Combination of SHS and Mechanochemical Synthesis for Nanopowder Technologies†

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Abstract

The combination of mechanochemical activation and self-propagating high-temperature synthesis (SHS) have widened the possibilities for both methods. For metallic systems, the investigation showed that a short-term mechanochemical activation of heterophase SHS products leads to single-phase and ultrafine intermetallides obtained from the elements by mechanical alloying. It was demonstrated that metastable phases, usually obtained by mechanical alloying, can be obtained from the equilibrium intermetallic compounds synthesized by SHS. Besides this, the investigations showed that preliminary mechanical activation, during which layered composites are formed from the initial elements, allows one to extend the concentration limits of SHS processes up to a solid solution region.

The preliminary mechanical activation also allows production of single-phase ultrafine complex oxides.

Introduction

Mechanochemical synthesis and mechanical alloying are in wide use as experimental methods for the production of highly dispersed powders and nanocomposites. Using mechanical activation we have managed to prepare nanocomposites in immiscible systems such as Cu-Bi, Fe-Bi, Fe-In. It is possible to get supersaturated solid solutions in many other intermetallic systems (Cu-Ga, Cu-In, Cu-Sn, Ni-In, Ni-Bi, Ni-Sn, Ni-Ge, Ni-Al) [1, 2]. However, from a technological point of view, mechanical activation poses a lot of problems which cannot be easily solved. The biggest problem is the low productivity of the techniques currently available, as well as the contamination of the end products caused by abrasion of the grinding media. The energy consumption should also be taken into consideration in some large-scale processes.

One of the alternatives to mechanochemistry may be self-propagating high-temperature synthesis (SHS), which is energy-saving and can be applied to the large-scale production of many intermetallic compounds or complex oxides (nitrides, carbides) [3]. Nevertheless, this method includes a combustion stage which requires very high temperatures. As a result, final products can be obtained only in the form of dense sintered or solidified products when SHS exceeds the melting point of reagents and/or products. To transform such products into commercially interesting powders, one needs to use milling as an unavoidable step. The grinding leads to further contamination and to additional energy consumption, which may be comparable with that required for the mechanochemical synthesis itself.

Another disadvantage of SHS is a relatively high temperature gradient near the combustion surface which leads to a non-uniform phase composition of the obtained products.

The shortcomings of these two methods can be overcome, and their advantages can be extended. This allows one to obtain the final products of required phase composition and disperse state, thus enabling the development of a new energy-saving and waste-free technology.

Experimental

The materials used in the investigation were: carbonyl nickel and iron, powdered aluminum, silicon, germanium, tungsten, molybdenum, titanium, and zirconium, pure gallium, barium peroxide, tungsten and molybdenum oxides.

A ball planetary mill AGO-2 [4] was used for the investigations. The volume of the mill drums was
250 cm³; the ball diameter was 5 mm, the ball load was 200 g and the weighed portion of powder treated was 10 g. In order to avoid oxidation of the metals, all the experiments on mechanical alloying were carried out in an argon atmosphere. The X-ray phase analysis was performed with a DRON-3M diffractometer with CuKα radiation.

IR absorption spectra were recorded with a SPECORD 75 IR spectrometer.

Electron microscopic studies were carried out using the JSM-T20 electron microscope and the high-resolution electron microscopes JEM-2010 and JEM-400.

The extent of aluminum recovery from intermetallic compounds was calculated as the ratio of the amount of hydrogen evolved in the reaction of samples with a 20% KOH solution to the amount of hydrogen that should be evolved in case of complete dissolution of the aluminum present in the sample. The amount of the evolved hydrogen was recorded automatically with a DAGV-70-2M volumeter.

1. Mechanochemical activation of SHS products in metal systems

1.1 Homogenizing effect of MA

Ultrafine single-phase intermetallic compounds are widely used in powder metallurgy for making heat-resistant materials, materials with a high corrosion stability and special magnetic properties. Single-phase intermetallic compounds are usually obtained by fusing or sintering followed by homogenizing and annealing for a long time [5]. The major disadvantages of these processes are deviations in the composition of the mixture in the case of high melting points of the initial components because of evaporation of the lower melting point ingredients. As a result, a long time interval is necessary for the process, and high energy consumption at the stage of homogenizing and annealing. Besides this, most of the powder intermetallides are obtained by grinding for a rather long time, which usually leads to substantial contamination caused by abrasion of the grinding media. In such cases, additional purification is required.

For metal systems with high enthalpies of the intermetallide formation, the SHS method can be applied; heterophase SHS products can be homogenized during mechanochemical activation at a simultaneous substantial decrease of the particle size, which should finally lead to finely dispersed material with a high structural defect content. This material is similar in its properties to that obtained by mechanical alloying of the elements; however, the time for mechanical treatment in the former case is several decades shorter.

