

Combustion of Mechanically Activated 3Ti + 2BN Mixtures

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Laws of self-propagating high-temperature synthesis in 3Ti + 2BN reactive mixtures after preliminary mechanical activation in a planetary ball mill are studied. A discontinuity caused by specific features of the dynamics of formation of mechanocomposites is observed on the plots of the burning rate and temperature versus time. Regimes of preliminary activation are determined, which ensure the solid-phase combustion regime. Results of x-ray diffraction phase analysis and electron microscopy of combustion products and initial mixtures for different times of mechanical activation are presented.

Key words: self-propagating high-temperature synthesis, mechanical activation, solid-phase combustion regime, titanium diboride, titanium nitride.

INTRODUCTION

It is well known that titanium nitride displays high resistance to oxidation and various acids, high thermal conductivity, and high hardness. Titanium diboride is also characterized by high hardness and strength at elevated temperatures and by anomalously high electric conductivity for ceramic materials. Ceramics based on the mixture of these two compounds has been used for a long time in various branches of industry. Methods for obtaining articles with high service properties have been developed. In particular, high stability of ceramics containing 40–50% (mole) of TiN to oxidation has been observed [1].

Nevertheless, TiN and TiB₂ have been obtained separately until recently. Methods of obtaining mixtures of these two compounds in a common process have been developed recently. Mixtures consisting of Ti, B, and BN are usually used for this purpose. For instance, Munir [2] reported data on obtaining TiB₂–TiN dense ceramics (up to 97.2%) with a nanometer grain size. Spark plasma sintering (SPS) of mechanically activated 2Ti + B + BN mixtures were used. Gotman et al. [3] and Shapiro et al. [4] used a specially developed facility for this purpose, which allowed a thermal explosion at

high pressures and reactive hot pressing (RHP).

Shim et al. [5, 6] reported obtaining TiN/TiB₂ composite powders as a result of mechanochemical synthesis in mixtures of titanium and boron nitride during 2–16 h. Such long activation times, however, inevitably lead to considerable contamination of the final product by the mill drum and balls owing to rubbing [7].

On the other hand, extremely high heats of formation of titanium nitride and diboride testify to the principal possibility of self-propagating high-temperature synthesis (SHS) in mixtures of titanium and boron nitride. For instance, Tomoshige et al. [8] reported results of obtaining ceramics with different ratios of TiB₂ and TiN by the SHS method. In that work, however, mixtures of titanium, boron, and boron nitride were again used in the SHS process. Of greater interest, however, are mixtures of titanium with boron nitride. This interest is inspired by both the necessity of expanding the range of raw materials for SHS processes and the search for effective methods of formation of a given microstructure of combustion products. It is known that replacement of elementary reagents by compounds normally leads to formation of a structure with finer grains [9]. The cost efficiency is another important factor. The cost of boron exceeds the cost of BN with a comparable purity by a factor of tens.

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Grigoryan and Rogachev [9] were the first to obtain SHS in a stoichiometric 3Ti + 2BN mixture. It was noted that this system is hard to ignite; therefore, it was necessary to use special high-temperature igniting compositions for stable initiation of SHS [9]. This fact agrees with the results of [3], where it was found that heating of samples with this composition even to a temperature of 1370 K does not initiate a self-propagating reaction.

It should be noted that the fact of a significant decrease in temperature of SHS initiation in mechanically activated reactive mixtures is well known at the moment. In some compositions, preliminary activation in energy-intensive planetary ball mills reduces the temperature of reaction initiation by hundreds of degrees [10–15]. Moreover, preliminary mechanical activation also leads to a decrease in the combustion temperature, which, in turn, promotes obtaining SHS products with a nanometer grain size and even a possibility of reaching a truly solid-phase combustion regime [10, 11, 14, 15].

Therefore, the objective of the present work is the study of the influence of preliminary mechanical activation of the 3Ti + 2BN mixture on the burning rate and temperature and on the phase composition of combustion products.

EXPERIMENTAL TECHNIQUE

The initial mixtures were prepared from titanium powders (98.5%) of the PTOM type and hexagonal boron nitride of the B type (98.4%). The titanium particle size was 1–30 μm ; coarser particles had a branching coral-shaped structure. BN particles were shaped as flakes with transverse sizes of 5–100 μm .

