Article

The Interaction Pathway in the Mechano-Ultrasonically Assisted and Carbon-Nanotubes Augmented Nickel–Aluminum System

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Abstract: The influence of mechano-ultrasonic activation (MUA) and nano-additives (carbon nanotubes-CNT) on the interaction pathway of nickel–aluminum powder mixture at high heating rates was investigated. The optimum conditions of the mechano-ultrasonic activation, along with the phase and structure formation peculiarities of nickel–aluminum and nickel–aluminum–carbon nanotubes mixtures by thermal analysis method, the so-called high-speed temperature scanner (HSTS), were found out. The optimum duration of mechanical and ultrasonic activation aiming to achieve homogeneous distribution in the agitated mixtures was determined. A shift in characteristic temperatures of MUA mixtures by the influence of both heating rate and ultrasound on the Ni + Al interaction pathway for the mechano-activated (1, 3, 5 min) and 1 wt% CNT containing mixtures was observed. The formation patterns of NiAl + Ni₃Al mixture or pure NiAl phase was manifested according to the interaction mechanism (depending on solid–liquid or solid–solid state of intermediates). The effective activation energy values for the Ni + Al exothermic reactions of all studied systems were determined by the isoconversional method of Kissinger.

Keywords: mechano-ultrasonic activation; carbon nanotubes; high heating rate; activation energy

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1. Introduction

Nickel–aluminum intermetallics, encompassing the compositional region between 40% and 80% of nickel, have attracted considerable interest owing to a favorable combination of properties, such as high melting point, low weight, high resistance to corrosion, and high-temperature strength [1–3]. The mechanical activation (MA) [4,5] and self-propagating high-temperature synthesis (SHS) are the most widely investigated techniques [6–8] among the versatile methods for manufacturing nickel aluminides. MA has already emerged as one of the productive and mature techniques for the solid-state synthesis of the nanocrystalline intermetallics uniform by the phase composition [9]. Additionally, MA is utilized to attain grain refinement, hardening and alloying through secondary phases, which have been found to be effective strategies to improve the mechanical behavior of these intermetallic compounds. Therefore, the utilization of MA allows us to overcome the challenges that arise in the melting or casting processes of nickel aluminides [10,11]. Mechanically activated SHS (MASHS) is a type of combustion process where preliminary mechanical activation significantly changes the structures of the SHS precursors. As a result of ball milling, an increase in the reserved energy of the system occurs and leads to a shorter ignition time and reaction initiation temperature; in addition, the evolution of nanostructures is favored [12].

A number of experimental and some theoretical works [13–16] are devoted to the influence of MA on SHS processes of the Ni–Al system. Recently, it was shown that ultrasound

treatment has a dramatic influence on the morphology of inorganic solids [17–19]. However, the intensive ultrasonic activation of the initial Ni–Al charge was considered in few works [20,21]. In particular, the surface area of the sonically treated particles considerably increases compared to untreated ones. Intensive treatment of Al under ultrasound causes the development of sponge-like particulates, stabilized by a thin layer of metal oxide. This sponge-like matrix would promote the reactivity of charge due to increased specific surface area. An experimental and theoretical study into the effect of intensive ultrasonic activation of the powder mixture on the phase and structure formation of Ni–Al intermetallics in the combustion wave will make it possible to obtain new scientific patterns and open up wide opportunities for a targeted impact on the fine and homogeneous microstructure of the final product. Therewith, a gap in the regulation of SHS processes is that they usually occur in a narrow range of parameters (size of initial particles, composition, sample's relative density, etc.) and cannot be controlled after initiation. Thus, it is pertinent to design a novel SHS process to grant in-situ control over the structure and features of the target compounds. From this perspective, the inclusion of nano-additives in the initial mixture and preliminary mechanical and ultrasonic activation (MUA) become promising [22].