Phase formation and morphological changes were investigated for the mechanochemical synthesis of intermetallides from elements and for the mechanochemical activation of heterophase products of the SHS process. For comparison purposes, systems were considered for which it is known that the SHS process can be performed, but the products of this synthesis are substantially different in phase composition:

- Ni-Al within the concentration region of NiAl phase existence. It is known that this phase can be obtained by SHS [3];
- Ni-Si, in which the SHS process is possible [6], but it is difficult to achieve single-phase composition during SHS synthesis;
- Ni-Ge in the NiGe intermetallide homogeneity region. Due to the rather high melting point of Ni (1455°C) and the rather low temperature of NiGe intermetallide decomposition (850°C), the homogeneity region is very narrow for this compound.

The X-ray investigation of the mechanical alloying of an NiAl intermetallide from a mixture of metal powders of the composition Ni 32 wt.% Al demonstrated that the synthesis started after mechanical activation for about 2.5–3 minutes. First, the Ni2Al3 intermetallide forms. Some amounts of unreacted nickel and aluminum still remain (Fig. 1a). After activation for 5–7 min., the amount of the formed Ni2Al3 phase starts to decrease and the reflections of the NiAl intermetallide increase (Fig. 1b). Then, the Ni2Al3 intermetallide disappears, the nickel and aluminum contents decrease gradually and the intensities of NiAl reflections increase. After mechanochemical
activation for 25–30 min., very broad reflections only of the NiAl phase are present in the X-ray diffraction patterns (Fig. 1c). The coherent scattering domains for this product are 8–10 nm.

The electron microscopic investigation of the products of the mechanical alloying of NiAl-based solid solutions in a ball mill demonstrated that after activation for 30 s, the initial nickel and aluminum particles could not be detected in the sample. The products consist of agglomerates of various shapes and sizes. An increase of the activation time to 1 min. leads to an increase of the fraction of coarse agglomerates which attain a plate-like shape as their density increases. Figure 2a shows a microphotograph of the cross section of the agglomerate, clearly exhibiting its layered structure. A further increase to the time of mechanical alloying causes a drastic change to the morphology of the product particles. The destruction of large layered agglomerates starts after mechanical alloying for 3 min.; whereas they disappear completely after 5 min. of alloying. The major part of the samples by this time is composed of rather dense agglomerates of irregular shape with a size of 2–50 µm. Larger particles (up to 50 µm) are also present. These agglomerates are composed of the layered particles 1–5 µm in size. It should be noted that according to XRD data, it is the mechanical alloying for 3 min. that causes the appearance of the Ni2Al3 intermetallide in the products, which is likely to be the reason of the significant change of the particle morphology. An increase in the time of mechanical alloying brings insignificant changes to the morphology of the formed products. The fine fraction (1–5 µm) content increases, the density of the formed particles increases (Fig. 2b).

The SHS of a metal powder mixture comprising Ni 32 wt.% Al results in the NiAl intermetallide with admixture of the Ni2Al3 phase; judging from the width of diffraction peaks, the formed products are well crystallized. Electron microscopic studies showed that the intermetallides were most likely crystallized

![Fig. 2](image1.jpg)

**Fig. 2** Microphotograph of a cross section cleavage of the layered composite of the system of Ni 32 wt.% Al after mechanical activation for 30 s (a), 25 min. (b).

![Fig. 3](image2.jpg)

**Fig. 3** Microphotograph of the SHS product in the system Ni 32 wt.% Al (a), the same product after mechanical activation for 1.5 min.
Mechanochemical activation of SHS products for 1.5 min. results in a material similar in morphology, particle size and coherent scattering domain to the material obtained by the mechanical alloying of nickel and aluminum powders for 25 min. This means that a short-time mechanochemical activation of a mixture of phases obtained by the SHS process in this system allows preparation of an ultra-fine single-phase intermetallic product (Fig. 3b). Similar products were observed for the Ni-Si system (Fig. 4).

X-ray analysis showed that a significant amount of the Ni$_3$Si$_2$ phase can be found in the products of the mechanical alloying of an Ni$_{55}$Si mixture corresponding to an Ni$_5$Si$_2$ intermetallic compound.

The X-ray diffraction investigation of the mechanical alloying of nickel and germanium at the ratio of Ni 55 wt.% Ge demonstrated that formation of the NiGe intermetallide starts within the first minute (Fig. 5a); a drastic increase in the intensity of the reflections from this phase starts after mechanical activation for 6—7 minutes (Fig. 5b); the maximum is achieved after 25 minutes of mechanical treatment (Fig. 5c). However, an admixture of the second phase (Ni$_2$Ge$_2$) appears during mechanochemical synthesis of the NiGe intermetallide; at first, the content of the second phase increases, then decreases and disappears completely after 12—13 minutes of mechanical alloying. By the end of the process (25—30 minutes) there is only one phase, which is the NiGe intermetallide, with a coherent scattering domain of 5—8 nm.

