Materials Science-Poland, Vol. 25, No. 1, 2007

Some aspects of mechanochemical reactions

K. WIECZOREK-CIUROWA*, K. GAMRAT

Cracow University of Technology, Institute of Inorganic Chemistry and Technology,
Warszawska 24, 31-155 Cracow, Poland

A classification of mechanochemical syntheses occurring in various states of aggregation is presented. Peculiarities of phenomena that take place under the action of mechanical impulses operating in high-energy ball mills are discussed.

Key words: *mechanochemical reaction; mechanical activation; mechanical alloying; nano-sized material; reactive milling*

1. Introduction

Mechanochemistry, a branch of chemistry concerned with the chemical and physicochemical transformations of substances in all states of aggregation induced by mechanical energy, was formulated by Heinicke [1] more than twenty years ago and is currently fully accepted. Recently, mechanochemistry has become the subject of ever-increasing interest in relation to the theory and preparation of advanced metastable solids – novel, high-performance, and low-cost composite materials with new properties such as better dissolution and leaching (especially important in the case of metals extracted from minerals), and faster decomposition and synthesis. Moreover, these materials also show an improvement in the sintering processes [2].

From the chemical point of view, the mechanical treatment of solids using high -energy impulses can cause mechanical activation, mechanical alloying, and reactive milling of solids. Communition, always the first step of these processes, is the multiple particle rupture which results in their size reduction and a simultaneous increase in the specific surface area and surface energy within the systems. Mechanical activation results in changes partly in the tension state and partly in the dispersion state. Milling can be viewed as a mechanochemical activation if these changes also involve alterations in the structure of the material, its chemical composition, and chemical

---

*Corresponding author, e-mail: kwc@usk.pk.edu.pl

reactivity. Mechanical alloying, invented by Benjamin in 1970 [3, 4], is the process in which mixtures of powders are milled to achieve alloying at the atomic level. Reactive milling is related to the process in which chemical reactions occur.

2. Theoretical considerations on mechanochemical treatment

2.1. How can mechanochemical treatment be realized?

The concept of mechanical treatment is very simple. Generally, it is the milling of the already powdered materials which involves a reduction of particle size. Intimate contact between the milled materials is utilized to greatly enhance diffusion and the chemical reactivity of solids. The most popular devices, in which mechanochemical processes can be conducted are vibratory, planetary, and attritor ball mills. They differ in their capacities, efficiencies of milling and additional arrangements such as cooling, special systems for measuring the temperature and/or pressure; they all also have certain features in common. In all these devices, the ground material is periodically thrown into zones of ball collisions. Energy transfer to the powdered particles takes place by shearing and/or impact action of the balls.

Grinding in these special mills is several times more effective than in conventional devices. For example, diminishing tungsten carbide particles from 2–3 mm pieces to particles of 3 μm conventionally takes 70 hours, while the process realized in a planetary mill takes only 3 minutes [5].

The estimation of the amount of energy to be supplied to the system in order to achieve the desired final products is not a simple task. There have been many attempts at solving this problem [6, 7]. The mechanochemical results depend on many parameters, such as the milling speed (rpm), milling time, milling atmosphere, the process control agent (PCA) and the ball-to-powder weight ratio (BPR), as well as the type of the mill, and the size and material of the grinding balls. All these variables are not completely independent. Therefore, it is necessary to optimise the milling conditions experimentally, because the results generally are not predictable á priori. Some examples illustrating the milling process under different conditions are presented below.

It is observed that the rate of chemical reaction increases along with increasing BPR value. For example, the reduction of $TiCl_4$ with Mg is complete after 48 hours using a BPR of 2:1, whereas with a 6-fold higher BPR value the process lasts few hours [3]. This indicates that in the latter case the frequency of collisions is higher.

A very important factor influencing the reactions induced by milling is the inert or oxidizing atmosphere. Milling in an inert atmosphere can result in gradual product formation and if milling is performed in air the oxidation of any component (e.g., reactive metal) can produce sufficient heat to initiate an appropriate chemical reaction, thus accelerating the overall process [3, 6, 7].

The reaction rate also depends on the presence of a process control agent (PCA). The application of the PCA slows down the reaction rate, which is useful in explosive processes. Most PCAs are organic compounds with low melting and boiling points. When high-energy ball milling takes place in mixtures with a reactive metal in the absence of a PCA, self-propagating reactions may occur spontaneously after the induction period. When the PCA is used, however, the reaction proceeds in a controlled manner and completes after a longer time. PCA may also inhibit inter-particle welding during each collision and may favour decrease in particle size [3].

