The influence of high-energy ball milling and nanoadditives on the kinetics of heterogeneous reaction in Ni-Al system

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Abstract. Kinetic studies were performed utilizing high-speed temperature scanner in the Ni-Al system including those with and without mechanical activation (MA) of different duration in a planetary ball mill, with and without using carbon nanoadditives (NA). The temperature profiles were taken and treated at different heating rates from 100 up to 2600 °C/min considering the influence of activation duration and the role of nanoadditive on the characteristic points of thermograms. Kissinger method allowed to evaluate activation energy (E_a) for non-activated, activated (1, 2, 3, 5 min), nanoadditive (1 wt.% containing nanoadditive (1 wt.%) and containing mechanonactivated (1, 3, 5 min) mixtures. The beneficial influence of NA on the interaction between Ni and Al in the non-activated and moderately mechanonactivated mixtures was demonstrated. The influence of MA and NA on the microstructure features and phase formation sequence at various heating rates were revealed. For all the mixtures under study, T* characteristic temperatures (the temperature, where the maximum exothermic effect was observed) were found to increase with increasing heating rates. It was unravelled that mechanical treatment leads to significant changes in the reaction kinetics and phase formation laws. Particularly, in an activated mixture, the formation of Ni\textsubscript{3}Al is followed by NiAl intermetallic, in contrast to non-activated mixture, where the reaction proceeds only with the NiAl formation. The both MA in 1 min and addition of 1 wt.% NA decreased the activation energy of the Ni-Al reaction, exhibiting commensurate impact on the effective activation energy value of the Ni-Al system. However, ≥3 min MA in the presence of 1 wt.% NA have prohibitive effect on the reaction in the Ni-Al system.

1. Introduction

Intermetallic compounds based on Ni-Al are being recognized as potential high temperature structural materials because of their low density (5.86 g cm\textsuperscript{-3}), high melting point (1911 K), excellent oxidation resistance up to 1573 K, as well as good thermal conductivity [1-2]. The combination of distinctive properties has made Ni-Al intermetallic compounds potentially useful for many structural applications, such as gas turbine hardware, corrosion resistant materials, heat treatment fixtures, high temperature dies, molds and cutting tools [3-4].

Previous studies have demonstrated the fabrication of nickel aluminides by means of powder metallurgy [5-9], mechanical alloying [10-12] and self-propagating high temperature synthesis (SHS) (also known as combustion synthesis (CS)) [13-16]. The synergistic influence of the both MA and SHS of nickel aluminides was manifested to be perspective in terms of phase regulation and impressive enhancement of intrinsic properties [17]. In [18, 19] the decrease in apparent activation energy of the reaction was attributed to the change of interaction pathway due to mechanically assisted combustion.
synthesis of Ni-Al. The preparation of Ni-Al intermetallic compound under the activated combustion mode was successfully implemented, as described in [20]. As a promoter, negligible amount of polytetrafluoroethylene (PTFE) was added into initial Ni-Al mixture.

Therefore, it is relevant to develop novel approaches for SHS processes to provide in-situ control on the phase and structure, as well as on the properties of target materials. In this regard, preliminary MA and the introduction of nanoadditives (NA) to the initial charge become promising.

Considering high temperatures and high self-heating rates of substances in the combustion front, the in-situ exploration of interaction mechanism of the combustion process is impeded. The modeling of the process at controllable conditions (e.g. with programmed heating rates and tuning the process within the time at conditions closer to heating rates and temperatures in the combustion wave) by thermal analysis methods will tackle the obstacle of mechanism examination.

High-Speed Temperature Scanner (HSTS setup) exclusively designed at the Institute of Chemical Physics NAS RA [21-23] for the kinetic investigations of the powder mixtures under high heating rates (up to 10000 °C min\(^{-1}\)) and temperature up to 1300 °C, was utilized to explore the influence of MA and NA on the structure and phase formation peculiarities in the Ni-Al system, as well as to estimate effective values of activation energies.