According to the data of the electron microscopic investigation, mechanical alloying in the mixture of a stoichiometric composition NiGe for 40 s results in the formation of rounded three-dimensional agglomerates with a maximal size of up to 400 μm, originating from particles of 0.2—1 μm in diameter. Besides this, separate particles of 0.2—1 μm in diameter are present; their number is rather large. An increase of the mechanical alloying time for this system to 5—7 minutes leads to the formation of very dense agglomerates; traces of a strong plastic deformation are sometimes observed on their surface. However, in this case the amount of separate fine particles is also rather larger. A further increase of the mechanical alloying time to 30 min. has practically no effect on the morphology and size of the resulting particles; it is only the fraction of coarse agglomerates which increases. The final product of mechanochemical synthesis NiGe is composed of rather dense particles with a size of 0.5—2 μm; they sometimes form larger agglomerates.

An SHS process was carried out in a mixture of this composition. According to XRD data, it is mainly the
equilibrium well-crystallized NiGe which forms, with an admixture of a second intermetallic (Ni$_5$Ge$_2$) (Fig. 6a). One can see from microphotographs that the final products are formed from the melt (Fig. 7a), which means that the SHS proceeds via the liquid phase.

The X-ray diffraction investigations of the mechanochemical treatment of the SHS products demonstrate that a broadening of the diffraction patterns starts after mechanical activation for 30 s. Phase homogenization of the system (NiGe) is achieved after 1.5—2 minutes (Fig. 6b). After mechanical activation for 3 min., the material exhibits a coherent scattering domain of 8—10 nm. Further mechanical activation leads to some narrowing of the peaks. According to the electron microscopic data, after mechanical activation of the SHS products for 30 s, the major part of the sample is composed of fine particles of irregular shapes, their size being 0.2—3 μm (Fig. 7b). Larger particles are still present, though they rarely occur in this case. A sintered agglomerate of fine particles starts to form. An increase of the treatment time causes an intensive formation of such agglomerates. Their density increases gradually. Traces of substantial plastic deformation are observed on the surface of some of these agglomerates. After mechanical activation for 3 min., the sample consists of agglomerates of different density and shape, their size being 1 to 400 μm.

Similar results were obtained for the Ni-Si system (Fig. 4a, 4b).

The investigation of the metallic systems showed that a short-term mechanochemical activation of heterophase SHS products leads to single-phase and ultrafine intermetallics obtained from the elements by mechanical alloying.

1.2 Formation of non-equilibrium phases by activation of SHS products

It is known that it is practically impossible to obtain non-equilibrium intermetallic compounds by SHS; however, highly reactive intermetallic compounds (which is exactly what metastable phases usually are) are used in hydrogen energetics, in preparation of Raney catalysts, metal cements, diffusion-hardening solder, metal dental materials, etc. Mechanochemical synthesis and mechanical activation are among the most efficient methods to obtain metastable phases in metal systems; it is known that a series of equilibrium intermetallic compounds can be transferred into non-equilibrium concentration regions by means of mechanical activation.

A comparative investigation of phase and microstructural transformations during the mechanochemical synthesis of non-equilibrium solid solutions from the elements and during mechanical activation of
equilibrium intermetallic compounds obtained by SHS was carried out. The Ni-Al system was selected for investigation, because it is known that the SHS process in the Ni-Al system can be carried out within a broad concentration range [3]. The limit solubility of aluminum in nickel ranges from 3.85 wt.% at 500°C to 10.3 wt.% at 1385°C. The structural similarity of the Ni$_2$Al intermetallic (cubic lattice of the Cu$_3$Au type) and β-nickel makes it possible to mechanochemically pass from the intermetallic to the non-equilibrium solid solution [7]. The structure of the Ni$_2$Al$_3$ intermetallic (40.8 wt.%Al) is close to that of NiAl. Aluminum atoms form distorted cubes in the rhombohedral lattice of Ni$_2$Al$_3$. Two-thirds of the positions in the centres of cubes are occupied by nickel atoms, the other positions are vacant. Disordering of these vacancies should lead to the formation of a supersaturated solid solution with a non-equilibrium concentration of vacancies.

The X-ray and electron microscopic studies of the mechanical alloying in a mixture of nickel and aluminum powders at a ratio of Ni 40.8 wt.%Al (calculated for the formation of the Ni$_2$Al$_3$ intermetallic) showed that the process is largely similar to the mechanical alloying of the Ni 32 wt.%Al mixture. At first, the Ni$_2$Al$_3$ intermetallic is formed; during further activation it is transformed into the supersaturated solid solution with a non-equilibrium concentration of vacancies based on the intermetallic compound NiAl. After mechanical activation for 30 minutes, the size of its coherent scattering domains is around 8 to 10 nm.

The X-ray diffraction patterns of the product of the SHS process in the Ni 40.8 wt.%Al mixture exhibit the formation of a well-crystallized Ni$_2$Al$_3$ intermetallic (Fig. 8a). Mechanochemical activation of this product for ~2 min., under the same conditions as those under which mechanical alloying was carried out, gives the diffraction patterns corresponding to the material obtained by mechanical alloying after 25–30 minutes (Fig. 8b), which has been mentioned above to be a supersaturated solid solution with a non-equilibrium concentration of vacancies based on the NiAl intermetallic. Further mechanical activation does not bring any substantial changes.

