

# Study of the effect of the size of the initial nickel powder on the structure formation of the mixture during mechanical activation of titanium and nickel

O A Shkoda

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

E-mail: [O.Shkoda@dsm.tsc.ru](mailto:O.Shkoda@dsm.tsc.ru)

**Abstract.** The structure and morphology of the mechanoactivated powder mixture has significant impact on the process of further synthesis. In this paper, the influence of the sizes of the initial powders on the formation of the structure of the mechanoactivated powder mixture during mechanical activation and the formation of layered agglomerates in the powder mixture of titanium and nickel is studied. The evolution of the formation of the size and density of layered agglomerates with the participation of both small and large nickel powder after different times of mechanical activation is studied. The study showed that the mechanical activation process leads to the formation of layered agglomerates and an increase in activity, which is associated with an increase in the contact surface of dissimilar particles, the number of defects. It is established that the use of initial nickel of different dispersion contributes to the formation of different structure of mechanoactivated powder mixture.

## 1. Introduction

The interest in research in the field of mechanical activation (MA) has increased due to the emergence of self – propagating high-temperature synthesis (SHS) - technology for the synthesis of inorganic compounds. The SHS process and its reactions depend on a number of physical and chemical parameters. These include thermodynamic parameters (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); physical parameters (the thermal conductivity of the powder mixture, the density of the briquette, the external gas pressure, the shape and size of the powder particles, the polydispersity of powders, the degree of hardening or defect of the structure of the component particles, the presence of external influences); technological (uniformity of mixing of the mixture components, the degree of activation of defects); chemical (the degree of moisture of powders, the concentration of adsorbed impurities and dissolved gases) [1, 2]. It is possible to influence the process of SHS by changing these parameters to obtain a particular product. Among the above methods of influence on the process of SHS and its regulation in recent years, such a method as mechanical activation is becoming increasingly common [3].

Special attention is paid to the mechanical activation of solids and reactions with their participation. Part of the mechanical energy transferred to the solid body during the activation process is stored in the form of energy of the fresh surface, linear and point defects on it, various radicals and other active centers. The general sequence of processes occurring during the mechanical activation of



a mixture of solids is reduced to the following stages: the dispersion of reagents, the mechanical mixing, the chemical interaction at the points of contact, increasing point contacts over the entire area, the destruction of the product layer and the formation of new fresh contacts, chemical interaction, etc., before the end of the interaction. The above effects and the use of the mechanical activation can positively assess its application for the intensification of the self-propagating high-temperature synthesis.

The use of the preliminary mechanical activation before sintering processes or SHS is becoming increasingly common [4-7]. Short-term mechanical activation, leading to a significant deformation of the lattice, followed by sintering above the polymorphic transition temperature promotes the formation of active embryos and intensifies the mass transfer process. Sintering processes of the preliminary mechanoactivated material can give qualitatively new results in the field of refractory compounds.

The mechanoactivation of the initial components is aimed at creating an energy reserve in them, thanks to which, with the subsequent transfer of thermal activation energy, it becomes possible to carry out a reaction in the mode of the self-propagating high-temperature synthesis. In the synthesis of materials by SHS technology, the temperature of the beginning of the interaction of components decreases, the amount of heat released increases, the mixing operation is excluded, the specified composition is provided.

Materials synthesized by the mechanical activation and the SHS method have different structure and different properties. The integration of these two methods helps to preserve the positive aspects of both processes and significantly reduce their disadvantages.

It is established that the implementation of solid-phase SHS is due to the formation of "layered composites(agglomerates)" from the powder mixture, in which the reagents are crushed to ultrafine sizes, the contact area is repeatedly increased and a high concentration of nonequilibrium defects is created. By means of the mechanical activation it is possible to use the phenomena occurring in solids at loads and high strain rates. This is a change in the structure, the acceleration of diffusion processes during plastic deformation, increasing the reactivity, the acceleration of solid-phase reactions, the formation of newly formed surfaces and active sites on them, the appearance of pulses of high local temperatures, etc. In the process of the MA be significant changes in the physico-chemical properties of materials, and, as a consequence, the increase of the reactivity.