This approach provides enhanced opportunities to reveal the stepwise nature of reactions in the Ni-Al system. By varying heating rates of reagents, it was possible to separate the main stages and analyze intermediate quenched compounds for the efficient exploration of interaction mechanism in the systems under study. Moreover, implementation of the process with different heating rates allowed to use the model-free non-isothermal Kissinger method [24, 25] to calculate Arrhenius parameters of the process.

This study is motivated by the need to investigate the influence of MA (1-5 min) and presence of NA (carbon nanotubes) on the structure formation patterns and interaction kinetics of the Ni-Al system (with 1:1 molar ratio of metals) at non isothermal conditions using HSTS technique.

2. Experimental

Nickel (PNK-1VL7, reagents grade, particle size \(\mu<10\ \mu m\)), aluminium (ASD-4, reagents grade, particle size \(\mu<40\ \mu m\)) and carbon nanotubes (CN) were used as precursors. Carbon nanotubes were synthesized by Chemical Vapor Deposition (CVD) method on a nickel-plated surface [26]. The substrate was a copper with a galvanic nickel coating with a thickness of about 5 \(\mu m\). The synthesis was carried out at atmospheric pressure. Heating was controlled by the temperature of the plate using a thermocouple. The operating temperature was 710 °C. The reactor was heated and cooled under constant nitrogen purging with a flow rate of 1.5 l·min\(^{-1}\) (the volume of the reaction chamber was 0.6 l). When the operating temperature was reached, vapors of the propane-butane mixture with a flow rate of 0.5 l·min\(^{-1}\) were fed into the reactor. The resulting carbon material was mechanically cleaned from the surface. The mass fraction of nickel in the CN was from 1.5 to 5 wt.\%. The material contained disordered filaments and fibers with a wide variation in a diameter (from dozen nanometers to several microns) (Fig. 1). The nanoadditive was added to Ni-Al mixture after mechanoactivation (\(m_{\text{nanoadditive}}=1\ \text{wt.\%}\)) by gently mixing in a ceramic mortar for 10 min.
Fig. 1. SEM images of carbon nanostructured material

MA of initial mixtures was carried out from 1 to 5 min in a planetary ball mill (RETSCH PM-100) at fixed rotation speed of 500 rpm. The mass charge ratio of milling media (10 mm steel balls) and powder was 20:1.

The experiments were carried out by HSTS setup under programmed high heating rates (100-2600 °C min⁻¹) and temperature up to 1300 °C. The reactive powder mixture (50-100 mg) was placed into the metallic envelope made from thin nickel foil with 0.1 mm thickness, and a K-type thermocouple (chromel-alumel) spot-welded directly to the foil in the central area of powder location. All measurements were conducted at 0.1 MPa argon (>99.98 %) pressure. The foil heater was heated by passing electric current with desired temperature time schedule provided by PC-assisted controller. Typical temperature profile for the inert experiment provides linear temperature time history, which defines the heating rate and coincides with the reactive T profile at low-temperature region when the reaction does not occur. The reaction onset temperature (T_o), the maximum peak temperature observed during self-heating (T_max) and the temperature prescribed by linear heating, where the maximum exothermic effect is observed (T*), were determined from the heating thermograms (Fig. 2).

Kissinger’s isoconversion method [24], based on the principle of temperature shift corresponding to the maximum advance on the DTA curve, as a function of heating rate (V_h), was applied to calculate the effective activation energy value for the process under study:

\[
\ln \left( \frac{V_h}{T_{\text{DTA}}^{\text{max}}} \right) = \ln A - \frac{E}{R} \left( \frac{1}{T_{\text{DTA}}^{\text{max}}} \right) \tag{1}
\]

where, V_h is the heating rate (K min⁻¹), T_{\text{DTA}}^{\text{max}} is the temperature corresponding to the maximum advance in the DTA curve (K), A is a constant, E is the effective activation energy of the process, (kJ mol⁻¹), R is the universal gas constant (8.31 J K⁻¹mol⁻¹).
The process was interrupted at different characteristic stages. Phase composition and microstructure of the cooled samples were examined. When interrupting the process, high cooling rates were achieved (up to 12000 °C min⁻¹) to exclude further interaction over the cooling stage.