Carbon nanotubes (CNT) were chosen as the nano-additive owing to their superior mechanical characteristics, such as axial elastic stiffness and tensile strength, which can be employed for structural applications. Embedding carbon nanoparticles in nanocomposites and homogeneous dispersion in ductile and lightweight metals, for instance, in the aluminum matrix, may contribute to enhanced mechanical properties. However, the low affinity of CNT to Al hinders dispersion and strong interfacial binding. MA and UA would help overcome this issue, together with the addition of metal (for example, nickel) bonding to sp^2 hybridized carbon and making the interfaces between CNT and nanoparticles comparatively stronger. On the other hand, the utilization of carbon nanotubes will play the role of the refiner for the metals' oxidized surfaces, in particular, for aluminum, and promote the interaction process.

Extreme conditions in the SHS wave (elevated temperatures and fast self-heating of substances in the combustion wave) impede the disclosure of interaction pathways in the SHS process and optimization of synthesis conditions. To tackle the challenge, the process in the Ni–Al system was modelled at guided conditions, in particular, at a programmed heating routine via tuning the interaction over the time and approximation of conditions to the combustion process, by the thermal analysis method, namely using a high-speed temperature scanner (HSTS) [23–25]. The influences of MUA ($t_{UA} = 0$ –55 min, $t_{MA} = 1$ –5 min) and heating rates on the kinetics, phase, and microstructure evolution pathway of Ni–Al and carbon-nanotubes augmented Ni–Al systems were examined. By changing the heating rates of systems from 100 to 2600 K min^{−1}, we succeeded in achieving homogeneity in the microstructure and complete phase formation in the Ni–Al system through the addition of CNT to the initial mixture and mechano-ultrasonic activation. The HSTS results were complemented by the characterization of phase and microstructure transformations based on SEM/EDS and XRD analyses results of quenched intermediates and calculations of kinetic parameters. This study aimed to disclose the interaction kinetics of the systems under study, unravel the relevance of MUA treatment and utilization of carbon nanotubes, as well as deduce the most favorable conditions (UA and MA duration, ignition temperature, heating rate, heating temperature, etc.) for the preparation of nickel aluminides.

2. Materials and Methods

Nickel (NPK, Yekaterinburg, Sverdlovsk region, Russia, particle size < 10 µm, purity 99.8%) and aluminum (ASD-4, Kyiv, Ukraine, particle size < 40 µm, purity 99.9%) powders were used as raw materials, and carbon nanotubes were used as nano-additives (CNT, from tens of nanometers to several microns in size produced by [22]). The mechanical activation of the Ni and Al green mixture (1:1 molar ratio) was carried out in a planetary ball mill (RETSCH PM-100, Haan, Germany) at different durations (1–5 min), using 10 mm-diameter steel balls as crushing-milling media, and $m_{ball}/m_{material} = 20:1$ ratio. Dry mixing in the air

was performed at a rotational speed of 500 rpm. The nano-additive ($m(\text{CNT}) = 1 \text{ wt\%}$) was mixed with the mechanically activated mixture in a ceramic mortar for 15 min. Ultrasonic activation of the powder mixture was performed with an ultrasonic cleaner (Stegler 6DT, 40 kHz, Shenzhen, China) with a duration of 1–55 min in ethanol medium. The agitated samples were dried at 373 K for 10 h.

As-prepared mixtures were subjected to high-speed heating using a high-speed temperature scanner (HSTS, Institute of Chemical Physics, Yerevan, Armenia, $V_h = 100\text{--}2600 \text{ K min}^{-1}$, $T_{\text{max}} = 1573 \text{ K}$). Thermal analysis equipment aimed to elucidate the role of the heating rate and temperature at non-isothermal conditions on the interaction mechanism in the system under study. This method is based on the electrically controlled high-speed heating of the sample under study and continuous recording of electrical power, as well as the sample's temperature during the process. In addition to recording the temperature curves, the process was discontinued at various distinctive stages of the interaction, and quenched samples were subjected to phase and microstructural examinations. When the heating process was interrupted, up to $12,000 \text{ K min}^{-1}$ cooling rate was achieved, impeding further possible interactions over the cooling process.