Mechanical activation of reactive 3Ti + 2BN mixtures was performed in an AGO-2 water-cooled planetary ball mill [16]. The volume of each of the two steel drums of the mill was 160 cm^3 . The ball diameter was 8 mm, the mass of the balls in each drum was 200 g, and the sample mass was 10 g. The centrifugal acceleration of the balls was 600 $\text{m} \cdot \text{sec}^{-2}$ (60g). To prevent oxidation during mechanical activation, the drums with the samples were evacuated and then filled with argon up to a pressure of 0.3 MPa. After mechanical activation, the samples were taken out from the drums in a box with an argon medium.

Samples without activation were prepared by simple stirring of the initial reagents in a porcelain mortar.

Reactive mixtures with moderate compaction (up to a relative density of 0.3–0.35) were loaded into a horizontally aligned ceramic container 15 × 15 × 60 mm. The container walls and the sample were separated with a

thin layer of electrotechnical asbestos.

The samples were burned in a flow-type SHS reactor with a volume of 6 liters. Prior to initiation, the reactor with the sample was purged with argon. During the SHS process and until complete cooling of the combustion products, argon with a flow rate of 9.5 liters/min was permanently supplied to the reactor. Combustion was initiated with a primer composition (Ti + 2B) + 35% (by weight) Ni with a mass of 0.5 g, which was ignited by a nichrome spiral heated by electric current. The burning rate (U_b) and burning temperature (T_b) were measured by tungsten–rhenium thermocouples [(W + 5%Re)/(W + 20%Re)] 100 μm in diameter fixed at a certain distance from each other. The signals from the thermocouples were recorded by an N-117/1 loop oscillograph.

The reactive mixtures after mechanical activation and SHS products were studied by methods of x-ray diffraction phase analysis (XDA), infrared (IR) spectroscopy, and scanning (SEM) and transmission (TEM) electron microscopy. The x-ray patterns were taken on a DRON-3.0 diffractometer with the use of $\text{CuK}\alpha$ -radiation. The electron microscopic study was performed with the use of JSM-T20 and JEM-2000 FX-II microscopes produced by JEOL. IR spectra were recorded by a Specord-75 IR spectrometer. Samples shaped as pellets pressed with addition of calcinated KBr were used.

RESULTS AND DISCUSSION

The adiabatic burning temperature of a stoichiometric 3Ti + 2BN mixture, which was calculated with the use of the data [17, 18], is equal to the melting temperature of titanium nitride (3223 K). Despite the high heat content of the composition, it is extremely difficult to initiate combustion in the initial samples that were not subjected to activation, even if a high-temperature primer is used, which completely agrees with the results [9]. For activated samples, the primer ensures stable initiation. Beginning from 5 min of mechanical activation, SHS can be initiated by the nichrome spiral only.

Figure 1 shows the burning rate and temperature as functions of the time of mechanical activation (t_a) of the 3Ti + 2BN mixture. It is extremely unusual to see a discontinuity on the U_b and T_b plots at activation times of 1–4 min. Combustion in these samples cannot be initiated with the primer used. None of the previously studied systems displayed such a character of variations of the SHS rate and temperature. The authors are not aware of such data in publications dealing with the ef-

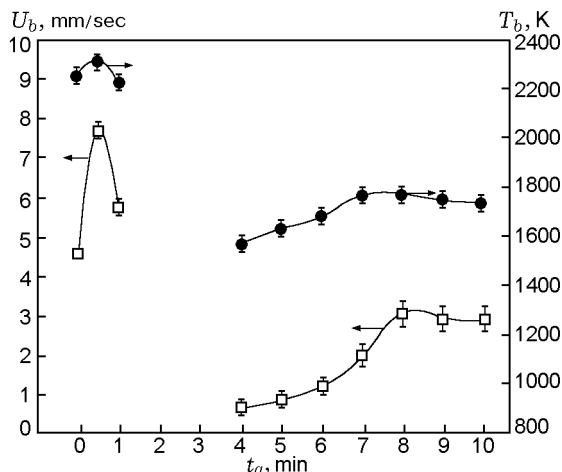


Fig. 1. Burning rate and temperature versus the time of mechanical activation of the 3Ti + 2BN mixture.

fects of preliminary activation on combustion processes. Obviously, this feature is caused by changes in the structure of the reagents and, possibly, the phase composition of the samples during their activation. Therefore, we studied the mechanically activated samples with the use of x-ray diffraction analysis, transmission and scanning electron microscopy, and IR spectroscopy.