Electron microscopic investigations showed that the formed porous fused SHS product (Fig. 9a) can be transformed mechanochemically within 2 min. into a product which is morphologically very similar to that formed at the final stage of mechanical alloying (Fig. 9b).

Metastable phases obtained by mechanical alloying and by mechanical activation of the SHS products have approximately equal reactivity.

For the example of a well-studied aluminum leach-
ing reaction, it was stated that non-equilibrium solid solutions based on NiAl, which were synthesized by mechanical alloying from metal powders within the concentration range of the Ni2Al3 intermetallide and activated for 1 min., exhibit a very high reactivity (Fig. 10). These samples exhibit similar dynamics to hydrogen evolution in leaching. This is one more confirmation of the fact that the formed metastable phases are identical. This means that the non-equilibrium solid solutions based on the Ni-Al intermetallide, with largely similar structure, particle morphology, coherent scattering domains, and reactivity can be obtained both by the mechanical alloying of the initial powders of the composition Ni 40.8 wt.% Al, and also by short-time mechanical activation of the Ni2Al3 intermetallide obtained by SHS. An important fact!

The X-ray diffraction studies of the mechanical alloying of the Ni 13.5 wt.% Al composition (the concentration region of equilibrium Ni3Al intermetallide) showed that a broadening and a slight decrease of the intensity of diffraction peaks related to metals occur within the first two minutes of activation. Diffraction reflections of the Ni2Al3 intermetallide appear after 2.5 minutes of mechanical treatment. The intensity of aluminum peaks decreases drastically while the intensity of Ni reflections decreases slowly. The Ni lattice parameter remains unchanged. Only after mechanical activation for 5 min. do the diffraction patterns of aluminum disappear completely. The diffraction reflections of nickel broaden substantially (which is especially noticeable in the large-angle region). Its lattice parameter increases (Fig. 11a), which is evidence of the incipient formation of a nickel-based solid solution. After 15 minutes of activation, the lattice parameter of the solid solution reaches its maximum \( a = 0.3590 \) nm. The coherent scattering domain of the resulting solid solution is 8–10 nm. Further mechanical activation causes a narrowing of the diffraction peaks. The formation of the Ni3Al phase, which is characteristic in this concentration range, was not detected at any stage of activation.

Electron microscopic investigations of the products of mechanical alloying in the mixture Ni 13.5 wt.% Al showed that the dynamics of particle morphology changes at the initial stages of the process is very similar to that observed for the composition Ni 32 wt.% Al. The formation of layered composites was observed, too. However, in this case they start to form as early as after only 30 s of mechanical alloying, which is much earlier than for the Ni 32 wt.% Al composition. The particles of the initial components are no longer detected at this moment. A substantial part of the resulting agglomerates look like plate-shaped particles with traces of strong plastic deformation on their surface. Relatively sintered and round-shaped agglomerates are also present. The maximal size of the plate-like agglomerates is 1–2 mm, while the rounded ones are between 1–2 and 40–50 \( \mu \)m in size. An increase of the mechanical treatment time to 15 min. leads to a decrease of the fraction of the smallest and the largest particles; they become more dense and uniform in size, almost monolithic.

A product of SHS in the mixture Ni 13.5 wt.% Al is an Ni3Al intermetallide. Diffraction patterns are evidence of a high order in the structure of the formed phase (Fig. 11b). Mechanical activation of the SHS product for only 30 s results in a significant decrease
of the intensity of diffraction peaks and to their substantial broadening. After 1.5 min., a non-equilibrium solid solution of aluminum in nickel is formed. Its lattice parameters are identical to those of the product formed in a mixture of initial powders mechanically alloyed for 15 min. (Fig. 11c). Further activation of this SHS product causes no change in diffraction patterns.

It was stated in electron microscopic studies that the particle size decreases sharply at the very first stages of the mechanical treatment of SHS products. After mechanical activation for 1.5 min., the product particles are practically identical in size and morphology to the products obtained from the initial Ni and Al powders after mechanical alloying for 15 min.

The investigation demonstrated that metastable phases, usually produced by mechanical alloying, can be obtained from the equilibrium intermetallic compounds synthesized by SHS.

Short-term activation following the SHS process therefore allows one to homogenize intermetallic phases and to obtain metastable structures. The final products are formed in the ultrafine state with minimal contamination caused by abrasion of milling tools.

This approach can also be used in the SHS synthesis of complex oxides, nitrides, borides, and carbides, etc. However, for this method of preparing ultrafine powders, the range of compounds is limited by the possibilities of the SHS method, i.e. involved are systems with very high temperatures of the final product formation.