The principle operation of the HSTS [23–26] device was based on the direct electrical heating of a cell made of a thin metal sheet containing a reactive mixture (Figure 1). The latter (50 mg) was poured into a thin envelope made from nickel (100 μm in thickness), installed in the reactor, and attached to electrical contacts. First, the reactor was vacuumed and filled with 0.1 MPa inert gas (argon, purity > 99.98%). The maximum heating temperature during the measurements did not exceed 1573 K.

Figure 1. The experimental steps for the kinetic studies using a high-speed temperature scanner. (a) envelope-heater with reactive mixture under study; (b) reaction chamber and controller: 1—reactive mixture, 2—boat made from nickel foil, 3—powder mixture in Ni boat, 4—envelope with mixture and thermocouple wire, 5—heated sample, 6—reaction chamber, 7—electronic unit and PC for control and registration [26].

The calculation of effective activation energy value for the reaction between nickel and aluminum was performed by the isoconversional method suggested by Kissinger [27]. The essence of methodology is the registration of the temperature shift that corresponds to the maximum advance on the heating curve at a given heating rate. The following expression (Equation (1)) is usually used to determine the effective activation energy value:

$$\ln\left(\frac{V_h}{(T^*)^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T^*}\right) \quad (1)$$

where V_h is the experimental heating rate (K min^{-1}), T^* —temperature on the inert curve that corresponds to the maximum advance on the heating profile, A —constant for a specific reaction, E —effective activation energy (kJ mol^{-1}), R —universal gas constant.

XRD data on the phase composition of the intermediates and final products were collected by Bruker diffractometer (D5005, Billerica, MA, USA) with monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). JCPDS-ICDD database [28] was used to process XRD data and identify the intermetallic materials from XRD patterns (Ni_PDF #65-2865 (Fm-3m), Al_#65-2869 (Fm-3m), NiAl_PDF 65-0431 (Pm-3m), Ni_3Al 65-0430 (Pm-3m)). The microstructural examinations were performed on the scanning electron microscopes (SEM, Prisma E and FE-SEM, Zeiss Evo MA15, Oberkochen, Germany) equipped with an EDS detector.

3. Results and Discussion

3.1. Ultrasonic Activation of Ni + Al Powder Mixture

Earlier, the influence of ultrasonic activation was investigated on the phase composition and microstructure transformation of the initial non-activated and mechano-activated Ni + Al mixtures of a 1:1 molar ratio. In order to determine the optimum UA duration, mechano-activated Ni + Al mixture ($t_{\text{MA}} = 1 \text{ min}$) was subjected to ultrasonic activation from 1 to 55 min. Prior to and after the activation, microstructural and EDS analyses of the corresponding samples were performed (Figure S1a,b). According to the results, in the case of ultrasonic activation for 25 min, a homogeneous, evenly distributed mixture of metal powders was obtained. This is evidenced also by the presence of sufficient intensities of the characteristic peaks of the constituents (Ni, Al) in the EDS spectrum and almost identical atomic percentages of metals in the selected microstructure with an area of $50 \mu\text{m}$.

According to the determined optimum conditions of UA, the non-mechano-activated and mechano-activated (for 1–5 min) mixtures, as well as the mixtures containing 1 wt% CNT, were subjected to ultrasonic activation for 25 min.

UA significantly affected the microstructural characteristics of the initial mixtures. As can be seen from Figure 2a,b, ultrasonic agitation in mechano-activated mixtures promoted the homogenization of the powder. The particle size reduction, phase segregation, and redistribution on the surface of particles given by sonomechanical action, along with homogenization of the powder mixture, occurred at up to 3 min MA and 25 min UA conditions (Figure 2c). However, a longer duration of MA caused agglomeration mainly of the ductile aluminum phase, and, despite UA treatment, agglomerates were not sufficiently dispersed (Figure 2d).