The use of preliminary MA before the self-propagating high-temperature synthesis allows to control the process in order to obtain the desired synthesized product. By changing the conditions of the preliminary MA can be adjusted modes of combustion and synthesis products. Despite the long-term use of preliminary MA for SHS, many questions remain poorly understood due to the variety of phenomena occurring during mechanical activation.

In recent years, in science, technology and medicine are increasingly 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 super-elasticity. The most striking and the best representative of such alloys are intermetallic alloys based on titanium nickelide NiTi. Therefore, the study of this material is of scientific and practical importance [8-21].

During MA, there are many different, simultaneous and often opposite processes, such as grinding the original powders, spreading the powder mixture on the grinding media, 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. In this paper, we investigate the effect of different sizes of the initial nickel powder on the structure formation of the mixture for MA.

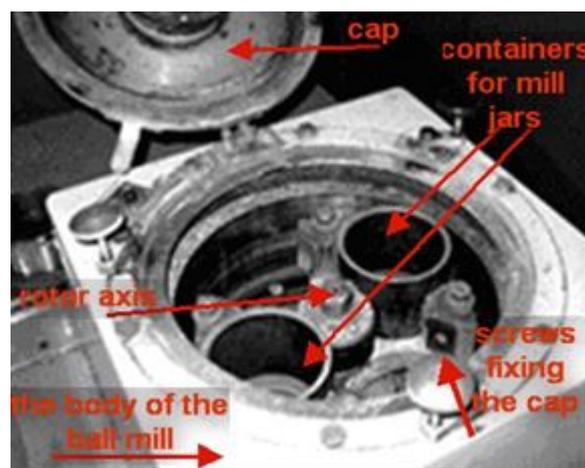
## 2. Experiment

Titanium powders of PTS with dispersion 100 – 300  $\mu\text{m}$  and nickel grades of PNE 1 (45 – 71  $\mu\text{m}$ ) and PNKL 7 (10  $\mu\text{m}$ ) were used in this work. Mechanical activation was carried out in a planetary mill with an energy intensity of 60 g with water-cooled drums (Figure 1). The planetary mill refers to the apparatus of impact-abrasion action. It is one of the most common and effective mechanical activators. Its working drum, rotating around its own axis, moves in a circular orbit around the main axis of the planetary mechanism. The material is crushed by the impact of grinding media, crushing or abrasion.

The walls of steel drums and balls with a diameter of 5 mm were pre-lined with shredded material to avoid rubbing with iron. The powders were loaded in the Ti – Ni ratio of 55.06 mass.%, then the mixture was dried at 1000<sup>0</sup>C in a vacuum for 120 minutes.

Mechanical activation was carried out in the air, the activation time varied from 1.5 to 5 minutes. Such MA time was chosen to study the processes of mechanical activation in time interval in which the formation of mechanochemically synthesized phases of titanium nickelide had not yet begun. The ratio of the mass of the powder to the mass of the balls in all experiments was 5 : 1. The formation of mechanosynthesized phases was monitored using x-ray phase analysis.

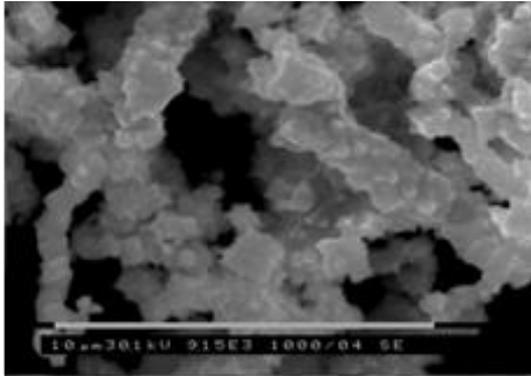
The structure and composition of activated powder mixtures and combustion products were studied by scanning electron microscopy (Philips SEM515) and x-ray phase analysis (Drone-UM).