2. The effect of preliminary activation on SHS process

2.1 Metal systems

A high exothermal effect of reaction and a strong Arrhenius-type temperature dependence of the reaction rate are of decisive importance for the feasibility of SHS processes. For diffusion-controlled processes, to which SHS processes also belong, another important parameter is the disperse state of the initial components, including the uniformity of their mixing and the surface area of contacts between the components. Mechanical alloying is known as a process which leads to the formation of layered mechanocomposites formed at the initial stage of the mechanical activation of metal mixtures (see Fig. 2a). Most metals exhibit good plasticity; under mechanical action in ball planetary mills where shock and shock-with-shear occur [8], the metal undergoes plastic deformation resulting in a change to the shape of the metal particles. They flatten, adsorption films on their surface are destroyed; components come into contact with each other by atomic-pure planes [9]. «Point» contacts of initial particles transform into flat ones, while the contact area increases considerably [10]. As a result, a short-term preliminary activation can extend the possibilities of reaction in a self-propagating regime even for systems where the SHS process cannot be carried out without preliminary heating.

In order to establish the lower limit of the conditions for the SHS process to occur with mechanical activation involved, we investigated the Ni-Al, Ni-Si, Ni-Ge systems, which are SHS systems and for which the lower concentration limits for silicon and aluminum in SHS without preliminary mechanical activation are known [11]. In the Ni-Al system, the limiting solid-phase solubility of aluminum in nickel is 10.3 wt.% at 1385°C and decreases to 3.85 wt.% at 500°C, but SHS cannot be performed in this concentration range. The minimal aluminum concentration at which SHS can be performed by the traditional method is 13 wt.%Al [3].

Preliminary mechanical activation in the Ni-Al system allows one to decrease the minimal content of Al in the initial mixture for the SHS process. This minimal Al content is 7 wt.% We succeeded in performing SHS in the sample compacted from the powder after mechanochemical treatment. The Ni₃Al, Ni₂Al₃ intermetallics and unreacted nickel were detected in the synthesis products. Subsequent mechanochemical activation homogenizes the product and leads to the formation of a solid solution only.

In the Ni-Si system, similarly to the Ni-Al system, the concentration range of the solid solution is strongly dependent on temperature; at room temperature, the solubility of silicon in nickel is ~5 wt.% while at 1150°C it is ~9.3 wt.%[12, 13]. It is not possible to realize an SHS process in the solid solution range without preliminary mechanical activation in this system.

Our investigations showed that in the solid solution range, the layered composites of nickel and silicon could be formed under activation within 1 min., though they do not look so dense as in the Ni-Al system. The SHS process was also performed in these mixtures containing 9 wt.%Si, the products being a mixture of the Ni₃Si, Ni₅Si₃ intermetallics and unreacted nickel. Similarly to the case of the Ni-Al system, subsequent mechanical activation results in a single-phase product which is a supersaturated solid solution.
In the Ni-Ge system, in which the limiting solubility of germanium in nickel is 13.8 wt.% [5, 14], we investigated the possibility of performing SHS also in the solid solution concentration range. Composites are formed in a Ni 13 wt.% Ge mixture after mechanical activation for 1.5 min. The Ni₅Ge₂ and NiGe intermetallics and unreacted nickel are the products of SHS. The formation of a single-phase solid solution is achieved by a subsequent short-term activation.

The investigations therefore showed that preliminary mechanical activation, during which layered composites are formed from the initial elements, allows one to broaden the concentration limits of SHS processes up to the solid solution region, perhaps due to reagent dispersion and an increase of contact area. The products of this synthesis are mixtures of intermetallics, the doping elements being completely consumed for their formation, and an excess of solvent metal. The conservation of the layered structure in SHS products allows us to assume that intermetallic compounds are formed locally inside the layered structure, its framework being built of solvent metal.

Using the discovered effect of preliminary mechanical activation on the possibility of performing SHS even in the concentration range of solid solutions, we tested it in the systems in which SHS cannot be performed without preliminary heating of the reaction mixture even in the range of intermetallic existence [3]. As an example, Figure 12 shows the combustion rate and the maximum combustion temperature plotted versus time of the preliminary mechanical activation for the Ni 45 wt.% Ti composition. The samples start burning at room temperature after 2.5 min. of mechanical activation. Similarly to all the systems considered above, an increase of the burning rate is connected to the formation of dense layered composites. A photograph of the sample after mechanical activation for 2.5 min. is shown in Figure 13. Increasing the time of mechanical activation also leads to a further increase of the density of the composites, a decrease of the grain size to <0.1 µm, and to the appearance of particles with traces of strong plastic deformation on the surface. The decrease of the combustion rate is connected to the start of destruction of the largest composites. Only NiTi (the main phase) and Ti₅Ni lines are observed in the diffraction patterns of the SHS products at any time of mechanical activation. No titanium or nickel lines are observed! The relative content of these phases in the products remains practically independent of the time of mechanical activation.