Figure 2 shows the x-ray patterns of the samples of the examined composition without activation and after 1 and 10 min of mechanical activation. As it follows from the data presented, the intensity of the lines of hexagonal boron nitride rapidly decreases with the activation time. At $t_a = 1.5$ –2 min, even the main line of BN (0.333 nm) almost completely disappears from the x-ray patterns, which shows that the major part of this reagent passed to an x-ray amorphous state.

A significant decrease in intensity and broadening of lines observed in the x-ray patterns in Fig. 2 are caused by the decrease in the particle size of the initial reagents and by generation of a large number of nonequilibrium defects and internal stresses in them owing to intense plastic deformation under conditions of activation in a planetary ball mill [10–15].

The TEM inspection did not reveal any anomalous changes in the sample structure at mechanical activation times corresponding to the discontinuity in the plots in Fig. 1. As the activation time was increased, a gradual and uniform decrease in the particle size of both reagents was observed. As an example, Fig. 3 shows a TEM photograph illustrating the internal structure of the sample activated during 2 min. It is seen that mechanical activation during 2 min decreases the BN and Ti particle sizes to 20–50 and 200–1000 nm, respectively. As the activation time is increased to 10 min, the tita-

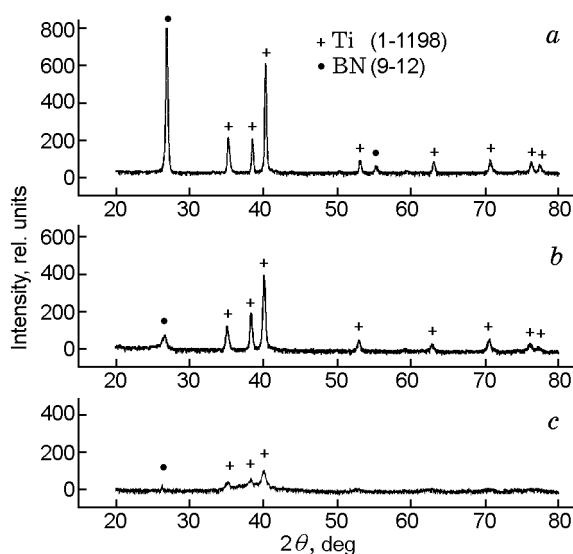


Fig. 2. X-ray patterns of 3Ti + 2BN samples without activation (a) and after activation during 1 (b) and 10 min (c).

nium particle size decreases to 10–50 nm (Fig. 4), and the size of amorphous boron nitride particles is smaller than 5 nm.

The electron diffraction patterns display broadened, but clear lines of BN after 3–4 min of mechanical activation. Real amorphization of BN begins at $t_a = 4$ –5 min, but some areas of crystalline boron nitride are also encountered in the samples even after activation during 10 min.

Thus, the results obtained show that there are no catastrophic changes in the BN structure at $t_a > 1$ min, when the beginning of the discontinuity is observed on the plots. This fact is also confirmed by the results of IR spectroscopy. As it follows from the IR spectra shown in Fig. 5, the molecular structure of BN is retained even after activation during 5 min. In the activated sample, all absorption lines are retained, but become strongly broadened. Their intensity decreases. The band of deformation oscillations ($\lambda = 820 \text{ cm}^{-1}$) becomes less steep toward smaller wavenumbers. This testify to changes in the angles of bonds in BN molecules. Broadening of the band of valence oscillations is caused by an increase in the defect concentration [19]. After mechanical activation during 10 min (spectrum c in Fig. 5), the width of the absorption bands increases further, and their intensity decreases very appreciably. These phenomena are caused by almost complete amorphization of BN at these activation times, which agrees well with the data of electron diffraction studies. A small shift of the minimum of the band of valence oscillations, as compared with the standard value of 1380 cm^{-1} for the

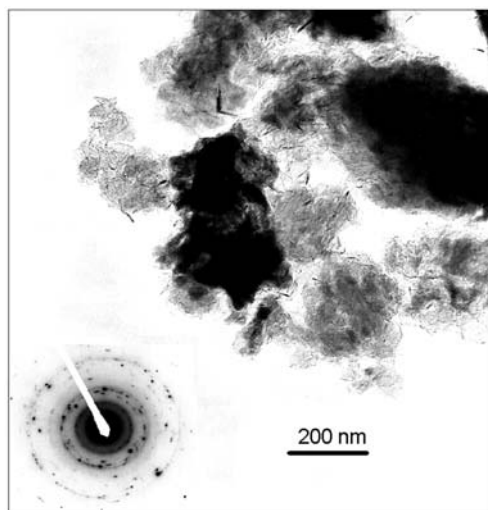


Fig. 3. Microstructure of the sample after activation during 2 min.