Higher magnification SEM images demonstrate the influence of both UA and MA on the metal's behavior in the mixture (Figure S2). In particular, 5 min MA leads to agglomeration of powder regardless of the UA treatment (Figure S2), and, in terms of the reduction in particle size, the UA treatment was beneficial for the mixtures mechano-activated for up to 3 min (Figure 2c,d).

Figure 2. SEM images of Ni + Al mixture; (a) $t_{MA} = 0$ min, $t_{UA} = 0$ min, (b) $t_{MA} = 0$ min, $t_{UA} = 25$ min, (c) $t_{MA} = 3$ min, $t_{UA} = 25$ min, (d) $t_{MA} = 5$ min, $t_{UA} = 25$ min.

According to the microstructural analysis results, the carbon nanotubes augmented powder after the simultaneous mechanical and ultrasonic activation was characterized, firstly, by particle size reduction, dispersion, and separation ($t \leq 3$ min), and then agglomerate formation ($t > 3$ min) (Figure 3). The influence of UA is more expressed on MA mixtures compared to non-mechano-activated mixtures.

Therefore, it can be argued that the effect of ultrasonic activation on the reduction in particle size in the presence of nanoadditives is also noticeable for up to 3 min of mechano-activated mixtures.

Figure 3. SEM micrographs of Ni + Al + 1 wt% CNT mixtures; (a) $t_{MA} = 0$ min, $t_{UA} = 0$ min; (b) $t_{MA} = 0$ min, $t_{UA} = 25$ min; (c) $t_{MA} = 3$ min, $t_{UA} = 25$ min; (d) $t_{MA} = 5$ min, $t_{UA} = 25$ min.

According to the results of the XRD analysis, the duration of mechano-activation did not change the phase composition of the UA mixtures, but the intensity and width of the characteristic peaks were modified. Based on the latter, the average size in the vertical direction of crystal for the component metals was calculated (Figure 4) according to Scherrer's formula (Equation (2)):

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

D is the dimension of the crystallite, K is a constant, which usually has a value between 0.89 and 0.94 and depends on the used peak fitting function, β is the half width at half maximum of the peak, θ is the scattering angle, λ is the wavelength (0.154 nm).

Figure 4. XRD pattern of 5 min activated Ni + Al mixture after 25 min ultrasonic activation.

From the comparison of samples without UA and UA agitated for 25 min, it is obvious that the simultaneous action of both mechanical and ultrasonic activation is more effective for grain dispersion than the separate application of each of these procedures. Moreover, for the mechanically activated mixtures for up to 3 min, a decrease in the size of nickel and aluminum crystallites was observed under the influence of UA (Table 1).

Table 1. Lattice parameters and average size of crystals according to Scherrer's equation for non-UA (Ni*, Al*) and 25 min UA subjected systems.

	#ICDD	Lattice Parameter, Å	Average Size of Crystals, nm			
		a = b = c	t = 0 min	t = 1 min	t = 3 min	t = 5 min
Ni	#652865	3.52	33	27	21	34
Al	#652869	3.74	42	26	26	38
Ni*	#652865	3.52	33	28	23	24
Al*	#652869	3.74	38	38	36	35

3.2. The Influence of Heating Rate on the MUA Ni–Al and Ni–Al-1 wt% CNT Systems

The impact of ultrasonic activation on the non-mechano-activated and mechano-activated Ni + Al and Ni + Al + 1 wt% CNT mixtures has been studied over a broad range of heating speeds ranging from 100 to 2600 K min^{−1}. Single-stage exothermic interaction corresponding to Ni + Al reaction was observed in all studied mixtures. In the studied interval of heating rates, in the UA agitated non-mechano-activated (Figure 5a, $t_{MA} = 0$ min, $t_{UA} = 25$ min; $T_o = 943$ K) and for up to 1 min mechano-activated mixtures (Figure 5a, $t_{MA} = 1$ min, $t_{UA} = 0$ min; $T_o = 938$ K, $t_{MA} = 1$ min, $t_{UA} = 25$ min; $T_o = 933$ K), the