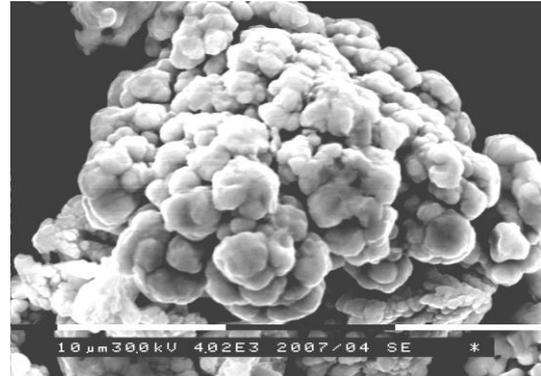
**Figure 1.** Appearance of high-tension planetary mill

## 3. Results

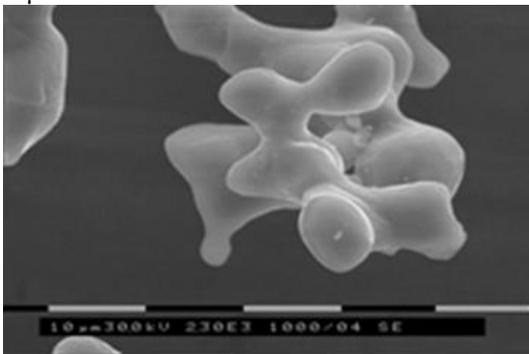
This paper presents a study of the effect of different sizes of the initial nickel powder on the structure formation of the mixture at MA. Figures 2, 3, 4 present the appearance of the initial powders of titanium and nickel type with different dispersion. After the first minutes of mechanical activation of the particles, both titanium and nickel lose their start shape, they are crushed, smeared on each other, forming layered agglomerates. Nickel is a more ductile material than titanium, so it first begins to spread on the particles and begins the process of formation in the process of mechanical activation of layered agglomerates.



**Figure 2.** Microstructure of initial powder of nickel PNKL type. x4580, scale bar represent 10  $\mu\text{m}$

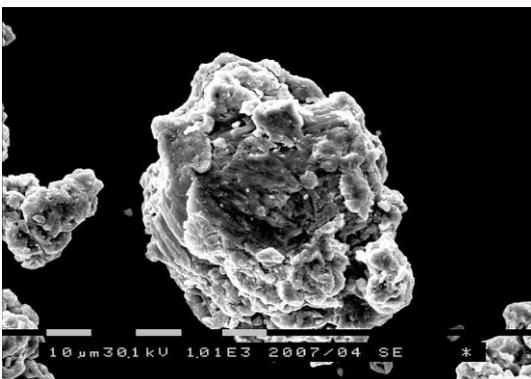


**Figure 3.** Microstructure of initial powder of nickel PNE1 type. x2020

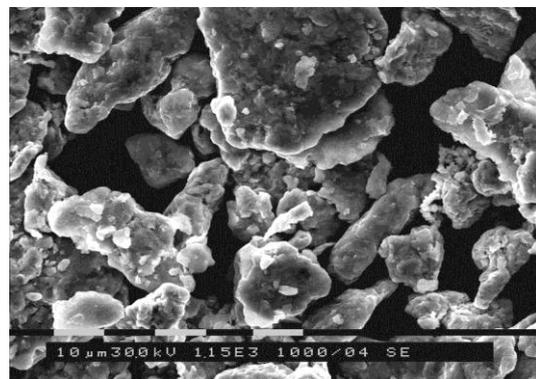


**Figure 4.** Microstructure of initial powder of titanium PTS type. x 23000, scale bar represent 10  $\mu\text{m}$

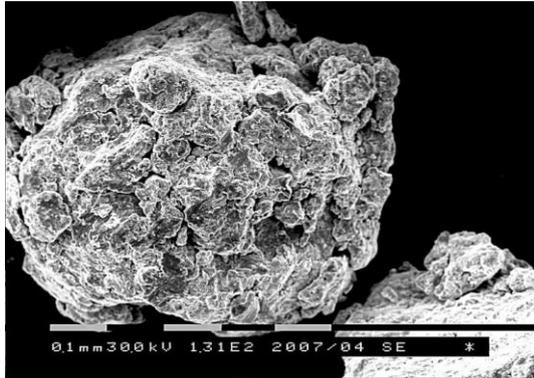
Figures 5, 6 show the structure after 2 minutes and Figures 7, 8 after 3 minutes of MA for different grades of original nickel. It is seen that after 2 min. MA and the use of nickel of different dispersion has a visible effect on the structure of the powder mixture, since the morphology of the powder mixture is markedly different from each other. Fine nickel particles are crushed faster and begin to form layered agglomerates faster. At mechanical activation with larger nickel after the same time (2 min) of mechanical activation of clearly formed agglomerates is not observed. But after 3 minutes MA the structure of the powder mixture is not much different from each other. Well-formed layered agglomerates are visible both when using fine and when using larger nickel.



