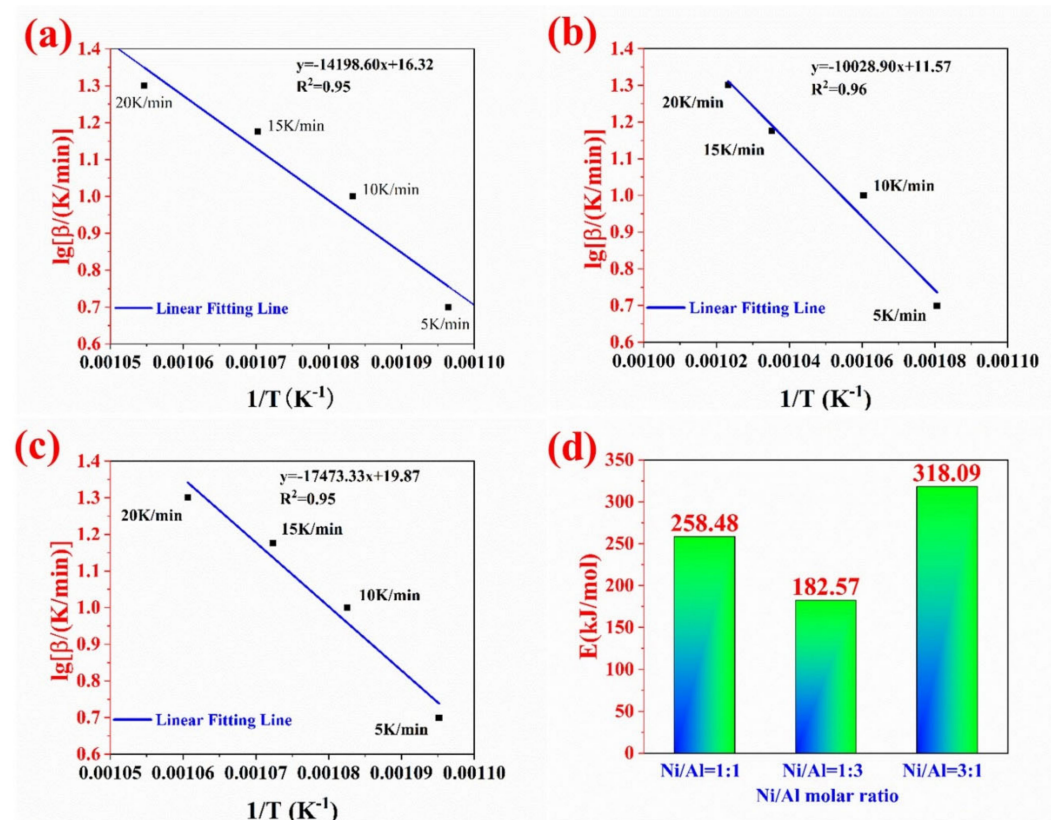


Figure 4. Linear fitting of samples at different heating rates (a) $\text{Ni}/\text{Al} = 1:1$, (b) $\text{Ni}/\text{Al} = 1:3$, and (c) $\text{Ni}/\text{Al} = 3:1$; (d) the apparent activation energy E of the samples.

Figure 4d showed that the apparent activation energy E of $\text{Ni}:\text{Al} = 1:1$, $1:3$, and $3:1$ are 258.48 kJ/mol, 182.57 kJ/mol, and 318.09 kJ/mol, respectively. When the contents of Al increased, the apparent activation energy E of Ni/Al materials reduced, resulting from the higher activity of Al than Ni. Moreover, when the melting of Al occurred, the liquid phase of Al increased the contact surface of Ni particles [31]. The higher quantity of Al would benefit from promoting the thermal reaction.

The Avrami–Erofeev reaction function f was generally used for energetic structural materials [6]. However, it was not a single reaction process; the segment fitting method was used here. The parameters in the reaction function were optimized for different segments. According to the theoretical calculation of the master curve method in Section 2.2, T_α was defined as the transition temperature of segmented reaction curves. The pre-exponential factor A was calculated for the different reaction stages at different heating rates based on Ozawa method.