interaction began after the aluminum melting. At a longer MA duration ($t_{MA} \geq 3$ min), the interaction initiated at the same temperature and proceeded prior to the melting temperature of aluminum, regardless of the heating rate (Figure 5a, Table 2). In CNT augmented Ni + Al mixtures, the reaction initiation temperature decreased with the increasing MA duration (Table 2, Figure 5b). With the presence of nano-additives in the nickel–aluminum mixtures under the influence of UA, the interaction occurred before the melting of aluminum, i.e., by solid+solid mechanism in both non-mechano-activated and mechano-activated mixtures. As a general pathway for all the study's mixtures, one may observe a decrease in the exothermicity of the main interaction as a result of the change in the system energy state (expansion of microcavities, friction, grain deformation, creation of new surfaces, etc.) occurring during the MA processing (Figures 5a,b and 6).

Figure 5. The interaction behavior of UA agitated Ni + Al ($0_{t_{MA}} = 0$ min, $1_{t_{MA}} = 1$ min, $3_{t_{MA}} = 3$ min, $5_{t_{MA}} = 5$ min) (a) and Ni + Al + 1 wt% CNT ($0'_{t_{MA}} = 0$ min, $1'_{t_{MA}} = 1$ min, $3'_{t_{MA}} = 3$ min, $5'_{t_{MA}} = 5$ min) (b) mixtures on the heating curves, $t_{UA} = 25$ min, $V_h = 600$ K min^{−1}.

Table 2. Characteristic temperatures (K) of various Ni + Al mixtures.

T_{MA} , min	Ni + Al			Ni + Al, $t_{UA} = 25$ min			Ni + Al + 1% CNT, $t_{UA} = 25$ min		
	T_0	T^*	T_{max}	T_0	T^*	T_{max}	T_0	T^*	T_{max}
0	933'	938	1428	943'	943	1423	923	943	1373
1	933'	938	1443	933'	933	1393	923	928	1353
3	893	903	1413	903	903	1373	888	893	1333
5	873	883	1323	878	888	1333	873	883	1273

Solid–solid and solid–liquid interactions were differentiated (' denotes the interaction by solid–liquid mechanism) according to the plateau observed on the thermograms and based on the reaction initiation temperature in the MUA Ni–Al systems (UA duration was kept constant—25 min).

Enforced by the mutual MUA influence, the heating curves are shifted to a lower temperature range, demonstrating the beneficial effect of MUA on the initiation of interaction (Figure 6).

Figure 6. The influence of MUA on the heating thermograms of Ni + Al + 1% CNT mixtures, $t_{UA} = 25$ min, $V_h = 600$ K min^{−1}: 0_ $t_{MA} = 0$ min, 0'_ $t_{MA} = 0$ min + UA; 3_ $t_{MA} = 3$ min, 3'_ $t_{MA} = 3$ min + UA; 5_ $t_{MA} = 5$ min, 5'_ $t_{MA} = 5$ min + UA.