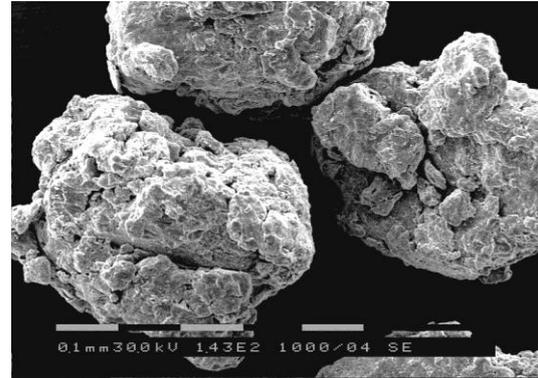
**Figure 5.** Microstructure of powder mixture after 2 minutes of mechanical activation with Ni – PNKL7.



**Figure 6.** Microstructure of powder mixture after 2 minutes of mechanical activation with Ni – PNE1.

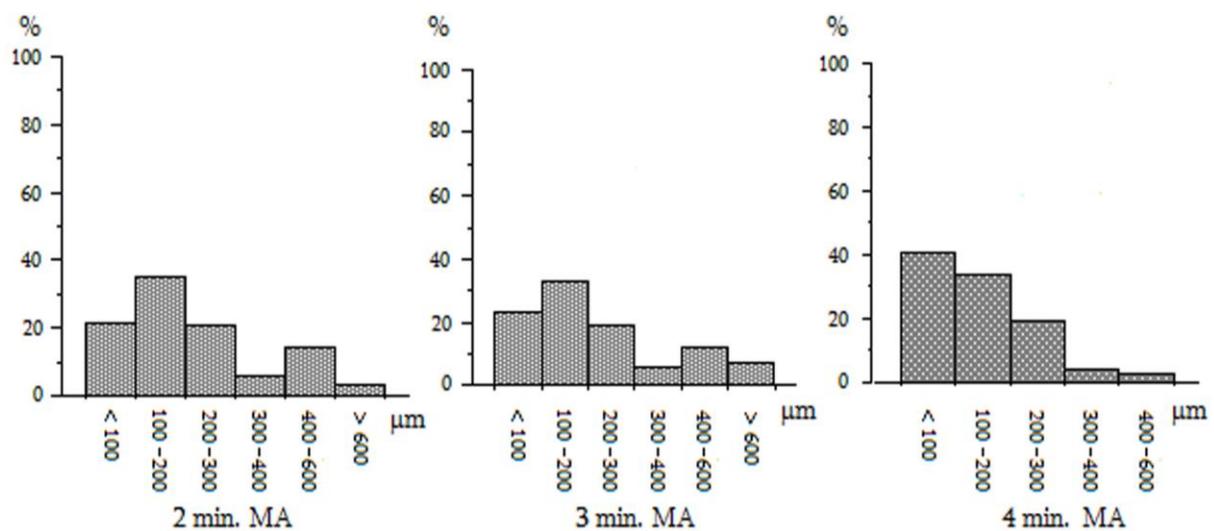


**Figure 7.** Microstructure of powder mixture after 3 minutes of mechanical activation with Ni – PNKL7.

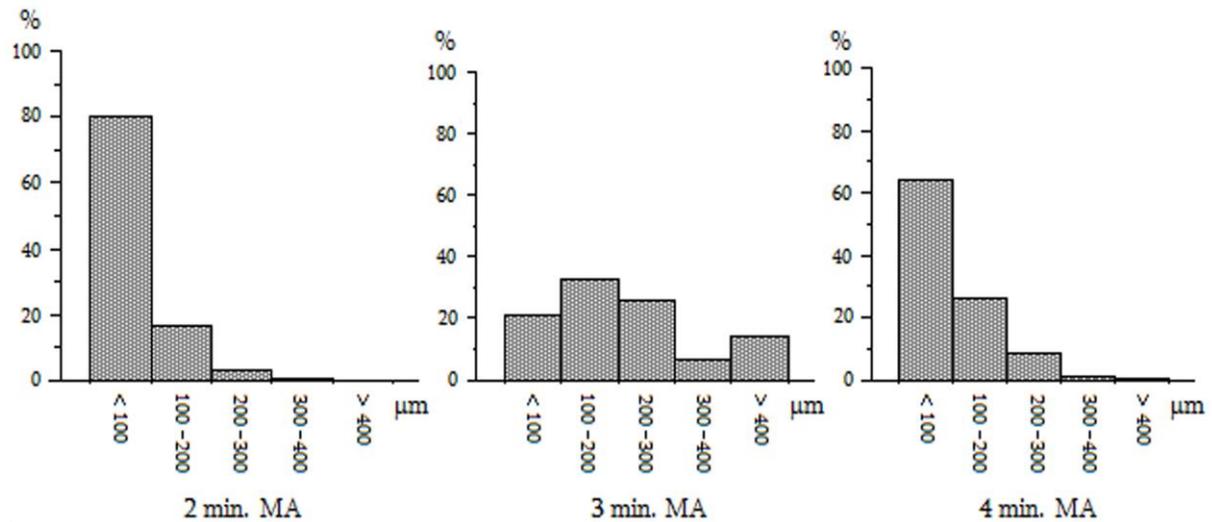


**Figure 8.** Microstructure of powder mixture after 3 minutes of mechanical activation with Ni – PNE1.

Figures 9 and 10 histograms of particle size distribution during mechanical activation of the mixture with fine and large nickel are presented. From the analysis of histograms, it follows that after 2 min. of MA the powder mixture with fine nickel contains almost 50% less than the smallest particles up to 100 microns. This suggests that at the earliest times of