Phase compositions of the intermediate and final products were analyzed by X-ray diffraction (XRD, DRON-3.0, Burevestnik, Russia) with monochromatic CuKα radiation (λ=1.5406 Å) operated at 25 kV and 10 mA. To identify the products from the XRD spectra, the data were processed using the JCPDS-ICDD database. The microstructure of powders was examined by BS-300 and LEICA440i scanning electron microscopes (SEM).

3. Results and discussion

3.1. Mechanical activation of Ni+Al powder mixture

The mechanical activation of initial Ni+Al powder mixture was implemented by dry mixing in air at different durations (from 1 to 5 min). The results of XRD examinations demonstrated no change in phase composition regardless the MA duration (Fig. 3). However, the characteristic peaks of metals were noticeably expanded with increasing the duration of MA.
According to microstructural analysis (Fig. 4), the increase in MA duration expectedly leads to a change in the form and size of particles. In particular, homogenization was observed at 1 min MA, while agglomeration of particles was registered at 3 and 5 min activation.

In figure 5 the microstructures of the initial mixtures in the presence of nanoadditive are shown before and after mechanical activation. The non-activated powder mixture is characterized by a smaller particle size (1-10 μm) compared to 3 min mechanoactivated mixture (10-20 μm).
3.2. Influence of mechanical activation and nanoadditives on the Ni–Al system at 2600 °C min\(^{-1}\) heating rate

Mechanical activation can lead to either increase or decrease in the efficiency of heat exchange between particles, which depends on the particle shape and size, on the particle size distribution, the interparticle contact surface area and the thermal resistance of interparticle contacts. The effect of activation duration is demonstrated on the typical temperature profiles of Ni+Al mixtures at 600 and 2600 °C min\(^{-1}\) heating rates. Single stage exothermic Ni-Al interaction was observed regardless the activation duration (Fig. 6). However, in non-activated mixtures and at the short duration of MA (up to 2 min) interaction starts after the melting of aluminum (630, 670 °C), while starting from 3 min of activation the process begins before the melting point of aluminum (at 580 °C). This pattern was observed regardless the heating rates (from 100 up to 2600 °C min\(^{-1}\)). The increase in self-heating temperature (characterizing the amount of heat released) in the 1 and 2 min mechanoactivated mixtures occurred as a result of increase in the contact surface area between particles of the mixture and intensification of bulk and grain boundary diffusion. The further decrease of self-heating temperature (3 and 5 mins) is in agreement with SEM analysis and is conditioned by the reduction of the specific heat release of the activated mixture and to blockage of the contact surface of the reactants.

The addition of 1%NA didn't have significant influence on starting temperature (T\(_{0}\)) of the processes (Fig. 7. 0 and 0', 3 and 3', 5 and 5'), however strongly contributed to the self-heating temperature of non-activated mixtures.

Fig 5. SEM images of (Ni+Al)+1wt%(NA) mixtures after mechanical activation, a) t\(_{MA}\)=0 min; b) t\(_{MA}\)=3 min
Fig. 6. The influence of MA and NA on heating curves of various Ni+Al mixtures with and without MA, \( a_{V_h}=600 \, ^\circ\text{C min}^{-1} \), \( b_{V_h}=2600 \, ^\circ\text{C min}^{-1} \): 0 _\_t_{MA}=0 \text{ min}; 0' _\_t_{MA}=0 \text{ min}+1\%\text{NA}; 1 _\_t_{MA}=1 \text{ min}; 1' _\_t_{MA}=1 \text{ min}+1\%\text{NA}; 3 _\_t_{MA}=3 \text{ min}; 3' _\_t_{MA}=3 \text{ min}+1\%\text{NA}; 5 _\_t_{MA}=5 \text{ min}; 5' _\_t_{MA}=5 \text{ min}+1\%\text{NA}

### 3.3. Influence of heating rate on the activation energy and phase formation of the various Ni–Al system

In the all studied non-activated Ni+Al mixtures the reaction \( T^* \) shifts to a higher temperature area from 625 to 750 \(^{\circ}\text{C} \) for \( T^* \) and from 1060 to 1160 \(^{\circ}\text{C} \) for \( T_{\max} \) with increasing the heating rate from 100 to 2600 \(^{\circ}\text{C min}^{-1} \), while the exothermic peak intensity of the reaction remains almost the same. Data obtained are close to the result of DTA/TG studies at low heating rates (5-20 \(^{\circ}\text{C min}^{-1} \), 650-750 \(^{\circ}\text{C} \); 159 kJ mol\(^{-1} \)) [20].