2.2 Oxide systems

The synthesis of nanocrystalline mixed oxides is among the major problems of advanced ceramic technology. Conventional processes for manufacturing multi component mixed-oxide ceramics involve high-temperature reactions between metal oxides or between metal oxides and carbonates. These diffusion-controlled processes require the application of high temperatures and the use of highly dispersed precursor powders; mixed oxides are formed in particles of 1 to 5 µm in size. Mechanochemical alloying partly removes the diffusion control. The consider-
able heat of the chemical reaction provides the high rate of the mechanochemical reaction. For example, for most reactions of mechanochemically assisted metal oxidation in a gaseous phase, the oxidation rate correlates with variations in Gibbs’ free energy [15]. For the exothermal reactions, the mechanochemical reaction rate of solid solution formation is a function of the enthalpy of formation of intermetallic compounds in equilibrium [16]. Therefore, if reactions with small decreases in Gibbs’ free energy are used in thermodynamically controlled mechanochemical synthesis, a large power supply and a long mechanical activation time would be necessary, by analogy with mechanochemical synthesis of mixed oxides from binary oxides, either alone or mixed with carbonates [17]. Efficient mechanochemical synthesis is not feasible unless in energy-intensive activators (steel drums and steel balls), and contamination of the product is inevitable. Therefore, mechanochemistry is almost useless for commercial ceramic processes with their extremely high purity requirements. The mechanochemical approach becomes practicable only with high rates of promoted reactions, i.e., those that are not only thermodynamically allowed, but that also give an energy gain. High rates of mechanochemical processes result in final products which are highly dispersed, and this can significantly influence the properties of the resultant ceramics.

The change of Gibbs’ energy in the synthesis of complex oxides from simple ones shows that all these reactions are thermodynamically allowed, while the majority of reactions with the participation of carbonates are available only at high temperatures (Table 1).

Some of these reactions were performed mechanochemically when a sufficient amount of energy was applied [17]. All the values obtained for the systems under consideration are approximately of the same order of magnitude, so the conditions for these reactions to proceed should be rather similar.

The use of peroxide compounds and oxides as the initial components of mixtures, as proposed by some authors [17], does not bring substantial changes to the ΔG of the reaction of complex oxide synthesis.

Among the methods to obtain oxides, the energetically most profitable ones are the direct oxidation of metals (or metal mixtures) by oxygen (Table 2). However, in reality one can hardly perform this type of synthesis mechanochemically due to the high plasticity of metals.

The most promising way seems to be the oxidation of metals by peroxide compounds, especially if we take into account that there is a rather large class of stable metal peroxides that can provide a couple for a proper metal to synthesize a complex oxide. In such cases, one should keep in mind that the mechanochemical interaction of metal peroxide with metals can follow two routes: either with the formation of complex oxides or with the formation of a mixture of

| No. | Reaction product M eO + MeO + CO2 | ∆G°298 kcal/mol | ∆G°1273 kcal/mol |
|-----|----------------------------------|----------------|-----------------|
| 1   | BaTiO3                           | 16.3           | -17.7           |
| 2   | BaZrO3                           | 24.2           | -10.0           |
| 3   | BaHfO3                           | 21.9           | -13.2           |
| 4   | BaMoO4                           | 2.5            | -30.5           |
| 5   | BaWO4                            | -4.2           | -42.6           |
| 6   | BaAl2O4                          | 26.5           | -16.3           |
| 7   | CaMoO4                           | -9.3           | -44.7           |
| 8   | SrMoO4                           | -6.6           | -41.7           |
| 9   | PbMoO4                           | -1.6           | -35.6           |

Table 2 Changes of Gibbs’ energy in the oxidation of metals or metal mixtures by oxygen or barium peroxide resulting in the formation of oxides and complex oxides.

| No. | Product of reaction M e + O2 | ∆G°298 kcal/mol | Product of reaction M e + O2 | ∆G°298 kcal/mol | Product of M e + BaO2 interaction | ∆G°298 kcal/mol |
|-----|------------------------------|----------------|------------------------------|----------------|----------------------------------|----------------|
| 1   | BaO                          | -251.1         | BaTiO3                      | -373.9         | BaTiO4                          | -231           |
| 2   | TiO2                         | -212.1         | BaZrO3                      | -402.0         | BaZrO3                          | -263           |
| 3   | ZrO2                         | -248.5         | BaMoO4                      | -334.9         | BaMoO4                          | -196           |
| 5   | MoO3                         | -159.7         | BaAl2O4                     | -364.5         | BaAl2O4                         | -225           |
| 7   | Al2O3                        | -378.0         | BaAl2O4                     | -556.3         | BaAl2O4                         | -390           |
simple ones, because both reactions are profitable from the thermodynamic viewpoint, and the change of Gibbs' energy is much higher than that for the synthesis from oxides and carbonates. The calculation of $\Delta G_{298}^\circ$ for the BaO$_2$ interaction with metals demonstrated that the decrease of Gibbs' energy was larger by 30−40 kcal/mol than when the products of the same reaction would be a sum of simple oxides. One can assume that synthesis will proceed to the formation of complex oxides.