3.3. The Phase Formation Patterns of the MUA Ni + Al Systems

The mechanism of interaction in the mechano-activated, as well as ultrasonically activated, Ni + Al and Ni + Al + 1% CNT mixtures depends on the temperature at which the exothermic reaction begins, in particular, on whether the process occurs with molten or solid aluminum. In the case of the nickel–aluminum interaction starting before the melting of aluminum (<933 K), the reaction was proceeded by the solid+solid mechanism, and immediately after the process, there were two phases in the XRD pattern of the quenched products: NiAl along with a trace amount of Ni₃Al. A further rise in temperature (up to 1573 K) promoted the development of a single-phase NiAl phase by the interaction of Ni₃Al with unreacted aluminum (considering the initial composition of metals 1:1 ratio). When the process started after the aluminum melting (>933 K), the reaction proceeded according to the solid + liquid mechanism. The molten aluminum dissolves nickel completely, and immediately after the exothermic reaction, there was a stoichiometric single-phase NiAl in the diffractogram of the quenched sample. Particularly, at a heating rate of 600 K min^{−1}, in UA agitated non-mechano-activated and 1 min mechano-activated Ni + Al and Ni + Al + 1% CNT mixtures, the reaction started after melting of aluminum (Ni + Al_ $t_{MA} = 0$ min, $t_{UA} = 25$ min, $T = 943$ K; $t_{MA} = 1$ min, $t_{UA} = 25$ min, $T = 933$ K; Ni + Al + 1% CNT_ $t_{MA} = 0$ min, $t_{UA} = 25$ min, $T = 943$ K; $t_{MA} = 1$ min, $t_{UA} = 25$ min; $T = 928$ K, Table 2). At a higher duration of MA (2–5 min) in mechano-activated mixtures at a heating rate of 600 K min^{−1}, the process began before the aluminum melted; the reaction was proceeded only by the solid+solid mechanism, leading to the formation of NiAl and Ni₃Al phases (Figures 7 and 8). Thereby, all CNT containing Ni + Al mixtures under UA decreased if the reaction initiation temperature occurred: the utilization of carbon nanotubes played the role of the refiner for the metals' oxidized surfaces, in particular, for aluminum, and promoted the interaction process. Moreover, in the 1 min mechano-activated mixtures, a change in the mechanism complemented by the emergence of different Ni–Al phases was observed. This was confirmed by XRD patterns of the products quenched at characteristic temperatures (Figures 7 and 8).

Figure 7. XRD patterns of the products derived from 1 min mechano-activated Ni + Al (a) and Ni + Al + 1% CNT (b) mixtures, $t_{UA} = 25$ min, $V_h = 600$ K min^{−1}.

Figure 8. XRD patterns of the products derived from 5 min mechano-activated Ni + Al (a) and Ni + Al + 1% CNT (b) mixtures, $t_{UA} = 25$ min, $V_h = 600$ K min^{−1}.

Microstructural examinations of the quenched samples after the exothermic interaction at 873 K (without grinding or sieving) in the Ni–Al and Ni–Al–1 wt% CNT mixtures revealed the formation of powder comprising agglomerates from 5 to 50 μ m (Figure 9).

Figure 9. SEM images of samples quenched at 873 K from Ni + Al (a) and Ni + Al + 1% CNT (b) systems; $V_h = 600$ K min^{−1}, $t_{MA} = 5$ min, $t_{UA} = 25$ min.

A higher magnification image (Figure 10a) of the Ni + Al system showed the sponge-like alloy formation under MUA processing, where the agglomerates consisted of up to 50 nm particles (Figure 10b). Samples quenched at 1473 K underwent sintering (Figure 10c). In some places, exfoliation of the sintered alloy was observed (Figure 10d).

Figure 10. SEM images of quenched samples from the Ni + Al system at 873 K (a,b) and 1473 K (c,d), $V_h = 600 \text{ K min}^{-1}$, $t_{MA} = 5 \text{ min}$, $t_{UA} = 25 \text{ min}$.

SEM images of CNT containing samples quenched at 873 K demonstrate the presence of finer particles in contrast to just the Ni + Al system (Figure 11a,b), revealing the positive effect of nanotubes on the alloy microstructure refinement under UA agitation. Sintered counterparts derived from CNT containing samples, i.e., samples quenched at 1473 K, exhibit an alloy microstructure with well-defined grains and needles of nm size (Figure 11c,d).

Figure 11. SEM images of quenched samples from the Ni + Al + 1% CNT system at 873 K (a,b) and 1473 K (c,d), $V_h = 600 \text{ K min}^{-1}$, $t_{MA} = 5 \text{ min}$, $t_{UA} = 25 \text{ min}$.

To confirm the phase composition of the formed product complementary to XRD examinations, EDS analysis was performed. The ratio of metals in the micrometer range is about 1:1, corresponding to composition of the NiAl intermetallic (Figures 12 and S3). It was not possible to detect 3:1 composition by EDS caused by a trace amount of the aforementioned phase (detected by XRD analysis).