Figure 5a–c show the fitting results of the test reaction curve at the heating rate 10 K/min. The two reaction curves revealed a good fitting effect. For the other heating rate conditions, it had a similar trend. In order to explore the mechanism on the occurrence of transition temperature, the transition data points of the samples are plotted in Figure 5d. It could be found that the transition temperature points were distributed in the Ni/Al liquid eutectic temperature range, which indicated that the transition from solid state to liquid state of Al was the critical factor, although the discrepancy was presented due to the reaction hysteresis at the high heating rates for Ni/Al = 1:3.

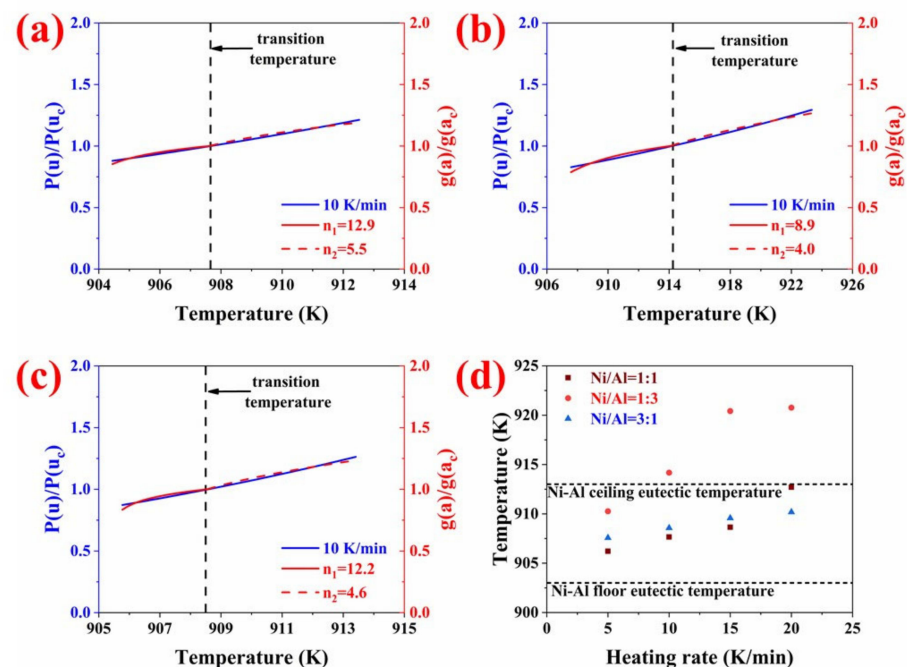


Figure 5. The comparison between the reaction curves and the test reaction curve at 10 K/min (a) Ni/Al = 1:1; (b) Ni/Al = 1:3; (c) Ni/Al = 3:1; (d) the transition temperature T_α .

Table 2 gives the reaction function parameter n and pre-exponential factor A of all the samples. For the Ni/Al powder samples with the same molar ratio, the different reaction parameters under different heating rates are collected in Table 2. It could be found that as the heating rate increased, both of the parameters n_1 and n_2 decreased. This is because the increase of the heating rate brought in the temperature accumulation of the sample, which included exothermic reaction. The weakened constraint between lattice atoms originated from the overheating effect, which was good for promoting the reaction process.

The reaction process was described by the Avrami–Erofeev reaction function with two sets of parameters and was divided into reaction stage I and II, according to the transition temperature. The schematic diagram of Ni–Al reaction mechanism with the two-stage reaction is shown in Figure 6. In the reaction stage I, both Ni particles and Al particles were solid, and the contact was similar to the point contact. This stage was considered as the hard contact stage. The reaction to generate Al_3Ni only occurred at the contact reaction zones. Therefore, the solid phase reaction was limited. Once the reaction temperature had been heated over the melting point, the solid state of Al started to transfer into the liquid state. The reaction entered the reaction stage II, where the liquid Al had a soft contact stage

with Ni particles. With a higher reaction temperature, the solid–liquid reaction between Ni and Al occurred at the surface of Ni particles. In this stage, the reaction rate become faster. In addition, the eutectic liquid would also exist at the reaction zones in the reaction stage II, as shown in Figure 6. The soft contact stage was also beneficial for promoting the thermal reaction of Ni/Al materials [32].