According to X-ray diffraction data, the mechanochemical interaction of barium peroxide with titanium for 5 min. results in the formation of a mixture of barium titanates. The reflections corresponding to BaO$_2$ and Ti disappear and reflections corresponding to Ba$_2$TiO$_4$, BaTiO$_3$ [18], etc. appear. No diffraction reflections from simple oxides of barium and titanium are observed.

The complex oxides were obtained for the system BaO$_2$-Me (Me=Zr, Al).

For the BaO$_2$-Ti mixture, an antisymmetric absorption band peaking at 700 cm$^{-1}$ and a very weak peak at 775 cm$^{-1}$ appear after 1 min. of activation. After 5 min. of activation, a shoulder of the 700 cm$^{-1}$ band appears at 550 cm$^{-1}$ (Fig. 14b). This band is assignable [21-23] to $\nu$ (Ti-O) stretches in [TiO$_4$] tetrahedra of barium titanates [23]. The positions of the peaks and the band shape do not correspond to $\nu$ (Ti-O) vibrations in various TiO$_2$ polymorphs [22, 24].

The BaO$_2$-Zr mixture mechanically activated for 5 min. exhibits an absorption band with a peak at 550 cm$^{-1}$ (Fig. 14c). This band can be assigned to barium zirconate [21, 23].

A broad asymmetric band with a maximum at 530 cm$^{-1}$ appears as a result of activation of a mixture of BaO$_2$ with aluminum (Fig. 14d). Magnesium aluminate exhibits a similar IR spectrum in this region [21, 26, 27], and the formation of barium aluminate can be assumed in the BaO$_2$-Al system under mechanical activation [28].

The electron microscopic investigation of the product of mechanochemical synthesis in a mixture of BaO$_2$ with Zr shows that activation for 1 min. results in the formation of particles of 0.3−1 µm in size. They are composed of small blocks of 6−12 nm in size (Fig. 15). The microdiffraction picture obtained from a separate particle also points to a developed microblock structure. The diffraction spots are shaped as rings, which is characteristic of polydisperse materials, while microdiffraction from a separate block gives a point, which is evidence of the single crystal state of the substance. Diffraction reflections in both electron diffraction patterns, though somewhat broadened, are point reflections, which is evidence of a rather high degree of crystallinity of the substance formed in mechanochemical synthesis. A similar picture was also observed for other complex oxides, with only a small difference in microblock size.

The investigations therefore demonstrate that the mechanochemical interaction of barium peroxide with
metals, which proceeds with a substantial decrease of Gibbs’ free energy, as it follows from thermodynamic calculations, allows one to synthesize complex oxides with nanocrystalline particles in a relatively short time.

The mechanochemical oxidation of metals by peroxide compounds allows the preparation of single-phase particles of complex oxides with nanometer-sized microblocks [29-32]. However, in the case of some metals such as tungsten, molybdenum, and tantalum, mechanochemical synthesis does not proceed to completion, whatever reagent ratio is taken, even after prolonged mechanical activation. Some part of the metal always remains unreacted. At the reagents molar ratio of BaO₂:W = 1:1, the products are BaWO₄ and Ba₂WO₅; unreacted W remains. At an increased barium peroxide content (up to 2:1), part of W also remains unreacted. A mixture of tungstates Ba₂WO₄, Ba₃W₂O₇ and Ba₃W₂O₈ is formed. At the reagents ratio of 3:1, only the content of complex oxide Ba₃WO₆ increases. Mechanochemical activation of the mixtures of BaO₂ with Mo, the molybdates BaMoO₄, Ba₃MoO₆ and Ba₅MoO₇ are formed. Similarly to the case of tungsten, a part of molybdenum remains unreacted.

The SHS process in these mixtures also results in the formation of a mixture of complex oxide phases; unreacted metal remains. The preliminary mechanical activation of the mixture has practically no effect on the phase composition of the SHS products although it does increase the process rate.

For BaO₂–M (M = W, Mo, Ta) systems, it was not possible to synthesize single-phase complex oxides, neither by mechanical activation nor by SHS.

IR spectroscopic investigations of the mechanochemical interaction of BaO₂ with WO₂ showed that the formation of a complex oxide starts within the first seconds of activation. The IR spectra of the initial mixture BaO₂+WO₂ contain one broad band at 850–550 cm⁻¹, without clearly exhibited maximums. It is assigned to the stretching vibrations ν (W-O) (Fig. 16a) [21]. The ν (Ba-O) band is below 400 cm⁻¹. After activation for 10 s, a clear band with a maximum at 810 cm⁻¹ is observed instead of the above-mentioned broad band; the intensity of this new band increases with increasing activation time (Fig. 16b, c). The similarity of the IR spectra of activated mixtures to the spectra of stolzite [21] allows us to assume that the activation of the BaO₂+WO₂ mixture results in the formation of BaWO₄ with a spinel structure. However, according to the IR spectroscopic data, the mechanochemical reaction of BaO₂+WO₂ → BaWO₄ does not proceed to completion, which is evidenced by the presence of noticeable absorption in the region 800–500 cm⁻¹ as a shoulder of the band with a maximum at 810 cm⁻¹ related to ν (W-O) of the lower tungsten oxide.

