

Nano-particles of Mechanochemical Synthesis

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Abstracts : A theoretical investigation of the solid phase mechanochemical synthesis of nano sized target product on the basis of dilution of the initial powdered reagent mixture by another product of an exchange reaction is presented. On the basis of the proposed 3 mode particle size distribution in mechanically activated mixture, optimal molar ratios of the components in mixture are calculated, providing the occurrence of impact friction contacts of reagent particles and excluding aggregation of the nanosized particles of the target reaction product. Derivation of kinetic equations for mechanochemical synthesis of nanoscale particles by the final product dilution method in the systems of exchange reactions is submitted. On the basis of obtained equations the necessary times of mechanical activation for complete course of mechanochemical reactions are designed. Kinetics of solid phase mechanosynthesis of nano TiCl by dilution of initial (2NaCl + Ti₂SO₄) mixture with the exchange reaction product (diluent, zNa₂SO₄, z = z* = 11.25) was studied experimentally. Some peculiar features of the reaction mechanism were found. Parameters of the kinetic curve of nano TiCl obtained experimentally were compared with those for the model reaction KBr + TiCl + zKCl = (z + 1) KCl + TiBr (z = z1* = 13.5), and for the first time the value of mass transfer coefficient in a mechanochemical reactor with mobile milling balls was evaluated. Dynamics of the size change was followed for nanoparticle reaction product as a function of mechanical activation time.

1. INTRODUCTION

The recent decade is a period of intense development of nanotechnologies [1-3], including solid-phase mechanochemical methods of obtaining nanosized systems [3-5]. There are two companies, that are exploiting successfully the mechanochemical synthesis of nanocrystalline powders: M.B.N., Italy and Advanced Nano Technologies (ANT). ANT is a joint venture between Advanced

Powder Technology (APT) of Australia and Samsung Corning of Korea.

APT has recently exploited some results in the field of displacement mechanochemical reactions. At the end of the reactions, nanocrystalline powders (grain size ~ 10 nm) within a soluble salt matrix are obtained. The final step is washing the salt matrix with appropriate solvents, allowing to obtain separated nanoparticles. The use of a diluent phase may be necessary to: a) avoid combustion

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reactions during milling [3]; b) reduce the volume fraction of nanoparticles (in this way, it is possible to avoid nanoparticles being agglomerated). However, the mass, volume or molar ratio of reagents to one of the products, which can be called a diluent, in the initial powder mixture is chosen only empirically, similarly to the conditions of mechanical activation (MA) of the prepared mixture (geometric and kinematic parameters of a mechanochemical reactor, comparative characteristics of the milling tools and material under treatment, kinetic parameters: time of MA, etc.). In the present paper, an attempt is made for the first time to provide a theoretical description of this method obtaining some quantitative estimations.

2. ESTIMATION OF KINETICS OF ABRASIVE-REACTIVE WEAR OF REAGENTS

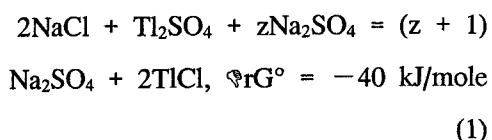
Reactions (1) analogue studied earlier exchange mechanochemical reaction $\text{KCl} + \text{NaNO}_3 = \text{KNO}_3 + \text{NaCl}$. Here we shall consider only specific features of application of the results of these works for an estimation of kinetics of abrasive-reactive wear of particles of MA substances

caused by the following differences:

- 1) Additive of one of products of reaction (diluent) to an initial mix of reagents;
- 2) Parities of mechanical properties of a diluent to those for reagents, for example, hardness;
- 3) Presence of 3-modal distributions on the sizes of MA particles.

3. EXPERIMENTAL SECTION

The practical realization of exchange reaction is hindered by the occurrence of reagents poorly soluble in water, both in the left and right sides of the above equation (TlCl and TlBr). Therefore, an experimental verification of theoretical results was performed on the reaction



carried out in an AGO-2 planetary mill under the conditions described for the reaction. Reaction (1) meets the conditions

of nanoparticle synthesis by the method of dilution with the reaction product. Solubility of the starting components for (1) is, in mass %: 21.925°C for Na₂SO₄, 35.8720°C for NaCl, and 4.8720°C for Tl₂SO₄. Detailed conditions for the test reaction (1) in an AGO-2 steel two-vial-type water-cooled ball mill are given in table 2 (m₃' denotes the mass of diluent Na₂SO₄ formed additionally). According to the values of hardness for the reagents (i = 1, halite NaCl; i = 2, thallium sulfate Tl₂SO₄; and i = 3 for the diluent, tennardite Na₂SO₄) the optimal dilution ought to be described by the value of z₁* equal to 11.25, as the values of hardness are usually higher for sulfates than for halides:

$$z_1^* = \rho_3 [2 \rho_2 m_1 R B_3 - \rho_1 m_2 (R M_3 + 2 R S_3)] / \rho_1 \rho_2 m_3 (R M_3 + 2 R S_3) \approx 11.25 \quad (2)$$

$$z_2^* = \rho_3 (2 \rho_2 m_1 + \rho_1 m_2) [2 R B_3 + 3 (R M_3 + 2 R S_3)] / R B_3 \rho_1 \rho_2 m_3 \approx 5.44 \quad (3)$$

Nevertheless, we chose both compositions for our experiments, to verify the theoretical results, and also because we failed to find the available value of

hardness for Tl₂SO₄ crystals. The mixtures of reagents of “chemically pure” quality and “pure” Tl₂SO₄, corresponding to the stoichiometric compositions with z = z₁* and z = z₂* = 5.44, were crushed and homogenized during an hour in a Fritsch Pulverisette mill, equipped with steel accessories (mortar of 9.45 cm and a ball of 5.16 cm in diameter). Initial average size of obtained particles of the mixture was within 0.005 – 0.015 cm, according to the optical microscopy, i.e. it was far from the particle size in the quasi-equilibrium state having been attained under MA: RB ≈ 1.25·10⁻⁴ cm. The products of MA were examined by the standard method of powder X-ray analysis (XRD) on a diffractometer with filtered CuK α radiation and scanning over 2θ angle rate of 1°/60 s.

The kinetics of transformation of (1) reaction was monitored by measuring the conductivity of water solutions of MA samples, 1 g per 10 ml of deionized water. Only poorly soluble product was TlCl, and this ensured a high enough accuracy of the measured drop of conductivity in the products relative to the initial homogenized samples. We have verified this method reliably for measuring the isomers separately when they are present in

solutions in a mixture of ammonium thiocyanate NH_4CNS , pseudohalogenide, and thiourea, non-conducting molecular crystal $(\text{NH}_2)_2\text{CS}$. A highly sensitive installation for the conductivity measurements was designed on the bases of an Impedance Meter BM507, Tesla, Brno, and a Pt-electrode, Conductometric Bell electrode, type OK-9023, Radelkis Electrochemical instrument, Budapest. Experimental error was defined from the following characteristics of the system: maximal content in a specimen of 1 g could be up to $4.491/20.77 \approx 0.216$ g of TlCl and $8.206/20.77 \approx 0.395$ g of Tl_2SO_4 .

48.7 mg of Tl_2SO_4 can be dissolved. Let us take that the solubility of MA TlCl particles is about 10 times lower than that of Tl_2SO_4 , i.e., in 1 ml of water ~ 5 mg of TlCl can be dissolved (as it is known, the solubility of MA salts can exceed their tabulated equilibrium solubility). Hence, from a specimen of 1 g, 10 ml of water can dissolve ~ 50 mg (0.05 g) of TlCl and all the other components of the system for sure. Therefore:

- experimental error in conductivity measurements could give the value of $0.05 / 0.216 \approx 23$ %, based only on the

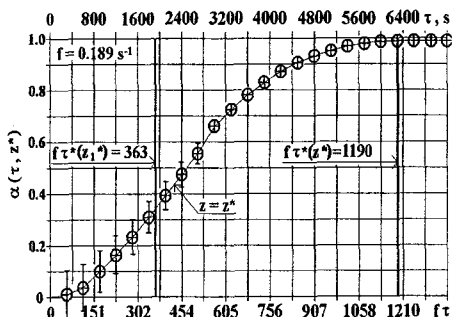


Figure 1. Kinetic curve $\alpha(\tau, z^*)$ for (1) reaction as a function of MA time τ and of the number ft of abrasive-reactive interactions of particles of reagents in the region $\pi r^2 \delta$ of impact action produced by a milling tools in an AGO-2 mill, defined by the conductivity measurements of the solutions of MA samples.

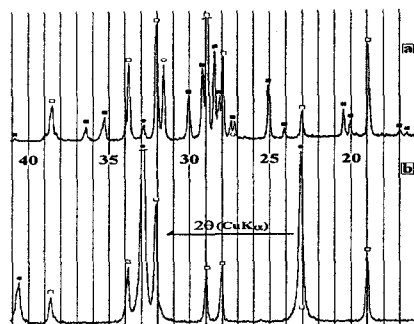


Figure 2. XRD patterns for samples:

a) charge for (1) after 1 h homogenization in a Fritsch Pulverizette mill, $z = z^* = 11.25$;
 b) MA in an AGO-2 mill during 7200 s.