Fig. 7. The activation energy of Ni-Al mixture with and without nanoadditives dependent on the duration of mechanoactivation
This type of thermal behavior is characteristic to exothermic systems with high activation energies. In particular, according to Kissinger’s method the activation energy of Ni-Al exothermic interaction was calculated to be 140.4 kJ mol\(^{-1}\) (630-750 °C, 100-2600 °C min\(^{-1}\)). The duration of mechanoactivation has detrimental effect on the effective activation energy value. In particular, 1 or 2 min activated mixtures demonstrated lower value of activation energy compared to that for non-activated mixtures and for the mixtures processed 3 and 5 min.

Considering the ductile nature of aluminum, it was preliminary expected that longer duration of activation (here it was only 3 min) may have reverse effect, i.e. lead to increase in particle size and decrease in the surface-to-volume ratio, or the specific surface area (SSA), which in turn affects the prevailing mechanism and hence the activation energy sensitive to particle size. Thus, effective activation energy decreases, and then increases vs activation duration (Fig. 7).

The change in interaction mechanism under the MA was disclosed by XRD examinations revealing that in the non-activated Ni-Al mixtures before the exothermic interaction, samples quenched immediately before the aluminum melting point (630 °C), contained only initial metals, whereas at 900 °C the product represented pure NiAl intermetallic compound (Fig. 8a). The mechanical activation promoted the formation of Ni\(_3\)Al intermetallic along with NiAl at 900 °C, while continuing the heating up to 1300 °C resulted in the formation of only NiAl intermetallic (Fig. 8b), which has a wide range of homogeneity according to the both parameters: composition and temperature. The formation of NiAl was predictable due to stoichiometry of the mixture (1:1), as well as by the studied temperature interval (up to 1300 °C). The formation of Ni\(_3\)Al intermediate in the mechanoactivated mixture might be explained by the lack of aluminum or diffusion barriers originated from aluminum agglomeration.

From other hand, the question about first formed phase in the Ni-Al interaction was discussed elsewhere and there is no unanimity about it, because some authors supposed NiAl\(_x\), Ni\(_3\)Al, NiAl, Ni\(_2\)Al\(_3\) as one, in addition the studied temperature interval was limited (up to 1000 °C). Enayati et al. [27] reported different behavior in Ni-Al powder mixture. They found that a Ni(Al) solid solution forms initially as an intermediate phase and then transforms to the Ni\(_3\)Al intermetallic compound on further milling. In [28] the increase of MA time had shown practical disappearance of Al with simultaneous increase of NiAl amount.
the process (900 °C) agglomerates of NiAl with average particle size of 20 μm were formed (Fig. 9c). Mechanoactivation in 3 min led to an agglomeration of Ni and Al particles in the initial mixture (Fig. 9a, 10a), but noticeable change was not observed before the exothermic peak at 590 °C. As in the mechanoactivated mixtures with a duration of 3-5 min the interaction proceeded in solid-solid mechanism, before the melting of aluminum, no additional coarsening was detected, and at the end of exothermic process (900 °C) fine-grained product (up to few microns) was registered.

The microstructural differences between the non-activated and mechanoactivated mixtures are associated with (i) the size of particles in the initial mixture and (ii) onset temperature of exothermic reaction (before or after Al melting). The recent is more presiding over the interaction mechanism (s+s, s+l) and the activation energy value.

