Study of thermal explosion parameters for mechanically activated powder mixture titanium – nickel at changing the characteristics of the thermal field

O A Shkoda

Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences, 10/3 Akademicheskii Prospekt, Tomsk, 634055, Russia

E-mail: O.Shkoda@dsm.tsc.ru

Abstract. The paper presents the results of an experimental study of thermal explosion characteristics of mechanical oactivated powder mixtures of titanium-nickel. It was found that the changes in the characteristic temperatures at different heating rates are wave-like regardless of the heating rate during the thermal explosion. The correlation of the cyclical changes in the thermal characteristics of the explosion and morphological changes of the powder mixture during mechanical activation was found. Nonmonotonic changes in the behavior of characteristic temperatures are associated with changes in particle powder sizes and layered agglomerates during mechanical activation. An increase in the critical temperature and a decrease in the maximum temperature occurs in the investigated time interval of mechanical activation with an increase in the heating rate in the subsequent thermal explosion. The decreases of the combustion temperature of the titanium – nickel activated mixture up to 400°C, and the realization of the synthesis in the solid-phase mode was recorded.

1. Introduction

Self-propagating high-temperature synthesis (SHS) is a type of combustion that produces practically valuable solids [1, 2]. One of the variants of self-propagating high-temperature synthesis is heating at a given rate, leading to a thermal explosion or setting a constant temperature in the surrounding reaction volume. The main feature of this method of the synthesis is that the initiation is carried out not only from the surface, but also due to the heating of the entire volume of the reacting substance. Depending on the ratio of the determining parameters, the maximum temperature can occur either in the center of the reaction volume, or between the center and the surface (transient modes to ignition, some modes of filtration self-ignition). In any of these cases, the temperature and concentration inhomogeneity forms one or two combustion fronts and in the future the process proceeds in a self-propagating mode. Under such conditions, the synthesis is carried out largely in the post-induction period. In the classical theory of the thermal explosion, post-induction periods were not considered, since the main practical application of the theory was to determine the safe conditions for the production, storage and processing of explosives and self-igniting systems. To do this, it was necessary to calculate the critical conditions of the thermal explosion and the induction period over the explosive limit. The study of the post-induction period began as a result of the development of research and improvement of the processes of self-propagating high-temperature synthesis and the need to understand the processes occurring during the synthesis in the mode of thermal explosion. The
spatio-temporal development of the thermal explosion (self-ignition) process depends on the heating rate. At low heating rates, the temperature rises slowly. Heating of the system, the thermal acceleration of the reaction is compensated by its kinetic inhibition, i.e. the fall of the reaction rate due to the burnout of the substance. With an increase in the heating rate, a certain critical speed is achieved, from which it is no longer possible to prevent an explosion. When self-ignition occurs near the surface of the maximum heating during the process moves to the center, and the temperature failure occurs in the center. With the increase in the heating rate, the maximum later gets to the center, and at some values of the heating rate, it gets to the center simultaneously with the explosion.

Interest in research in the field of the thermal explosion also arose in connection with the emergence of one of the varieties of self–propagating high-temperature synthesis—technology—synthesis of inorganic compounds in the thermal explosion. A. G. Merzhanov [3] expressed the opinion that the method of synthesis in the mode of thermal explosion refers to the processes of SHS, as it has a significant stage of self-propagation. The most common method of the synthesis in the mode of thermal explosion is linear heating at a constant speed. This method synthesized a number of systems, mainly intermetallides and composites. The process of SHS and its reactions depend on a number of physical and chemical parameters. These include various thermodynamic parameters such as the heat of formation of a chemical compound, the heat capacity of the reaction products, the initial temperature of the process, the composition of the mixture; some physical parameters such as the thermal conductivity of the powder mixture, the density of the briquette, the external pressure of the gas, the shape and size of the powder particles, the polydispersity of powders, the degree of hardening or defect of the particle structure of the components, the presence of external influences; technological parameters: uniformity of mixing of the components of the mixture, the degree of activation of powders, chemical: the degree of moisture content of powders, the concentration of adsorbed impurities and dissolved gases. By changing all these parameters, you can influence the process of SHS to obtain a particular product with a given structure and properties. Among the above methods of influence on the process of SHS and its regulation in recent years, such a method as preliminary mechanical activation has become increasingly common.

Interest in research in the field of mechanical activation (MA) increased due to the emergence of SHS technology for the synthesis of inorganic compounds [4, 5]. The use of preliminary MA before sintering processes or SHS is becoming increasingly common [6-13]. Preliminary mechanical activation of different time, leading to a significant deformation of the lattice, with subsequent sintering and SHS facilitates the formation of active embryos, and intensifies the process of mass transfer. Sintering and synthesis processes of pre-mechanically activated material can give qualitative new interesting results in the field of refractory compounds.

The mechanical activation of the initial components creates a reserve of additional energy in them, thanks to which, with the subsequent transfer of thermal activation energy to them, it becomes possible to carry out a reaction in the mode of self-propagating high-temperature synthesis. In the synthesis of materials by SHS-technology with preliminary mechanical activation, the temperature of the beginning of the interaction of the components decreases, the amount of heat generated increases, the mixing operation is excluded, the specified composition is provided, and it becomes possible to carry out the synthesis in solid-phase mode.