2.2. What kind of materials can be activated and obtained by milling for practical applications?

Generally, it is possible to indicate the usefulness of mechanical treatment for the production of intermetallic compounds and alloys in metallurgy, composites and complex oxides for materials applied in engineering, nanocrystalline substances for catalysis, and nanomaterials as fuel cells and other active materials for the production of fertilizers, building materials, pigments, etc.

For example, mechanical alloying in order to obtain a homogenous alloy at room temperature involves material transfer. The alloying process is independent of the melting points of the elements used, hence high temperature melting and thermally unstable alloys can be prepared. This technique was developed for producing oxide dispersion strengthened (ODS) Ni-base superalloys for gas turbine applications [6]. Another application of the mechanical activation process is the preparation of materials that have large surface areas and/or exhibit structural defects which may lead to the strong enhancement of their catalytic properties [8–10].

2.3. The principles of two types of mechanochemical reactions

Most reactions in the solid state are slow and complex. Their characteristic feature is that they involve product formation at the interfaces of reactants. Furthermore, product growth requires the diffusion of reactant phase atoms through the product which constitutes a barrier preventing further reaction. Thus, in order for this kind of reaction to proceed for a reasonable time, it should be realized at high temperatures. Moreover, in most cases a solid phase reaction requires charge transfer to be initiated. This can be carried out either thermally or via non-thermal routes including a mechanochemical procedure. It has been established that high energy ball milling of powder or powder mixtures may significantly accelerate chemical reactions between two solids, a solid and a liquid, or a solid and gas, making it possible for the reaction to occur at temperatures lower than those of conventional synthesis [11–13].

Mechanochemical processes do not proceed in the bulk. This means that chemical transformations occur in a different definite region of the particle each time. The size of these sites is usually estimated to be 10^{-5}–10^{-6} m [13].

It is evident that ball milling induces changes in the specific surface area of solid particles and/or the emission of exoelectrons. This is due to the repeated formation of fresh interfaces at any time between the reacting phases. This formation is brought about by means of dynamic deformation, fracturing, and cold welding of the solid particles [13, 14].

The impact energy usually reaches fractions of a Joule, the inelastic collisions last for 10^{-4}–10^{-5} s, and the amount of the matter in the collision zone is close to 10^{-9} m^3. The temperature and pressure increase, especially at the collision points between the solids. Two kinds of temperature effects during mechanical treatment are usually taken into account: local temperatures due to ball collisions, and the overall temperature in the milling vial. The local temperature impulse is approximately equal to the collision time (10^{-5} s). This temperature is defined as a flash temperature. It is the maximum local temperature generated at some points of colliding particles and balls or other grinding bodies. The flash temperature occurs at areas of real contact due to the frictional heat dissipated over these areas. The flash temperature occurs even when the overall temperature rise is lower, and its pressure can reach 10^6 Pa [14].

In the processes of plastic deformation, fracture and friction during ball collisions, the impact energy is converted into other forms of energy which induce structural defects, broken bonds, and other excess energy effects. These instances accumulate and a new, active state of the substances is produced. Such excited states are formed, because the rate of the energy release exceeds the rate of the energy dissipation. Consequently, the chemical reactivity of solids increases considerably. The ignition of the chemical reaction occurs after a period of milling, when the powder reaches a critical level of activation.

The kinetics of the mechanochemical reaction depends on the conditions of the milling process. The application of appropriate milling conditions allows the mechanical reaction to be conducted in two different kinetic ways – as a self-propagating reaction that is initiated when the reaction enthalpy is sufficiently high and develops slowly with each collision or as the one that results in a gradual transformation of the substrates [3, 7, 15–19]. The first type requires a critical time for the ignition of the reaction. It has been observed that the temperature of the vial initially increases slowly with time. After a certain period of milling, the temperature increases abruptly, confirming that ignition has occurred. The time at which a sudden increase in temperature occurs is referred to as the ignition time. After that time the reaction occurs within seconds. The ignition temperature is a function of the enthalpy change and microstructure parameters, e.g. interfacial area between the reactants [18].

It was assumed that after a period of comminution mixing and activation agglomerates begin to form and increase in size. The reaction starts in a single agglomerate or in the powder layer coating a milling ball or on the wall of the vial. One reaction front propagates into other parts of the powder. The powder can be attached to the surface of a milling ball or the inner wall of the container. When a ball hits this layer, a part of the kinetic energy is transferred to the powder as heat, increasing its temperature [3]. The stress inside the powder is not uniform but concentrated in few points. The result is the formation of thermodynamically unstable zones, where the reaction can start even if the average temperature of the powder is not sufficient to initiate the reaction front.

Intimate contact between the reactant phases is an essential requirement for self -propagating synthesis. This condition is easy to achieve when mechanical activation is conducted in a system of ductile-brittle substances. The ductile component is flattened by a micro-forging process whilst the brittle is fragmented. One can assume that the brittle particles of the materials are dispersed in the ductile matrix. If both milled materials are brittle, however, this phenomenon is not observed.