mechanical activation, up to 2 minutes of fine nickel slightly crushed and reaching the size of less than 10 microns, begins to act like a surfactant and contribute to the rapid formation of agglomerates.



**Figure 9.** Histograms of distribution of the particles of the powder mixture, with small (10  $\mu\text{m}$ ) nickel

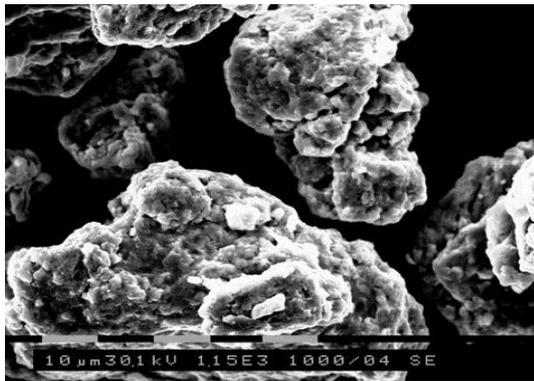


**Figure 10.** Histograms of distribution of the particles of the powder mixture, with large (45-71  $\mu\text{m}$ ) nickel

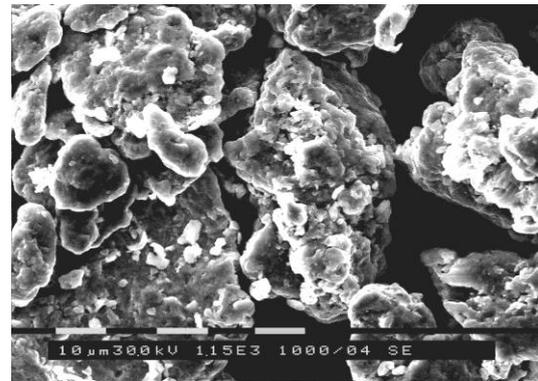
Also, the small particles of nickel can self-lined, that is stick to the walls of the drums and the grinding steel balls. While larger nickel need time to be crushed to a similar size. This time is close to 3 min. of the mechanical activation. It is seen that after 3 minutes that the histograms for small and large nickel have a qualitatively and quantitatively similar appearance.