The use of preliminary MA before self-propagating high-temperature synthesis allows to control the process in order to obtain the desired synthesized product. The mechanical activation with a large number of variable parameters gives additional leverage on the impact of the subsequent synthesis, and additional opportunities to control and control the synthesis, and hence the structure, composition and characteristics of the resulting material. Despite the long-term use of pre-MA for SHS, many questions remain poorly understood due to the large variety of phenomena occurring during the mechanical activation.

In recent years, in science, technology and medicine are widely used multifunctional materials with desired properties - materials that under the influence of external factors and operating conditions (temperature, mechanical load, etc.) can be controlled to change their properties. These materials
include alloys with unique physical and mechanical properties - the effect of thermomechanical shape memory and superelasticity. The most striking and the best representative of such alloys are intermetallic compounds based on titanium nickelide NiTi. Therefore, the study of this material is of scientific and practical importance [6 - 8, 14 - 20].

During MA there are many different, simultaneous and often opposite processes, this grinding of the initial powders, spreading the powder mixture on the grinding bodies, the formation of layered agglomerates and their breaking. And the whole complex of phenomena can be influenced by various factors, including the dimension parameter of the initial components is very important and can have a significant impact on the formation of the structure of the mechanoactivated powder mixture and the subsequent synthesized product. The use of the thermal explosion after the mechanical activation helps to understand the processes occurring during the mechanical activation and their influence on the subsequent synthesis.

2. Experiment
For the mechanical activation powders were used: titanium grade PTS (100-300 microns) and nickel grade PNCL7 (10 microns). MA was carried out in a planetary mill with an energy density of 60 g. Powders were loaded in the ratio Ti-Ni 55.06 mass.%. The mechanical activation was carried out in an air medium, the activation time varied from 30 seconds up to 5 minute. This time MA was chosen to study the process of the mechanical activation in this time interval, which has not yet begun the formation of mechanochemically synthesized phases in titanium nickelides. The formation of mechanosynthesized phases was monitored using x-ray phase analysis. Synthesis in the mode of thermal explosion of mechanoactivated mixtures was carried out at the installation of a constant volume (V=5 l) in argon medium. The activated mixture (4-4.5 g) was poured into a cup of thin steel mesh with a diameter of 1.1 cm and a height of 2.2 cm the sample was heated by a resistance furnace with a temperature measurement in the center of the sample with a chromel-aluminum thermocouple with a diameter of 100 µm. Thermocouple readings were recorded using an electronic potentiometer KSP-4. The structure and the composition of activated powder mixtures and combustion products were investigated by scanning electron microscopy (Philips SEM515) and x-ray phase analysis (Drone-UM).

3. Results
The appearance of the initial titanium and nickel powders is shown in figures 1 and 2. Initial powders differ from each other not only in size (titanium is larger), but also in shape. Coral-elongated titanium particles are markedly different from sharp-angled nickel.

But already in the first seconds of the mechanical activation of titanium and nickel the particles lose their original shape and structure, they break, crushed and smeared on each other. The process of grinding and spreading of particles occurs constantly and simultaneously. And this alternation from the earliest times of the mechanical activation forms layered agglomerates, which are layers of dissimilar source titanium and nickel.

Figures 3 and 4 show the microstructures of the powder mixture of titanium and nickel after 2 and 4 minutes of the mechanical activation. After 2 minutes of the mechanical activation, the powder mixture of titanium and nickel is the mixture consisting of separate large particles of irregular shape, on which individual small particles are glued. These fine particles are basically not particles of one component, but a mixture of particles stuck on each other. That is also the layered agglomerate, but much smaller. Such small particles – agglomerates are broken off parts of the large agglomerate. At the initial time of the activation of the layered agglomerates do not have time to form a dense structure. Layers of dissimilar source components did not have time to roll to each other. Therefore, parts of such the agglomerate can easily break off and form smaller ones.

Figure 4 shows the microstructure of the powder mixture after 4 minutes of the mechanical activation. Here, layered agglomerates are denser formations with larger dimensions compared to the powder mixture after 2 min MA. During this time, the layers in the agglomerate had become thinner,
more tightly cling to each other and the agglomerate became more rounded, disappeared, broke off the angular edges. The processes of agglomeration and destruction occur continuously throughout the period of mechanical activation.

The effect of preliminary mechanical activation of the nickel – titanium system on the combustion parameters in the layered (wave) mode is described in detail in [9]. In particular, the dependence of the initial combustion temperature for different compositions of the initial mixtures activated in the attritor with balls and without balls is established. It is shown that the mixture Ti-50 at% Ni after machining with balls does not require preheating. The mechanical activation was performed before the formation of mechanosynthesized phases. The formation of mechanosynthesized phases was controlled by indications of x-ray phase analysis.