The second type of mechanical synthesis concerns reactions proceeding more slowly up to the point at when processes become a function of the milling time [3, 7, 15]. If ignition does not occur, collisions between the milled material and grinding medium contributes to the comminution, mixing, and defect formation. The formation of the final product occurs step by step.

3. Practical examples of mechanochemical synthesis in various aggregation systems

3.1. Solid-solid systems

Synthesized Pb(Zr,Ti)O_3, lead zirconate titanate (PZT), of a perovskite structure is widely used in various sensing and actuating devices. The traditional method of obtaining this material is a solid-state reaction between stoichiometric mixtures of the constituent oxides – PbO, TiO_2 and ZrO_2 followed by calcination at high temperature. This procedure often leads to an incomplete reaction. Obtaining the PZT phase from $Pb(NO_3)_2$, $TiCl_4$, and $ZrO(NO_3)_2$, however, is possible by mechanical activation using a high-energy shaker mill operated at 900 rpm for 20 h [20].

It is known that modified thermal, optical and electrical properties of the material can be obtained when the powder particle size falls into the micro- or nanoscale. Thus, fine metal silver powders with particle sizes ranging from 50 to 100 nm, which allow the concentration of silver in the conducting composite materials to be reduced, were synthesised in a mechanochemical process by inducing a solid-state displacement reaction between AgCl and sodium in a planetary mill in an argon atmosphere [21]. The reaction is completed after 20 minutes of milling, whereas 2 hours of milling was required to obtain silver in a nanocrystalline form.

For building materials, silicate hydrates (CSHs) such as afwillite ($Ca_3(SiO_3(OH)_2\cdot 2H_2O$) and tobermorite ($Ca_5(OH)_2Si_6O_{16}\cdot 4H_2O$) were used. These compounds are usually synthesized by hydrothermal reactions between lime and silica in the presence of water at high temperatures in an autoclave. The new method of CSH synthesis is based on grinding the initial components with water at room temperature. Grinding was carried out in a planetary mill at 700 rpm. It was shown that afwillite is almost completely formed within 120 minutes of milling, while tobermorite forms within 180 minutes [22].

Binary oxides such as Ag–V and Cr–V have been extensively studied due to scientific and practical interest. For example, compounds of the Ag–V–O system doped with lithium can be applied as positive electrode materials [23], while the Cr–V–O system tested by us [24] has a number of applications in the field of heterogeneous catalysis, sensors, magnetic and ceramic technologies. In both cases, it was found that pure oxides, i.e. Ag_2O, V_2O_5, and Cr_2O_3, reveal strong stability during mechanochemical treatment. Their milling in mixtures composed of Ag_2O with V_2O_5 and Cr_2O_3 with V_2O_5 involved the formation of different spinel phases. In the former case, the presence of $Ag_4V_2O_7$ and Ag_3VO_4 in the milling products was detected, and the presence of $CrVO_4$ and $Cr_2V_4O_{13}$ in the latter one. X-ray diffractometry indicates that spinel phases appear in the milling products after several hours.

Zirconium phosphates (NZP) can be used as catalysts for skeletal isomerization and dehydroaromatisation. The prospective method of its synthesis is based on the mechanical activation of crystallohydrates of ammonium phosphate and zirconium oxochloride or oxonitrate. Materials prepared via the mechanochemical route possess a lower density of acid sites as compared to samples obtained using the sol-gel method, while mechanically synthesized NZP reveals the presence of the strongest Lewis centres [25].

Cr_2O_3 powders have a wide range of applications, including green pigments. Particles smaller than 50 nm can be used as transparent colorants. The reduction of Cr_2O_3 particles is also needed for improving sintering. Various methods of synthesizing nano-sized chromium oxide can be applied, including gas condensation, sol-gel, or laser induced pyrolysis. In a previous study [26], mechanochemical nanomaterial treatment was used. The mechanochemically realized process occurs according to the reaction:

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4$$

Ten minutes of milling of the reactant mixture involved an abrupt increase in the vial temperature, confirming that Cr_2O_3 particles are formed in a combustion process during milling (with a large negative enthalpy change of $\Delta H = -562$ kJ/mol).