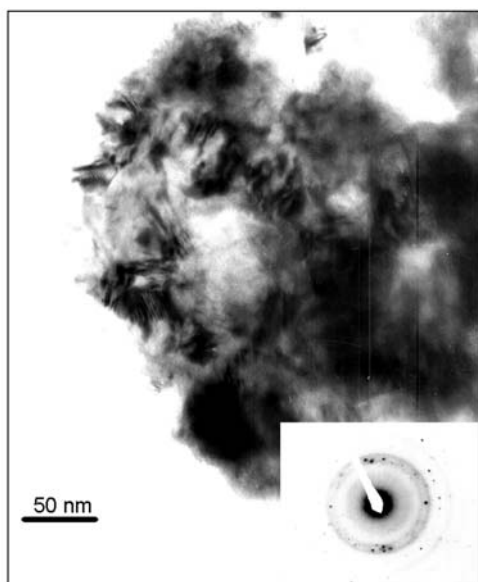


Fig. 4. Microstructure of the sample after activation during 10 min.

hexagonal modification of boron nitride, indicates that the length of the B—N bond becomes shorter. It follows from here that the molecular structure of BN persists even after activation during 10 min, but all bonds become strongly deformed.

Thus, the data obtained show that boron nitride only transforms to an x-ray amorphous state at activation times corresponding to the discontinuity in Fig. 1; this transition is caused by a significant decrease in

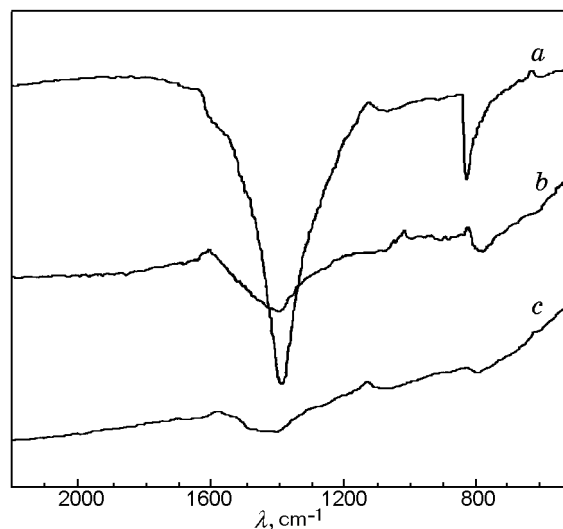


Fig. 5. IR spectra of 3Ti + 2BN samples without activation (a) and after activation during 5 (b) and 10 min (c).

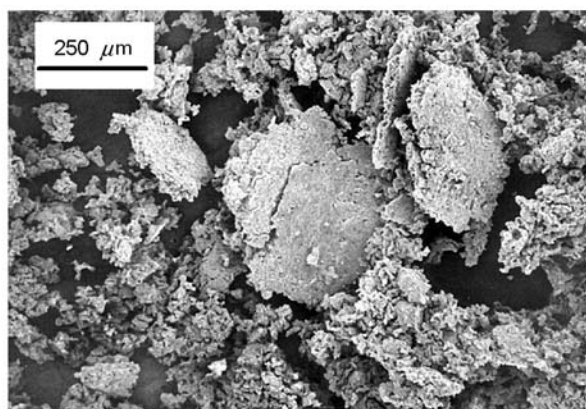


Fig. 6. Microphotograph of mechanocomposites formed after mechanical activation of the initial mixture of reagents during 30 sec.

the particle size of this reagent, whereas the molecular structure of BN remains unchanged.

More significant changes were found in studying the morphology of the products of mechanical activation. SEM investigations show that agglomeration starts at the very first stages of activation of the powder mixtures of the initial reagents. At the beginning, these particles are not dense and have irregular shapes. After activation during 30 sec, the sample contains flake-shaped denser particles in addition to irregularly shaped and friable agglomerates (Fig. 6). An increase in the activation time to 1 min leads to an increase in the size, density, and number of such particles. The maximum transverse size of these composites is 250–500 μm.