Table 2. The reaction function parameter n and pre-exponential factor A of all the samples.

Sample	Stage	n/A	Heating Rate (K/min)			
			5	10	15	20
Ni/Al = 1:1	I	n_1 $A_1 (\times 10^{14} \text{ min}^{-1})$	27.6 1.3639	12.9 1.3590	10.3 1.3567	5.5 1.3504
	II	n_2 $A_2 (\times 10^{14} \text{ min}^{-1})$	12.2 1.3585	5.5 1.3467	4.8 1.3436	2.2 1.3389
Ni/Al = 1:3	I	n_1 $A_1 (\times 10^9 \text{ min}^{-1})$	14.5 3.4174	8.9 3.4045	4.9 3.3773	2.9 3.1903
	II	n_2 $A_2 (\times 10^9 \text{ min}^{-1})$	6.5 3.3921	4.0 3.3638	2.1 3.2979	1.9 2.8624
Ni/Al = 3:1	I	n_1 $A_1 (\times 10^{17} \text{ min}^{-1})$	23.5 3.9351	12.2 3.9216	8.2 3.9079	6.3 3.8954
	II	n_2 $A_2 (\times 10^{17} \text{ min}^{-1})$	10.1 3.9157	4.6 3.8754	3.1 3.8400	2.4 3.8085

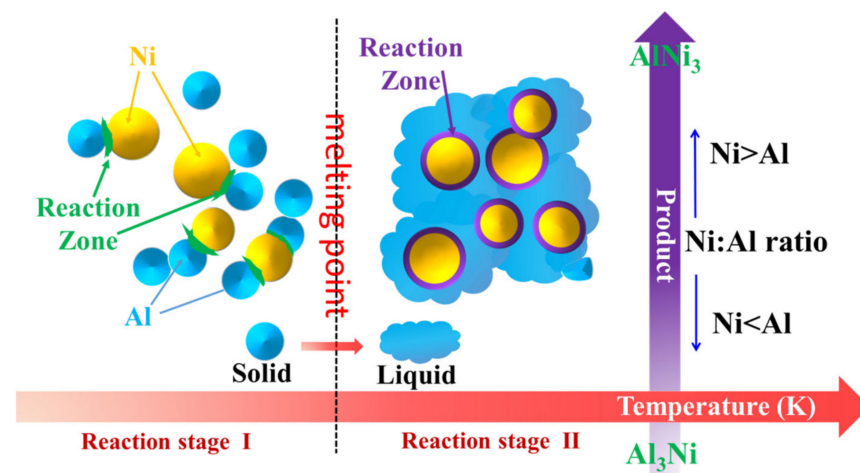


Figure 6. Schematic diagram of the reaction mechanism of Ni/Al materials.

4. Conclusions

In summary, a novel understanding of the thermal reaction behavior and mechanism of Ni/Al energetic structural materials was demonstrated. Depending on the melting point of Al, the thermal reaction stages of Ni/Al were divided into two stages: the hard contact stage and the soft contact stage. The thermal reaction behavior of Ni/Al energetic structural material powder was studied based on the DSC test, XRD characterization, and chemical reaction kinetics analysis. The reaction kinetic parameters and specific reaction mechanism were determined to describe the reaction process for Ni/Al powder. The parameters were used to determine the difficulty and mode of reaction. For the specific kinetic parameters, as the ratio of Al increased, the apparent activation energy of the material significantly reduced. Otherwise, as the ratio of Ni increased, the apparent activation energy increased. It could be found that the exothermic reaction function between Al and Ni was described by Avrami–Erofee segment reaction function. The transition of Al from solid to liquid was the critical factor affecting the establishment of segment reaction function. In addition, the

thermal reaction mechanism of Ni/Al energetic structural material was provided based on the hard contact stage and soft contact stage. This work offered a new idea to understand the thermal reaction behavior and mechanism of Ni/Al energetic structural materials under different temperature stages.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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