Reactive ball milling is almost an ideal method for preparing nano-sized metal matrix composites (MMCs) because of its simplicity and the possibility of composite formation characterized by uniform distribution of grain sizes. Moreover, such an *in situ* route of synthesis results in the production of materials that have more homogenous microstructures and are more thermodynamically stable than those synthesized using conventional *ex situ* techniques. For example, this kind of material consisting of ceramic and intermetallic phases, namely $Cu–Al/Al_2O_3$ and $Ni–Al/Al_2O_3$, can be obtained by milling mixtures of Cu(Ni) hydroxycarbonates with aluminium [27, 28]. The formation of these multiphase materials is a consequence of many complex, simultaneous and subsequent chemical reactions occurring during milling in air. These mechanochemical processes are described below:

- mechanical decomposition:

$$M_2(OH)_2CO_3 \rightarrow 2MO + H_2O\uparrow + CO_2\uparrow$$

- aluminothermic reduction:

$$3MO + 2Al \rightarrow 3M + Al_2O_3$$

- mechanical alloying:

$$xM + yAl \rightarrow M_xAl_y$$

where M is Cu or Ni.

The factor facilitating these reactions is heat emission in the process of rapid aluminium oxidation during its activation in air. It may be assumed that this heat ($\Delta H_{298} = -1675$ kJ/mol) accelerates the decomposition of hydroxycarbonates, induces the alluminothermic reaction, and enhances the alloying of the two metallic phases. The initiation temperature of the aluminothermic reaction can be monitored by differential thermal analysis (exo-effects).

3.2. Solid-gas

There are some examples of mechanochemical reactions that proceed in solid–gas and solid–liquid systems. One of them is the production of rutile (TiO_2) from the mineral ilmenite $FeTiO_3$. For this purpose, ilmenite powder is milled in vacuum and air. In vacuum, no structural changes are observed. Activation carried out in air, however, involves ilmenite transformation to $Fe_2Ti_3O_9$ according to the reaction:

$$6FeTiO_3 + 1.5O_2 = 2Fe_2Ti_3O_9 + Fe_2O_3$$

where Fe_2O_3 is hematite and $Fe_2Ti_3O_9$ ($Fe_2O_3{\cdot}3TiO_2$) is a new iron titanate phase. This phase is thermally metastable and forms Fe_2TiO_5 and TiO_2 after a further annealing [29].

Another example of a solid–gas system is the synthesis of TiN which takes place during the ball milling of Ti in a pure nitrogen atmosphere [30]. It was proposed that nitrogen absorption in the milled metal powders occurs at the moment of ball collision, and the quantity of nitrogen absorbed during one collision event is proportional to the energy supplied to the powder from the colliding balls.

The phase evolution in this kind of systems under mechanochemical treatment is influenced by the initial pressure of the gas component.

3.3. Solid–liquid

The mechanochemical destruction of polyhalogenated pollutants or pure polyhalogenated compounds by pure metals (e.g., sodium, magnesium, aluminium, zinc, iron, alloys) and some suitable hydrogen donors (e.g. alcohols) is shown below:

$$\text{R–Cl (toxic)} + \text{Na} + \text{hydrogen donor} \rightarrow \text{R–H (biphenyl)} + \text{NaCl (harmless)}$$

Such pollutants can be eliminated at room temperature at times ranging from minutes up to one hour in a single step. The whole process can be characterized as a reductive dehalogenation facilitated by mechanochemical treatment [31].

Other researchers [32] have tested high energy milling as a method for lowering the amount of chlorinated compounds in contaminated soil. They used two substances, namely $NaBH_4$ and $LiAlH_4$ as reducing agents. $LiAlH_4$ proved more efficient, reducing poly(chlorobiphenyls) (PCBs) by over 9% in three hours.

Different kinds of processes occurring in solid–liquid systems can be represented by the mechanical treatment of a mixture of Al and Ti with pyrazine ($C_4H_4N_2$) [33]. Milling of this system in benzene solution (PCA) brings about the formation of the metal matrix composite Al–TiN. This was formed in two steps, i.e. at the beginning Ti was milled with pyrazine. After 48 hours of milling two kinds of nitrides, Ti_2N and TiN, were identified, and then Al was added to the nitrides. A homogenous Al–TiN composite was obtained after an additional 96 hours of milling.

4. Selected experimental methods of identifying and characterizing materials synthesized mechanochemically

A comprehensive study of the physical and chemical processes that occur during mechanical treatment by means of high-energy ball milling appears to be possible only if a reliable identification of solids and quantitative phase analysis of the activated products are performed. Due to the complexity of mechanochemical reactions, the nature of the obtained solids is closely related to the milling conditions, they should therefore be well-defined. Moreover, it is very important to determine the factors influencing the activation effects. Another difficulty arises from the fact that these reactions are composed of many successive stages, which are very different in many cases. The experimental methods required for identifying and characterizing materials synthesized mechanochemically involve not only techniques applicable to solids, but also those particularly adapted to the nanostructured character of the milling products. Thus various types of analytical methods must be applied [34–40].