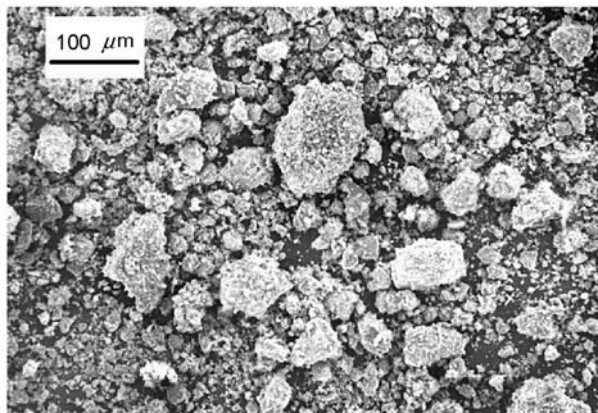


Fig. 7. Microphotograph of mechanocomposites formed in the initial mixture of reagents activated during 8 min.

At activation times longer than 1 min, a drastic change in the morphology of the activation products is observed. Large flake-shaped composites become almost completely destroyed. After activation during 1.5–2 min, the products consist of shapeless and friable particles 0.5–5 μm in size.

An increase in the activation time to 3–4 min again leads to formation of denser particles; these particles have a roundish shape and a size of 1–5 μm . In addition, coarse particles up to 50 μm begin to appear. They are still rather friable low-density agglomerates of smaller spherical particles. A further increase in the activation time is accompanied by gradual compaction of these agglomerates and by an increase in their number and size. Figure 7 shows a microphotograph of the sample after activation during 8 min. In addition to coarse particles having an irregular oval shape and a size of 20–150 μm , the sample contains a large number of smaller particles. Flake-shaped composites are rarely encountered in these samples. After activation during 10 min, the density and number of large mechanocomposites increase further. Nevertheless, approximately one half of the sample volume at these activation times is filled by small, but already extremely dense particles having an almost spherical shape and a size of 1–5 μm .

The combustion products of non-activated samples form a well-melted high-porosity low-strength cakes.

The height of the samples after mechanical activation during 30 sec increases during their combustion approximately by a factor of 1.5–2. The SHS products form a cake that has even higher porosity and lower strength (it disintegrates into a powder). The electron microscope study shows that the main part of these products consists of flake-shaped particles whose shape and size coincide with those of initial mechanocomposites. As is shown in Fig. 8, the surfaces of these particles

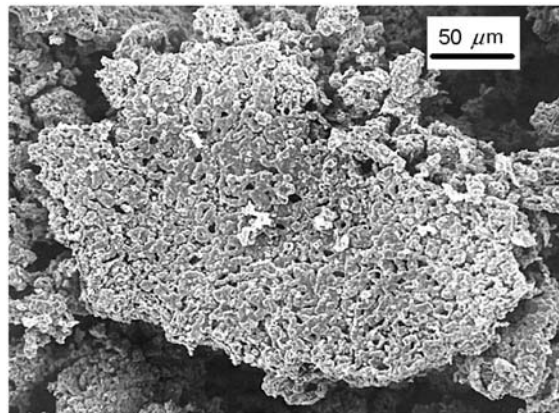


Fig. 8. Microphotograph of combustion products formed after preliminary activation of the initial mixture of reagents during 30 sec.

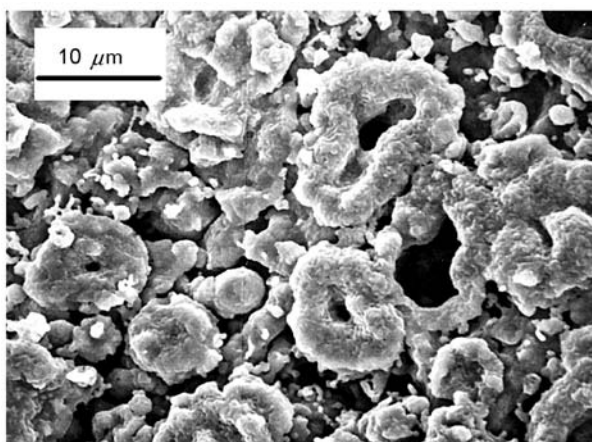


Fig. 9. Microphotograph of the channels through which the gas phase escaped to the surface of combustion products.

clearly display the traces of melting of interaction products. Channels with well-melted edges through which the gas phase escaped are often observed (Fig. 9). These particles, however, do not form a single cake.