![Fig 9](image)

**Fig 9.** SEM images of quenched samples (Vₜ= 600 °C min⁻¹) for non-activated Ni+Al mixtures a - initial mixture, b - 630 °C c - 900 °C

![Fig 10](image)

**Fig. 10.** SEM images of quenched samples (Vₜ= 600 °C min⁻¹) for 3 min mechanoactivated Ni+Al mixtures; a - initial mixture, b - 590 °C c - 900 °C

### 3.4. The influence of nanoadditives on the activation energy and phase formation of the non-activated and activated Ni–Al system

The addition of 1% of carbon nanotubes has stimulating influence on the non-activated Ni-Al mixture. As a result, Ni-Al interaction started earlier and exhibited increase in maximum temperature, as compared to the non-activated mixture without nanoadditives. According to the activation energy values calculated by Kissinger method, the addition of nanoadditives to a non-activated mixture significantly lowered the activation energy value from 140.7 to 127.2 kJ mol⁻¹. As it can be seen from the microstructural analysis of the samples cooled at 640 and 900 °C (Vₜ=600 °C min⁻¹) the introduction of nanoadditives into the system led to a significant decrease in the particle size of the product (Fig. 11) conditioned by the small grain size of the initial mixture and the homogeneous distribution of carbon nanotubes. This fact, in turn, affects the heterogeneous reaction and the crystallization of the alloy from a "short" existing melt, changing the composition and structure of the resulting material, contributing to the formation of a more homogeneous granular structure of the product (Fig. 11c).
Fig. 11. SEM images of quenched samples (V_h = 600 °C min⁻¹), a - initial mixture, b - 640 °C c - 900°C

The addition of 1% nanoadditives to the mechanoactivated mixture of a duration in 1 min led to an increase in characteristic temperatures (T_o=595-680 °C, T*_c=600-780 °C, T_max=1000-1160 °C) according to heating rate (V_h=100-2600 °C min⁻¹), however as compared to the nanoadditive containing non-activated mixtures, T_max temperatures are lower in the studied heating rate region (Fig. 12).

Fig. 12. Heating curves of a mixture containing Ni+Al+1%NA activated for 1 min V_h=100 (1), 300 (2), 600 (3), 1200 (4), 2600 (5) °C min⁻¹

According to XRD analysis results, regardless of the presence of nanoadditive in the non-activated mixtures (Ni+Al+1%NA and Ni+Al), one phase NiAl product was observed in the product quenched immediately after the exothermic peak. Ni3Al was observed along with NiAl in the mechanoactivated mixtures with any duration (1, 3, 5 min), immediately after the exothermic reacton, and single-phase NiAl was formed at the end of the heating at 1200 °C (V_h=600°Cmin⁻¹).

Conclusion
The characteristic temperatures derived from the thermograms of the Ni+Al powder mixture, as well as the activation energies of the processes significantly depend on both the mechanoactivation duration and the presence of the nanoadditives. The increase in the mechanoactivation up to 2 min leads to the decrease in the activation energy (E_a) values. In the non-activated mixtures and at the short duration of MA (up to 2
(1 min) interaction starts after the melting of aluminum (630, 670 °C), while starting from 3 min of activation the process begins before the melting point of aluminum (at 580 °C) regardless the heating rate (from 100 up to 2600 oC min\(^{-1}\)). The both MA in 1 min and addition of 1 wt.% NA decreased the activation energy of the Ni-Al reaction, exhibiting commensurate impact on the effective activation energy value of the Ni-Al system. Mechanical treatment leads to significant changes in the reaction kinetics and phase formation laws. Particularly, in an activated mixture, the formation of Ni3Al is followed by NiAl intermetallic, in contrast to non-activated mixture, where the reaction proceeds only with the NiAl formation. In the non-activated mixtures the interaction process started after the melting of aluminum, then particle coarsening occurred from 660 °C up to 900 °C, and at the end of the process (900 °C) agglomerates of NiAl with average particle size of 20 μm were formed. As in the mechanoactivated mixtures with a duration of 3-5 min the interaction proceeded in solid-solid mechanism, before the melting of aluminum, no additional coarsening was detected, and at the end of exothermic process (900 °C) fine-grained product (up to few microns) was registered.

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