The first type are thermal analysis methods. Such techniques as thermogravimetry and differential thermal analysis are very useful for describing mechanically activated substances, because they make it possible to identify highly defected, finely crystalline or even amorphous phases formed during milling, which might be difficult to achieve using other methods. Moreover, thermal analysis allows the quantitative phase composition of the activated mixture to be estimated, which enables, for example, estimating the consumption of initial components of the tested mixtures. Moreover, in some cases thermoanalytical experiments may be used for simulating the reactions that occur during reactive ball milling. Such simulations, done for mixtures of

Cu–hydroxycarbonate with aluminium (Fig. 1), simplified the estimation of the reaction mechanism that yields the composite Cu–Al/Al_2O_3 during milling. DTA curves reveal that $Cu_2(OH)_2CO_3$ thermally decomposesd into CuO, and that then copper oxide is reduced by Al. The consequence of such a process is the formation of Cu and a large amount of heat. This heat may accelerate the alloying of Cu with Al into intermetallic phases.

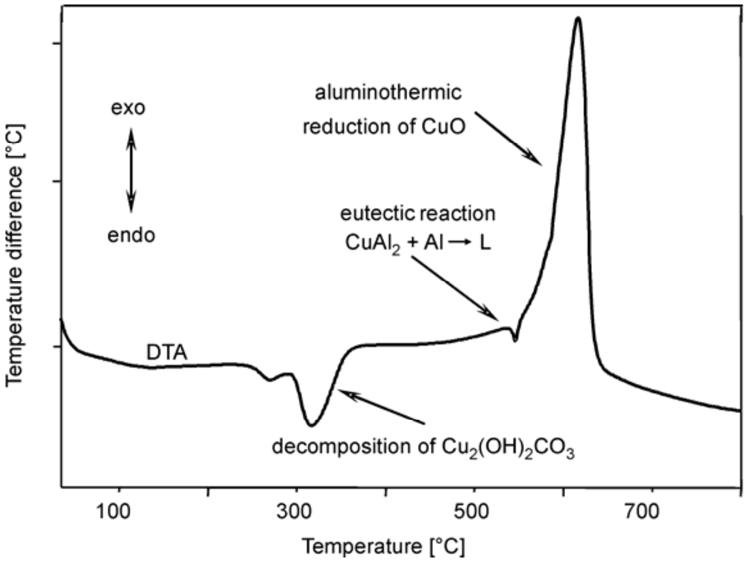

Fig. 1. DTA curve (non-oxidizing atmosphere) of the $Cu_2(OH)_2CO_3$–Al system simulating the reactions that may occur under mechanical action

Information about the qualitative phase composition of mechanically activated materials can be obtained from X-ray diffractometry. The technique is ideal for monitoring the progress of the process occurring during milling, if the materials are in their crystalline forms.

When the materials are in their fine or even amorphous forms, mechanosynthesis can be followed by using IR spectroscopy. An example of the special usefulness of IR spectroscopy for estimating the time in which the mechanosynthesized products start to form is the spinel synthesis of mechanically treated mixtures of Cr_2O_3 and V_2O_5. We observed $CrVO_4$ in the milled products after 1.5 hours of milling, which is confirmed by the stretching vibration of the VO_4^{3-} observable in the IR spectra shown in Fig. 2. The amount of spinel phases, however, is very small and can be detected without doubt by using X-ray diffractometry. Another useful spectroscopic technique is Mössbauer spectroscopy, used for substances with magnetic properties. It provides information on the magnetic states and local coordination of magnetic ions [37, 38].

Results obtained using thermoanalytical methods – X-ray diffractometry and IR spectroscopy – are useful especially for bulk analysis, however they must be supplemented with results from other analytical methods that provide more accurate data about the composition and structure of mechanically treated materials.

