Theory of Nanoparticles Mechanosynthesis

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ABSTRACT

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 nanoparticles 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 mechanoactivation of nano-TiCl
dilution of initial (2NaCl + Ti3SO4) mixture with the exchange reaction product (diluent, ZnNa2SO4, \( z = 11.25 \)) was studied experimentally. Some peculiar features of the reaction mechanism were found. Parameters of the kinetic curve of TiOCl obtained experimentally were compared with those for the model reaction \( KBr + TiCl_3 + ZnCl_2 = (z + 1) KCl + TiBr_2 (z = 13.3) \), 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 dilute phase may be necessary to: a) avoid combustion 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.

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

Reactions (1) analogue studied earlier exchange mechanochemical reaction KCl + NaNO3 = KNO3 + 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.

2. 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 (TiCl3 and TiBr3). Therefore, an experimental verification of theoretical results was performed on the reaction

\[ 2NaCl + Ti_3SO_4 + ZnNa_2SO_4 \rightarrow (z + 1) Na_2SO_4 + 2TiCl_3 + \Delta \cdot (\theta = 40 \text{ kJ/mole}) \]

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 %: 21.92\% for Na2SO4, 35.87\% for NaCl, and 4.87\% for Ti3SO4. Detailed conditions for the test reaction (1) in an AGO-2 steel two-vial-type water-cooled ball mill are given in table 2 (\( m_0 \)) denotes the mass of diluent Na2SO4 formed additionally). According to the values of hardness for the reagents (\( n = 1 \), halite NaCl, \( i = 2 \), thallium sulfate Ti3SO4, and \( i = 3 \) for the diluent, tennantite Na2SO4) the optimal dilution ought to be described by the value of \( z^* \) equal to 11.25, as the values of hardness are usually higher for sulfates than for halides:

\[ z^* = \frac{2p_2M_1R_3^3}{\Delta (R_1^3 + 2R_2^3)} \]

\[ \Delta = 11.25 \]

\[ z^* = \frac{2p_2M_1 + p_1M_2}{R_1^3 + 3R_2^3} \]

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 Ti3SO4 crystals. The mixtures of reagents of “chemically pure” quality and “pure” Ti3SO4, corresponding to the stoichiometric compositions with \( z = z_1^* \) and \( z = z_2^* = 5.44 \), 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 particles obtained from 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: \( R_0 = 1.25 \times 10^{-4} \) cm. The products of MA were examined by the standard method of powder X-ray analysis (XRD) on a diffractometer with filtered CuKα 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 TICI, 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 NH₄CNS, pseudohalogenide, and thiourea, non-conducting molecular crystal (NH₃)₂CS. A highly sensitive installation for the conductivity measurements was designed on the bases of an Impedance Meter BMS07, Tesla, Bino, 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 = 0.216 g of TICI and 8.206/20.77 = 0.395 g of Tl₂SO₄. In 1 ml of water ~3 mg of TICI and 48.7 mg of Tl₂SO₄ can be dissolved. Let us take that the solubility of MA TICI particles is about 10 times lower than that of Tl₂SO₄, i.e., in 1 ml of water ~5 mg of TICI 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 TICI and all the other components of the system. Therefore:

- experimental error in conductivity measurements could give the value of 0.05/0.216 = \(23\%\), based only on the 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 = \(7\%\);
- by means of correction factor 2, obtained by averaging over the composition or on one half of the transformation degree \(a\), the error could be diminished to \(4\%\) (diameter of the experimental points on kinetic curve just corresponds to the latter).

![Figure 1. Kinetic curve \(a(t, z^*)\) for (1) reaction as a function of MA time \(t\) and of the number \(n\) of abrasive-reactive interactions of particles of reagents in the region \(r^2\) of impact action produced by a milling tools in an AGO-2 mill, defined by the conductivity measurements of the solutions of MA samples.](image)

![Figure 2. XRD patterns for samples: a) charge for (1) after 1 h homogenization in a Fritsch Pulveronette mill, \(z = z^* = 11.25\); b) MA in an AGO-2 mill during 7200 s. o - NaCl, • - Tl₂SO₄, □ - Na₂SO₄, ● - TICI.](image)

7. 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 \(\gamma\) for the reaction nanoscale target product, nano-TICI. The only reflection free from overlapping is that (11) of TICI (figure 3). We used this advantage here below.

For calculating the crystallite size \(D\) and strain \(\gamma\), we used widely known methods:

1) half-width of (222) line for initial Na₂SO₄ powder (2\(\theta = 38.6^\circ\), \(\Delta 2\theta = 0.233\) nm, see also figure 2a) was near to the TICI (111) reflection by 2\(\theta\) and \(\Delta 2\theta\) and was used for calculating of \(B_\gamma\) value of the half-width of TICI (111) reflection of MA samples using Scherrer formula, as well as for calculating of a standard broadening \(B_\gamma\) caused by a device using Warren formula;

2) 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 \(\gamma\) by the Gauss formulas. Integral intensities of peaks \(B_\gamma\) were used.

![Figure 3. Characteristics of reaction (1) dynamics and crystallite size change as a function of MA time \(t\) 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 TICI for the times: c) 600 s, d) 900 s, e) 3600 s, f) 5400 s, g) 300 s (vertical scale enlarged by \(-3-4\) times).](image)

The reflections from (110) plane were overlapped, and also with some of Na₂SO₄ reflections (cf. figures 2 and 3), so the application of Bcos\(\theta\) = (\(0.9A/D\)) + Ysin\(\theta\) was hindered, where \(A = 0.5418\) 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 \(\gamma\) 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 \(z = z^* = 11.25\) 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-TICI.

8. 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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REFERENCES