The height of the sample activated during 1 min increases even more during combustion. The SHS product is a friable powder with no signs of sintering. In terms of morphology, it resembles the previous sample. Probably, the only difference is the fact that the liquid phase on the composite surface is observed only around the channels of gas-phase exhaustion.

Samples activated during 4 min exhibit very slow and unstable burning. Sometimes, the combustion front stops before it reaches the end of the sample. An increase in the activation time to 5 min stabilizes SHS wave propagation. The process of combustion of these

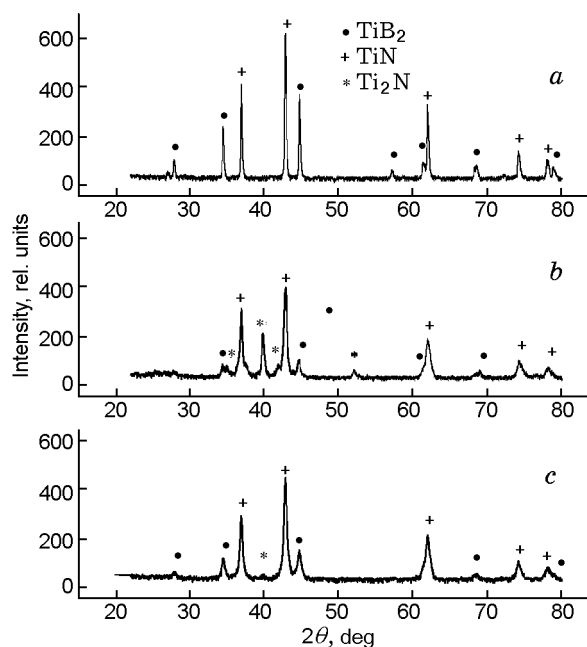


Fig. 10. X-ray patterns of combustion products of the 3Ti + 2BN mixture without activation (a) and after activation during 4 (b) and 10 min (c).

compositions is accompanied by rather intense ejection of hot particles from the SHS wave.

During combustion of mixtures activated for more than 6 min, the particle size of the products being formed is reduced in the flow of the gas phase released and are partly entrained from the reaction zone in the form of fine-particle dust. After 10 min of mechanical activation, almost the entire SHS product is entrained away from the container. Combustion of such mixtures remains stable, but the values of U_b in parallel experiments cannot be well reproduced. A significant scatter between the extreme values is observed.

The products of combustion of the mixture mechanically activated during 4–10 min do not display any signs of melting. These products can be hardly distinguished from the initial samples. The only difference is the fact that some large composites become less dense.

Figure 10 shows the x-ray patterns of combustion products of the samples without activation and with activation during 4 and 10 min. We can conclude from the intensity of lines in these x-ray patterns that the main phases in the SHS products are TiN and TiB₂, independent of the activation time. Mechanical activation during 4 min decreases the intensity of the TiB₂ lines and leads to the emergence of the Ti₂N line (Fig. 10b).

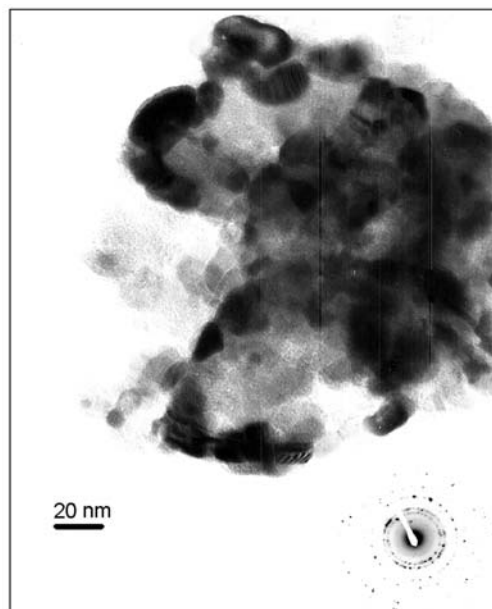


Fig. 11. Microstructure of combustion products formed after preliminary activation of the initial mixture of reagents during 10 min.