○ - NaCl , ■ - Tl_2SO_4 , □ - Na_2SO_4 , ● - TlCl .

In 1 ml of water ~ 3.5 mg of TlCl and

conductivity of the solutions of MA

specimens;

- calibration dependence of conductivity on the composition of mixture of initial components allowed us to lower the error down to $(0.05 - 0.035) / 0.216 \approx 7\%$;

- by means of correction factor 2, obtained by averaging over the composition or on one half of the transformation degree α , the error could be diminished to $\sim 4\%$ (diameter of the experimental points on kinetic curve just corresponds to the latter).

4. CALCULATIONS ON THE BASE OF XRD DATA

Figure 3 shows the results of XRD method for samples used in evaluation of the crystallite size D along with the lattice strain Y for the reaction nanoscale target product, nano-TiCl. The only reflection free from overlapping is that (111) of TiCl (figure 3). We used this advantage here below.

For calculating the crystallite size D and strain Y , we used widely known methods]:

I) half-width of (222) line for initial Na₂SO₄ powder ($2\theta = 38.6^\circ$, $d_{222} = 0.233$ nm, see also figure 2a) was near to the TiCl (111) reflection by 2θ and $dhkl$ and was used for calculating of B_s value of the half-width of TiCl (111) reflection of MA samples using Scherrer formula, as

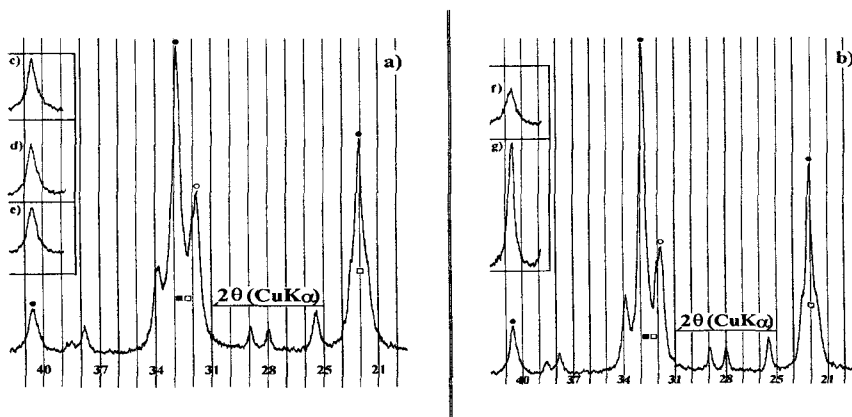


Figure 3. Characteristics of reaction (1) dynamics and crystallite size change as a function of MA time τ obtained by XRD method: a) $\tau = 1800$ s, b) $\tau = 2100$ s. Insets in figures 3a and 3b give the reflections (111) at $2\theta = 40.65^\circ$ for TiCl for the times τ : c) 600 s, d) 900 s, e) 3600 s, f) 5400 s, g) 300 s (vertical scale enlarged by $\sim 3-4$ times).

well as for calculating of a standard broadening B_{st} caused by a device using Warren formula;

II) only one Voigt line was used for approximation, assuming that the contribution of D into the line profile is described by the Cauchy and that of Y by the Gauss formulas. Integral intensities of peaks B_i were used.

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The reflections from (110) plane were overlapped, and also with some of Na_2SO_4 reflections (cf. figures 2 and 3), so the application of $B\cos\theta = (0.9\Lambda/D) + Y\sin\theta$ was hindered, where $\Lambda = 0.5418$ nm for $CuK\alpha$ radiation. The second orders of reflections (222, 444) were very weak because of high dispersion, distortion and redistribution of intensities because texturing of reagents and so useless for

unambiguous separation of D and Y effects. As a rule, all the methods described are illustrated by the original XRD patterns, as it is done also in this work.

Thus, the following numerical regularities were found at MA and nano-particles formation by the method of dilution with the end product, as a result of experimental study of (1) reaction: the theoretical value of mole dilution $z = z1^* = z^* = 11.25$ was proved; the kinetic curve of the reaction was obtained; the coefficient of mass transfer by mobile balls in an AGO-2 mill was found; the dimensions of crystallite sizes and of lattice strains were calculated for the end-product, nano- $TiCl$.

5. SUMMARY

Numerical modeling of the conditions of nano-particles mechano-synthesis by an end-product diluent method is carried out. Satisfactory conformity of theoretical estimations with the available and obtained experimental data is received.

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