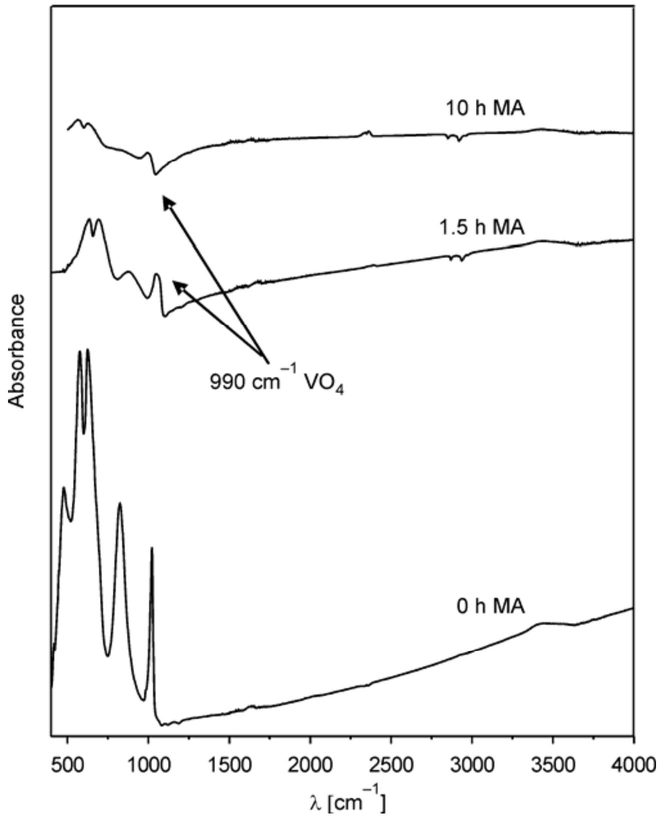

Fig. 2. IR spectra for the V_2O_5–Cr_2O_3 system after mechanochemical treatment

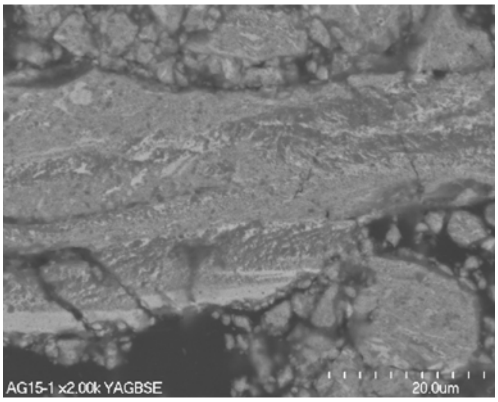

Fig. 3. SEM microphotographs of the $Cu_2(OH)_2CO_3$–Al mixture after mechanochemical syntheses of the Cu–Al/Al_2O_3 composite, characterized by a lamellar structure

One of the techniques used for this purpose is scanning electron microscopy with backscattered electron imaging and quantitative energy dispersive X-ray elemental microanalysis (EDS). By combining the grey tone levels with the results of EDS, a single compound can be quickly identified and localized. For example, this technique reveals that mechanosynthesis in the $Cu_2(OH)_2CO_3$–Al systems involves the formation of a composite characterized by a lamellar morphology (Fig. 3). Moreover, on the basis of EDS analysis it was possible to estimate that such a material is composed of aluminium oxide and intermetallic phases. The disadvantages of scanning electron microscopy include low spatial resolution and the inability to image individual grains, dislocations, and defects in the tested material.

Another microscope method useful for analysing mechanically activated substances is transmission electron microscopy (TEM). TEM measurements can be applied for estimating the composition and microstructure of mechanically alloyed products. A high resolution obtained in this type of microscopy allows single grains of the products to be observed. Such single grains of mechanosynthesized copper can be seen in Fig. 4. Electron diffraction patterns unquestionably confirmed that the detected phase is nanocrystalline Cu (Fig. 4c).

Larger prospects in the analysis of nanometric substances can be achieved using high-resolution transmission electron microscopy (HRTEM). HRTEM allows the atomic structure of grain boundaries to be probed and atomic coordinate positions to be estimated. The final point to consider in preparing HRTEM and TEM specimens, however, is how closely representative the thin films are of the bulk material [39].

X-ray photoelectron spectroscopy (XPS) can provide characteristics of surface mechanochemically obtained materials. This technique gives information about the elements present on the surface and on their amounts. The exact description of surface composition is important for materials used as catalysts because their action depends on active sites localized strictly on the surface [40]. Therefore, the analytical method must give information about layers only several nanometers deep. This special usefulness of XPS spectroscopy can be demonstrated in the case of Cr_2O_3–V_2O_5 mixtures mechanochemically treated in argon (dry conditions) and ethanol (wet conditions). The tested mixtures were mixed at a ratio of V/Cr equal to 0.1. Only XPS shows that on the surface of the sample activated in the dry medium (V–Cr–O/Ar) the ratio V/Cr is fourfold higher than the theoretical one or that detected for the sample activated in wet conditions (V–Cr–O/Et) (Table 1). This suggests that the surface of the sample was enriched in vanadium when treated in argon. Due to this, one can conclude that mechanical activation in dry conditions involves the segregation of phases by covering Cr_2O_3 grains with a V_2O_5 layer.

It was necessary to find suitable analytical procedures to characterize phases in mechanochemically activated systems. The task appeared to be rather complex, however, because of the multiphase and nanocrystalline character of the reactive ball milling products. Therefore, a coupled analytical system should be applied in many cases. Such systems are especially useful for catalytic materials because they can test catalysts in action, such as UHV surface analyses systems equipped with catalytic reactors, X-ray photoelectron and Auger electron spectroscopy.