As the time of preliminary mechanical activation is increased, a gradual decrease in intensity of the lines of this semi-nitride is observed. An extremely weak line of the most intense reflection of Ti₂N is, nevertheless, present in the x-ray patterns of combustion products of the samples activated during 10 min (Fig. 10c).

The lines of all products in the x-ray patterns of the activated samples are much broader than the lines of TiN and TiB₂ in Fig. 10a. This broadening can be caused only by the small particle size of the SHS products, because all internal stresses and defects are expected to be annealed at temperatures reached in the combustion wave of these compositions. The results of a TEM study of combustion products confirm this conclusion. As an example, Fig. 11 shows a TEM photograph of the SHS products formed from the initial mixture of reagents activated during 10 min. It is seen that the combustion products consist of individual grains 10–30 nm in size, which are surrounded by particles of a finer fraction, with a size of several nanometers. It was found by the dark-field image method that the coarser crystals consist of TiB₂, and the finer fraction consists of titanium nitride.

Thus, we can conclude that a truly solid-phase combustion regime is formed in reactive mixtures activated during 4–10 min [20], and the resultant products have a nanometer grain size.

The results obtained show that two separate regions on the dependences of the burning rate and tem-

perature on the time of preliminary mechanical activation of the examined composition in Fig. 1 correspond to different combustion mechanisms. Combustion with participation of the liquid phase occurs in the first region, while the second region is associated with the solid-phase SHS regime. These two regions are separated by an area in which combustion cannot be initiated despite a significant decrease in the grain size of the reagents at these activation times. It is difficult to understand the reason for this phenomenon from the viewpoint of available concepts on the mechanism of interaction of powder reagents in the SHS wave. It is well known that a decrease in the grain size of the reagents in conventional powdered SHS compositions leads to an increase in the burning rate [20].

The results obtained show that the unusual discontinuity in Fig. 1 is caused only by the specific features of morphology of the activated samples, namely, by the fact that dense mechanocomposites formed at small activation times become suddenly destroyed if the activation time exceeds 1 min. The destruction is caused by very substantial fragmentation of BN particles, which is evidenced by the transition of the major part of this reagent to the x-ray amorphous state. Apparently, this transition leads to significant changes in mechanical properties of the activated medium. This, in turn, is the reason for destruction of large mechanocomposites formed at smaller times of mechanical activation. Thus, we can conclude that combustion cannot be initiated only because there is no sufficient amount of dense composites in the sample, despite the decrease in the particle size continued in the activation interval of 1–4 min.

It should be noted here that the governing role of the formation of composites on SHS processes in activated mixtures was first noted in [14] for samples of the Fe–Si system. Though the heat of formation of FeSi₂ is even slightly higher than that of FeSi (19.4 and 17.6 kcal/mole, respectively [21]), combustion can be initiated in an activated Fe + Si composition and cannot be initiated in a Fe + 2Si composition. The only difference between these samples is the fact that mechanocomposites are not formed with a large content of low-plasticity silicon.

All these results lead us to conclude that it is also possible to ensure SHS in activated mixtures of the examined system only if the samples contain a sufficient amount of dense mechanocomposites. The grain size of the reagents is of secondary importance.

It is well known that a significant decrease in the grain size is not the only process in mechanocomposites being formed. The contact area increases multiply, and a high concentration of nonequilibrium defects is

formed [10–15]. All these factors increase the reactivity of the mixture.

The mechanism of interaction of reagents in the combustion wave is not yet absolutely clear. The maximum burning temperatures reached in the samples activated during 4–10 min and the results of the electron microscope studies testify that the initial reagents and reaction products in the SHS wave are in the solid state. On the other hand, the ejection of the products observed during combustion indicates partial gas release. This gas phase in the system considered can be only nitrogen. First of all, this is evidenced by partial formation of the product of incomplete nitriding of titanium (Ti₂N) after SHS in activated compositions. Control experiments with burning the same samples in a nitrogen environment showed that Ti₂N is not formed in this case. The products consist of TiN and TiB₂ only. These data confirm that the gas phase released during combustion of activated samples consists of nitrogen.

Thus, the results obtained show that solid-phase interaction between nano-sized particles of the initial reagents with partial release of nitrogen occurs in the combustion wave of the activated samples of the system considered. All these facts allow us to conclude that the examined system is a new type of the solid-phase SHS reaction with partial gasification of one of the reagents.

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