Samples after MA were placed in a special furnace filled with argon. The furnace was heated and the temperature curves were observed on the recorder-thermograms of which determined the temperature of the beginning of heat release $T_0$, the critical temperature of the thermal explosion $T^*$ and the maximum temperature of $T_{\text{max}}$. A typical thermogram of the process is shown in Fig.5. At $T_0$, heat is released in the system, at the critical temperature - the process becomes uncontrollable and the maximum temperature is the maximum values that the temperature reaches during self – heating and explosion.

Figure 1. Microstructure of initial powder of titanium of PTS type.

Figure 2. Microstructure of initial powder of nickel of PNCL7 type.

Figure 3. Microstructure of the powder mixture after 2 min MA

Figure 4. Microstructure of the powder mixture after 4 min MA
Figure 5. The typical thermogram of synthesis in Ti-Ni system after preliminary mechanical activation, $T_0$ - initial temperature of the thermal explosion, $T^*$ - critical temperature of the thermal explosion, $T_{\text{max}}$ - maximum temperature of the thermal explosion.

For the analysis of the arising dependences the graphs of characteristic temperatures (the temperature of the beginning of heat release, the critical temperature and the maximum temperature) on the MA time at different heating rates were constructed (Fig. 6).

Figure 6. Dependences of the characteristic temperatures of thermal explosion from the time of the preliminary MA at:
a - heating rate of 350 deg/min.
b - heating rate of 600 deg/min.
c - heating rate of 800 deg/min

On the graphs you can see all the curves have a wave-like nature and the general tendency to decrease of the temperature with increasing time of MA, regardless of the heating rate. The higher the heating rate, the lower the values of $T_0$, $T^*$ and the higher the $T_{\text{max}}$ with increasing MA time. The temperature difference i.e. how much the characteristic temperature decreases with increasing time MA depends on the heating rate. The graph of the temperature difference from the furnace heating rate was constructed (Fig. 7). It can be seen that the critical temperature ($T^*$) increases almost monotonically, the maximum temperature ($T_{\text{max}}$) decreases, and the initial temperature drops sharply to the certain point, then also...
increases sharply with increasing heating rate. At any heating rate, non-monotonic changes in the range of 3 to 4 min. of MA can be seen on the charts. The critical temperature equal to eutectic (940 °C) for the unactivated mixture is reduced to 400 °C and the synthesis proceeds in the solid-phase mode.

The structures of the mixture were studied for explain the observed changes of characteristic temperatures in the thermal explosion. Changes in particle size and layered agglomerates after different MA times were analyzed. The smallest agglomerates and particles were less than 100 µm and the largest reached 300 µm or more. To identify the behavior of layered agglomerates, they were divided into several groups: less than 100, from 100 to 200, from 200 to 300, and more than 300 microns. The results of the study of changes in the number of layered agglomerates with different sizes are shown in figure 8. It was found that after 1 min. MA in the mixture is dominated by fine powder, with the size to 100 microns. The amount is to 60 % after 1 min. MA and reaches to 80 % after 2 min. MA. After 3 min. MA, the amount of fine fraction decreases to 20 %. The number of layered agglomerates of other larger fractions does not differ much from each other and amounts to 16% of the fraction with the size from 100 to 200 microns after 2 min. MA. The number of larger fractions is even smaller. Thus, in the time interval up to 2 min. MA in the mixture there are active processes of titanium grinding, the initial dimensions of which were from 100 to 300 microns on the debris which smeared nickel particles. Ground, crushed titanium particles, connecting with nickel begin to form layered agglomerates. After 3 min. of MA, the number of agglomerates from 100 to 200 microns increases to 30%, as well as the number of agglomerates with sizes from 200 to 300 microns to 25% increases. At the same time, the amount of fine fraction to 100 µm sharply decreases from 80% to 20%. This indicates that most of the small particles stuck and formed the layered agglomerate. After 4 min of MA, the dimensional situation in the mixture changes again sharply and resembles the situation after 2 min MA. There is an increase in the amount of fine fraction up to 60% and decrease in the number of large agglomerates. There is a change of the system behaviour after 3 minutes MA. Up to 3 min. is dominated by grindings, after 3 min. MA - agglomeration processes. This change in agglomerates influences the of characteristic temperatures in a subsequent thermal explosion.

Figure 7. The dependence of ΔT on the heating rate, where ΔT-the difference in temperatures
- maximum temperature (T_max)
- critical temperature (T*)
- start temperature of heat (T_0)

Figure 8. Change number of fractions as a function of the time of the mechanical activation
4. Conclusion

Changes in the characteristic temperatures are wavelike with increasing time of preliminary mechanical activation, regardless of the heating rate.

The increase in the critical temperature difference and the decrease in the maximum temperature occurs in the investigated time interval of the mechanical activation with an increase in the heating rate during the subsequent thermal explosion.

The critical temperature of the thermal explosion equal to eutectic (940°C) for the unactivated mixture Ti – Ni is reduced to 400°C in the activated system and the synthesis proceeds in the solid-phase mode.

Nonmonotonic changes in the behavior of characteristic temperatures are associated with changes in particle sizes and layered agglomerates during the mechanical activation.

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