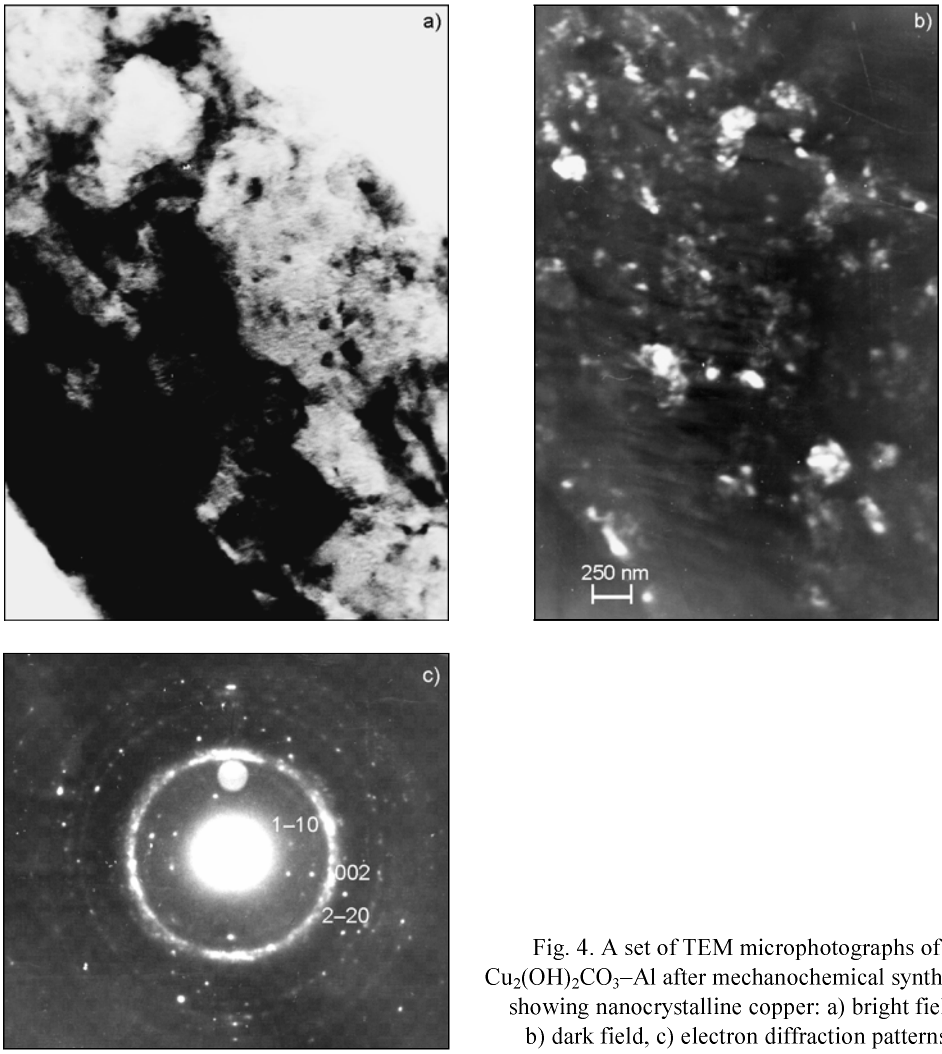

Fig. 4. A set of TEM microphotographs of $Cu_2(OH)_2CO_3$–Al after mechanochemical syntheses, showing nanocrystalline copper: a) bright field, b) dark field, c) electron diffraction patterns

Table 1. XPS data for mixtures of the oxides V_2O_5 and Cr_2O_3, not milled (V–Cr–O) and milled in dry and wet conditions (V–Cr–O/Ar and V–Cr–O/Et)*

Sample	BE, eV				V/Cr
	Cr 2p	(*N*)	V 2p	(*N*)	
V–Cr–O	576.1 578.3	(14582) (1570)	–	(*)	0
V–Cr–O/Ar	576.2 578.7 581.7	(13132) (2647) (617)	517.5	(6765)	0.41
V–Cr–O/Et	575.9 577.8	(13228) (3810)	517.1	(1636)	0.10

*(N) – relative amount of atomic form of elements, (*) - below the limit of detection.

All the above-mentioned methods are useful tools for obtaining information regarding the composition and localization of phases. Moreover, the complete phase analysis of mechanically activated products leads to a better understanding of the mechanism of chemical reactions under high-energy ball milling that provide materials with desired properties.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education, Project No. PB 1234/H03/2006/30.