Figure 12. SEM/EDS analysis results of quenched samples from Ni + Al (a) and Ni + Al + 1% CNT (b) systems at 873 K, $V_h = 600 \text{ K min}^{-1}$, $t_{MA} = 5 \text{ min}$, $t_{UA} = 25 \text{ min}$.

It should be noted that, according to literature data, Ni_3Al phase formation was also observed via solid + liquid mechanism [29]; in addition, experimental studies of another work [30] indicate that Ni_3Al formation strongly depends on the change in the particle size of nickel powder. In particular, the decrease in nickel particle size as a result of MUA processing promotes the formation of the Ni_3Al phase according to the $\text{NiAl} + 2\text{Ni} > \text{Ni}_3\text{Al}$ scheme.

3.4. The Calculation of Effective Activation Energy of the Ni + Al Reaction by Kissinger Method

The variation of effective activation energy values (Equation (1)) estimated for the exothermic interaction between metals under the MUA agitation is presented in Table 3. The calculation is based on the shift of characteristic temperatures of the Ni + Al exothermic reaction versus heating rate (Figure 13).

Table 3. The effective activation energy values for the Ni + Al reaction in the different systems.

t_{MA} , Min	Effective Activation Energy, E_a (kJ mol ^{−1})	
	Ni + Al, $t_{UA} = 25 \text{ min}$	Ni + Al + 1% CNT, $t_{UA} = 25 \text{ min}$
0	218 ± 13	148 ± 12
1	120 ± 11	129 ± 8
3	229 ± 9	172 ± 9
5	183 ± 5	297 ± 9

Figure 13. Heating curves of UA agitated 1 min mechano-activated Ni + Al + 1% CNT mixture at different heating rates: A— $V_h = 100 \text{ K min}^{-1}$, B— 300 K min^{-1} , C— 600 K min^{-1} , D— 1200 K min^{-1} .

The increase in the MA duration of the MUA mixtures was accompanied first by a decrease in the E_a activation energy, then by an increase, which was caused by the expansion of the specific surface area of the particles in the case of short MA processing and by the formation of aluminum agglomerates in the case of a higher duration of MA. The behavior of the activation energy in the studied systems is in harmony with the change in the interaction mechanism from solid + liquid ($t_{MA} = 0 \text{ min}$, 1 min) to solid + solid ($t_{MA} = 3 \text{ min}$, 5 min). The addition of CNTs had a significant effect on the activation energy of the non-mechano-activated mixtures, which was due to the change in the reaction mechanism by shifting the interaction process to the lower temperature range. A decrease in activation energy value was observed in the Ni + Al + 1% CNT system under MA and UA influence for 1 min activated mixtures, but a further increase in the MA duration increased the activation energy regardless of the UA processing.

The activation energy values indicated that the effect of UA in the samples mechano-activated up to one minute was significant in terms of particle size reduction, mixture homogenization, and exothermicity of the interaction. The latter is the result of acoustic cavitation at the surface, which generates high-velocity microjets of liquid that invade the surface, causing surface erosion, defects, and localized heating [31]. Increasing the duration of MA led to certain structural changes for the precursors; therefore, the exothermicity of the peak was lower, although the process was stimulated to be initiated at a lower temperature. For comparison, the ultrasonic activation of 1 min mechano-activated mixtures had approximately the same effect as the 1% CNT addition. In the case of a long duration of mechano-activation, it was necessary to apply ultrasound energy of a higher intensity for sufficient dispersion of the particles.