The agglomerates formed after 3 min MA, although they have similar dimensions for different types of nickel, their density varies. In Figures 7 and 8 can be seen that the agglomerates formed with the participation of larger nickel look less dense, the layers are not in close contact with each other, unlike the mechanoactivated mixture with fine nickel. And as the MA time increases to 4 minutes, the less dense agglomerates begin to break down again, which reflects the histogram after 4 minutes in Figure 10. There is again an increase in the amount of fine fraction with size up to 100 microns. Thus, when using the initial nickel with different dispersion, it is possible to obtain a different structure of the mechanoactivated mixture with different size factor. That will have an impact on the subsequent processes of synthesis. Figure 11 shows the microstructure of the powder mixture with fine nickel after 4 minutes of the mechanical activation. Quite large layered agglomerates are visible here. But if you compare with the previous microphoto of this powder mixture (Figure 4) it can be seen that after less time of the mechanical activation, namely after 3 minutes, the layered agglomerates look denser.

Figure 12 shows the microstructure of the powder mixture containing the initial large nickel powder. And here you cannot see such large layered agglomerates as in the previous picture. Thus, it turns out that the powder mixture containing the initial large nickel powder, after 4 minutes of the mechanical activation forms smaller layered agglomerates. Conversely, the powder mixture containing the initial fine nickel powder after 4 minutes of the mechanical activation forms the structure that contains larger layered agglomerates. When mapping visible data of photographs and the results of the histogram, you can see that they fit together well.



**Figure 11.** Microstructure of powder mixture after 4 minutes of mechanical activation with Ni – PNKL7.



**Figure 12.** Microstructure of powder mixture after 4 minutes of mechanical activation with Ni – PNE1.

Histograms (Figures 9 and 10) it is shown that after 4 minutes of the mechanical activation, the powder mixture containing small initial nickel has the smaller amount of the smallest fraction up to 100  $\mu\text{m}$  (Figure 9) than the powder blend containing large initial nickel (Figure 10). This powder mixture, after 4 min of the mechanical activation contains more than 20 % more fine fraction. This amount of fine fraction was formed due to chipping from large agglomerates, which do not look very strong in Figure 8.

Thus, this study involving two types of nickel, large and small, showed not only the effect of the size of one initial component on the entire structure of the powder mixture after the different time of the mechanical activation. It helped to trace the evolution of the structure formation that occurs during the mechanical activation inside the activator. This study revealed the periodicity of changes in the size and structure of layered agglomerates and the sequence of transformations that occur with them.

And by varying the dimension of the initial nickel powder, it is possible to change the structure and density of layered agglomerates, thereby forming the structure of the powder mechanoactivated mixture in the desired direction for subsequent synthesis. The obtained data on the structure must be taken into account in the further synthesis and production of the material.

#### 4. Conclusion

The study showed that the process of the mechanical activation leads to the formation of the layered agglomerates and an increase in activity, which is associated with an increase in the contact surface of dissimilar particles, the number of defects, regardless of the size of the nickel powder.

Smaller nickel powder with initial dimensions up to 10  $\mu\text{m}$  in the initial times of the mechanical activation (up to 2 minutes) contributes to a faster formation of the layered agglomerates with a denser structure.

Larger nickel at its initial size from 45  $\mu\text{m}$  up to 71  $\mu\text{m}$  forms the layered agglomerates, which upon further activation is able to again crushed.

The use of the initial nickel of different dispersion contributes to the formation of different structure of the mechanoactivated mixture

#### Notification

- MA - mechanical activation,
- SHS - self – propagating high-temperature synthesis,
- PTS - the titanium powder average
- PNE - the electrolytic titanium powder
- PNKL - the titanium powder carbonyl

SEM - Scanning Electron Microscope  
Dron-UM - x-ray powder diffractometer

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