References

[1] Heinike G., *Tribochemistry,* Academie-Verlag, Berlin, 1984.
[2] Boldyrev V.V., Tkačova K., J. Mater. Synth. Proces., 8 (2000), 121.
[3] Takacs L., Mandal S.K., Mater. Sci. Eng. A, 304–306 (2001), 429.
[4] Benjamin J.S., Metall. Trans., 1 (1970), 2943.
[5] Bobkov S.P., Frolov A.N., Izv. Vuzov, Khim. i Khim. Tekhnol., 34 (1991), 93.
[6] Murty B.S., Ranganathan S., Intern. Mater. Rev., 43 (1998), 101.
[7] Suryanarayana C., Progress Mater. Sci., 46 (2001), 1.
[8] Avvakumov E., Senna M., Kosova N., *Some Theoretical Aspects of Mechanochemical Reactions. Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies*, Kluwer, New York, 2002.
[9] Tkačova K., *Mechanical Activation of Minerals*, Elsevier, Amsterdam, 1989.
[10] Rougier A., Soiron S., Haihal I., Aymard L., Taouk B., Tarascon J.-M., Powder Technol., 128 (2002) 139.
[11] Urakaev F. Kh., Boldyrev V.V., Powder Technol., 107 (2000), 93.
[12] Courtney T.H., Maurice D., Scripta Mater., 34 (1996), 5.
[13] Butyagin P., Coll. Surf. A, 160 (1999), 107.
[14] Kajdas C. K., Tribology Intern., 38 (2005), 337.
[15] Welham N.J., Mater. Sci. Eng. A, 255 (1998), 81.
[16] Tokumitsu K., Solid State Ionics, 101–103 (1997), 25.
[17] Shaffer G.B., McCormick P.G., J. Mater. Sci. Lett., 9 (1990), 1014.
[18] Korchagin M.A., Grigor'eva T.F., Bokhonov B.B., Sharafutdinov M.R., Barinova A.P., Lyakhov N.Z., Comb., Expl. Shock Waves, 39 (2003), 51.
[19] Zhang D.L., Zhang Y.J., J. Mater. Sci. Lett., 17 (1998), 1113.
[20] Junmin X., Wang J., Weiseng T., J. Alloys Comp., 308 (2000), 139.
[21] Keskinen J., Ruuskanen P., Karttunen M., Hannula S.P., Appl. Organometal. Chem., 15 (2001), 393.
[22] Saito F., Mi G., Hanada M., Solid State Ionics, 101–103 (1997), 37.
[23] Kittaka S., Nishida S., Ohtani T., J. Solid State Chem., 169 (2002), 139.
[24] Wieczorek-Ciurowa K., Gomułczak A., Rakoczy. J., Stoch J., Gamrat K., Sawłowicz Z., Polish J. Appl. Chem., 49 (2005), 253.
[25] Pavlova S.N., Sadykov V.A., Zabolotnaya G.V., Maximovskaya R.I., Zaikovskii V.I., Tsybulya S.V., Burgina E.B., Chaikina M.V., Agrawal D., Roy R., Solid State Ionics, 141–142 (2001), 683.
[26] Tsuzuki T., McCormick P.G., Acta. Mater., 48 (2000), 2795.
[27] Wieczorek-Ciurowa K., Gamrat K., Sawłowicz Z., J. Therm. Anal. Cal., 80 (2005), 359.
[28] Wieczorek-Ciurowa K., Gamrat K., Fela K., Solid State Ionics, 164 (2003), 193.

[29] CHEN Y., J. Alloys Comp., 257 (1997), 156.
[30] PUCLIN T., KACZMAREK W.A., J. Alloys Comp., 266 (1998), 283.
[31] ARESTA M., DIBENEDETTO A., PASTORE T., Abstracts P-I-03. p. 69. IV Intern. Conf. of Mechano-Chemistry and Mechanical Alloying. 7–11 Sept. 2003. Braunschweig (Germany).
[32] BALEMA V.P., PECHARSKY V.K., DENNIS K.W., J. Alloys Comp., 13 (2003), 69.
[33] ZHANG F., KACZMAREK W.A., LU L., LAI M.O., Scripta Materialia, 43 (2000), 1097.
[34] WIECZOREK-CIUROWA K., GAMRAT K., SHIROKOV JU.G., Thermochim. Acta, 400 (2003), 221.
[35] WIECZOREK-CIUROWA K., GAMRAT K., PARYŁO M., SHIROKOV JU.G., J. Therm. Anal. Cal., 70 (2002), 165.
[36] WIECZOREK-CIUROWA K., GAMRAT K., PARYŁO M., SHIROKOV JU.G., J. Therm. Anal. Cal., 69 (2002), 237.
[37] ŠEPELAK V., WISMANN S., BECKER K.D., J. Magn. Magn. Mater., 203 (1999), 135.
[38] BECKER K.D., Solid State Ionics, 141–142 (2001), 21.
[39] MULLER D.A., MILLS M.J., Mater. Sci. Eng. A, 260 (1999), 12.
[40] FIERRO G., JACONO M. LO, INVERSI M., DRAGONE R., PORTA P., Topics Catal., 10 (2000), 39.

Received 23 June 2006
Revised 29 September 2006