A comparative overview allowed us to comment on the strong dependence of microstructure evolution on mechanical and ultrasonic agitation. For example, intense HEBM (694 rpm, 40:1 ball–powder ratio, 6 mm steel balls as a milling media) resulted in the formation of a fine lamellar composite structure and a decrease in reaction onset temperature up to 573 K after 5 min MA [32]. It was obvious that the interaction started during the milling and would not achieve the homogeneous phase and microstructure formation, as well as an accurate determination of the activation energy value. However, at certain MA and UA conditions, it will be possible to avoid new phase formation during the agitation and achieve the homogeneous dispersion of metallic particles. For the temperature range 923–1123 K, effective activation energy value was calculated to be 155 kJ mol^{-1} for non-activated mixtures by HSTS method for finer metal precursors, but by electrothermal explosion method for non-activated Ni–Al mixture, $\sim 200 \text{ kJ mol}^{-1}$ was obtained [33], which is in accordance with the current work. In the current research, 25 min UA treated mixtures under 1 min

MA demonstrated a decrease in apparent activation energy with and without the CNT addition. Ultrasound-assisted electrocatalyst preparation reported in [34] demonstrated the UA influence on commercially available alloys at high-intensity ultrasound (HIUS) processing in both water and ethanol. AlNi intermetallic particles modified under HIUS in water and ethanol–water mixture were not expected to possess improved electrocatalytic properties compared to unmodified AlNi particles caused by surface passivation via metal oxide (surface areas were 125 and 48 m² g^{−1}, respectively). This proves the necessity of preliminary ultrasound agitation of precursors, but not the alloy, and the necessity of the careful selection of UA media (not to cause oxidation of the metal's or alloy's surface). In the presence of ethanol, it was possible to avoid additional oxidation during cavitation, but limited segregation of particles was feasible. Overall, the simultaneous utilization of MA and UA enhances the liquid-surface mass transport and the reactivity of a nickel and aluminum mixture as reagents for the synthesis of intermetallics.

4. Conclusions

Through the influence of mechano-ultrasonic activation and carbon nanotubes as nanoadditives, the interaction pathway of nickel–aluminum powder mixture, phase, and structure formation peculiarities at high heating rates were revealed. The optimum conditions for MUA processing were deduced (25 min UA for 1 min MA mixtures), demonstrating the relevance of UA treatment for MA mixtures over non-mechano-activated ones and the expediency of simultaneous application of both mechanical and ultrasonic activation, instead of the separate application of each of these procedures. Along with the microstructural homogenization of the precursor mixture, MA for up to 3 min decreased the size of nickel and aluminum crystallites under the influence of UA without changing the phase composition of the initial mixtures. The increase in the heating rate shifted the characteristic temperatures of single-stage exothermic interaction to the higher region for the non-mechano-activated, mechano-activated (1, 3, 5 min), and CNT (1 wt%) containing mixtures under UA agitation. The change in the interaction mechanism from solid–liquid (non-MA, 1 min MA mixtures) to solid–solid (3 min MA, 5 min MA, CNT containing mixtures) altered the phase composition of the products and accompanied the formation of NiAl+Ni₃Al mixture (s + l) or pure NiAl (s + s) after the exothermic interaction. The mutual MUA agitation shifted the heating curves to a lower temperature range, and the addition of CNT led to a decrease in the reaction initiation temperature, demonstrating the beneficial effect of MUA and CNT on the initiation of interaction. The effective activation energy values for the Ni + Al exothermic reactions showed that the lower E_a values were received for the Ni + Al and Ni + Al + 1% CNT systems under 1 min MA and 25 min UA influence. Hence, increasing the duration of MA under UA led to certain structural changes in the precursors; therefore, the exothermicity of the peak was weaker, although the process was stimulated to be initiated at a lower temperature.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met12030436/s1>, Figure S1: SEM (a) and EDS (b) images of Ni + Al mixture after 25 min ultrasonic activation; Figure S2: SEM images of Ni + Al mixtures; t_{MA} = 0 min, t_{UA} = 0 min (a), t_{MA} = 0 min, t_{UA} = 25 min (b), t_{MA} = 5 min, t_{UA} = 0 min (c), t_{MA} = 5 min, t_{UA} = 25 min (d); Figure S3: EDS analysis results of the quenched samples from Ni + Al mixtures at 1473 K, V_h = 600 K min^{−1}, t_{MA} = 5 min, t_{UA} = 25 min.

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