According to the XRD data, a growth of the reflections from the BaWO₄ phase starts at the second minute of activation and reaches its maximum by 5 minutes (Fig. 17 a, b). But, with increasing activation time, the intensity of the diffraction peaks of the complex oxide does not increase, and the intensities of the peaks related to the initial tungsten oxide do not decrease. This means that the result of mechanochemical interaction between BaO₂+WO₂ is a mixture of phases.

For the interaction of BaO₂ with MoO₂, the IR spectra and XRD also reveal a mixture of phases.

The relatively high temperatures of formation of the complex oxides in the system involving the oxidation of the lowest tungsten oxide with barium peroxide allows one to perform these reactions by means of SHS. However, pretreatment of the barium peroxide and sometimes heating of the initial mixture are necessary [33]. This is due to the fact that BaO₂ particles entrained in air become coated with a layer of barium carbonate and hydroxide. This layer prevents an SHS reaction. One can assume that a short-term prelimi-
nary mechanochemical activation of the initial mixture leads to the destruction of these barrier layers and provides a substantial increase of the area of contact between the oxides and the barium peroxide.

An investigation of the effect of the preliminary mechanochemical activation of commercially available BaO₂ with WO₂ showed that the maximal temperature and rate of SHS process are achieved after activation for 2 min., and the single-phase complex oxide BaWO₄ is formed (Figs. 16d and 17c). A disadvantage of the resulting substance was the large particle size (300–500 nm) and in some places even partial agglomeration (Fig. 18a). Electron microscopic studies show that subsequent mechanical treatment of the product for 2 minutes in a high-energy activator of planetary type produces a material with a particle size of 20–30 nm (Fig. 18b) without changes of phase composition (!).

Similar results were also obtained for the BaO₂+MoO₂ system, in which the maximal rate of the SHS process with the formation of the complex oxide BaMoO₄ is achieved after preliminary mechanical activation for 30 s.

The structural similarity of the higher oxide WO₃ and barium tungstate BaWO₄ and rather high temperature of the reaction BaO₂+WO₃ → BaWO₄+1/2 O₂ (−128 kJ/mol) allow us to assume that this reaction

Fig. 17 X-ray patterns of an initial mixture of barium peroxide with WO₂ (a), after its mechanical activation for 5 s (b) and of the SHS product in this mixture (c).

Fig. 18 Microphotograph of the SHS product of a BaO₂+WO₂ mixture (a), the same product after mechanical activation for 2 min. (b).
can be conducted mechanochemically. It follows from the analysis of the IR spectra (Fig. 19). Similarly to the case of the lower oxide, the reaction starts during the first seconds of activation. The shape of the $\nu$ (W-O) band of WO$_3$ (1000–500 cm$^{-1}$) and the ratio of intensities of their maximums are changed. After activation of the mixture for 1 min., the IR spectrum of the sample contains only one intensive band with a maximum at 810 cm$^{-1}$. This band relates to $\nu_3$ vibrations of WO$_4$ tetrahedrons of the reaction product BaWO$_4$.

X-ray phase analysis showed that the growth of the intensity of the BaWO$_4$ phase reflections was accompanied by the decrease of the WO$_3$ reflections intensities till their complete disappearance after activation for 5 min. (Fig. 20). Microphotographs suggest that the initial stage of the process involves intensive dispersion of the particles; their aggregation starts at the second minute of the process. After activation for 5 min., complex oxide particles are formed; the size of their blocks is 20–30 nm (Fig. 21).

The mechanochemical activation of BaO$_2$ with MoO$_3$ results in the formation of the complex oxide BaMoO$_4$. The complex oxide with the same composition (BaMoO$_4$) can be obtained via SHS between barium peroxide and the higher molybdenum oxide, both reagents being activated preliminarily for 30 s.

**Conclusion**

Our investigations show that a combination of the SHS process with the mechanical activation both of reagents and products could be rather attractive for
technological applications. The preliminary activation facilitates combustion, making it possible even in the concentration region where conventional SHS is never observed. In other cases, the very short mechanical activation of SHS products allows us to prepare uniform single-phase products.

For complex oxides, the picture is very similar if we can only provide the energetic conditions for SHS. There is usually quite a wide variety of precursors available for ceramic synthesis, which makes it possible to find an energetically efficient root.

The complex oxides can be obtained by mechanochemical synthesis, by SHS, and by a combination of mechanical activation and SHS.

The combination of mechanical activation and SHS brings advantages to both methods. As a result, the short-term mechanochemical activation of SHS products becomes an extremely convenient method for manufacturing nanopowders.

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