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ENERGETIC APPROACH TO KINETICS OF MECHANOCHEMICAL PROCESS*

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Abstract

Kinetics of a mechanochemical process is proposed to describe quantitatively with a problem set-up scaled to energy instead of time. This makes possible the comparability of experimental data obtained in machines with different intensities of treatment.

Keywords: energetic efficiency, intensity of treatment, kinetics, mechanochemical process

Introduction

Today the theory of kinetics of mechanochemical transformations in solids is regarded as being behind the practical needs [1]. The present work has been undertaken to meet the requirement of the quantitative description of kinetics of a mechanochemical process, with respect to a machine in which the process takes place. (The term 'mechanochemical process' is considered as the general one, by which either mechanical activation, mechanochemical reaction, or comminution is meant.)

With few exceptions, the kinetics of a mechanochemical process is considered in literature with respect to time of treatment. However, formation of a process outcome depends first of all on the energy dose taken up in a treated substance (so called 'energy yield' [2]).

This can be illustrated with the following example. In Fig. 1a the increase of the specific surface area of graphite against the energy dose under various specific power inputs [3] is presented. Obviously, one and the same law describes the grinding of graphite in spite of different conditions of treatment.

The same dependence recalculated against the time of treatment is shown in Fig. lb. It looks as if presenting three different processes of different kinetics. It is quite opposite to Fig. la.

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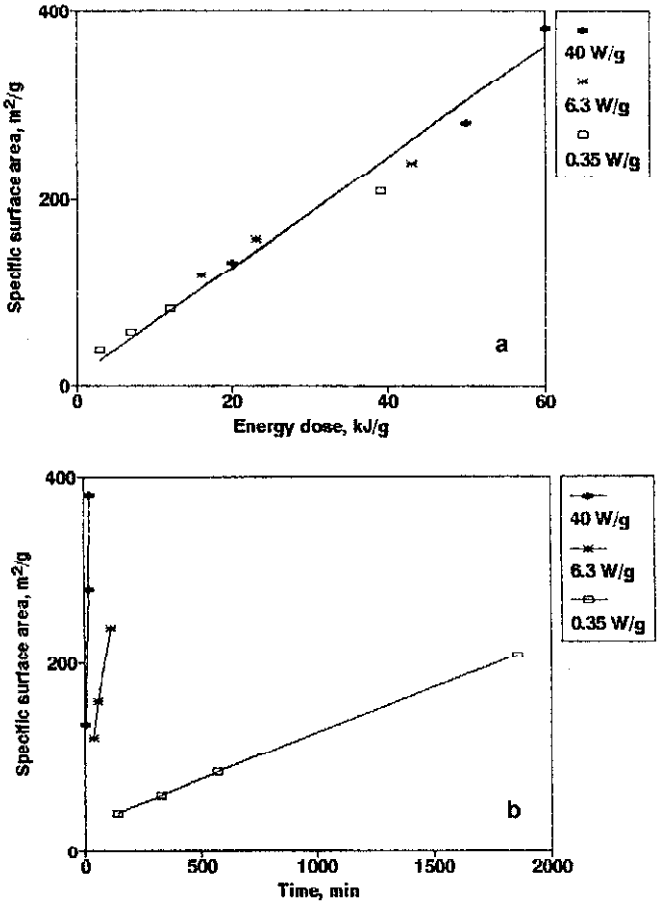

Fig. 1 Kinetics of comminution of graphite under various power inputs: a – against the energy dose; b – against the time of treatment

So, in a general way, the data obtained in different conditions with respect to time are incomparable and, consequently, irreproducible. In order to attain the reproducibility, one has to use the scale of the current energy as an argument of the process rather than that of the current time. Correspondingly, one has to move to other kinetic regulations than those concerned with time [4]. This kind of kinetics can be termed 'energy-scaled kinetics'.

Relationships of energy-scaled kinetics

For clarity of presentation and for definiteness of dimensions of quantities, the following is set out in terms of chemical reaction. For any one of the other outcomes (e.g. solubility, or specific surface area, etc.) all one needs to do is to substitute 'mole' by the respective dimensions.

In terms of energy-scaled kinetics the dimensions of the rate of a reaction product formation should be $[w]$=mol J^{-1} ; this quantity can be termed 'energy-scaled rate', the definition of which is the following:

$$w = \mathrm{d}W\mathrm{d}\varepsilon \tag{1}$$

that is the derivative of a concentration magnitude with respect to the energy taken up in a substance.

Consequently, the current concentration of a product is given by:

$$W = \int_0^\varepsilon w\mathrm{d}\varepsilon \tag{2}$$

where ε – the current energy taken up.

Now one has to determine the energy-scaled rate of formation of a product of chemical reaction.

Formally this rate has to obey the general law of chemical kinetics – the law of mass action: at constant temperature the rate of the reaction is proportional to the concentration of a substance taking part in the reaction:

$$-\frac{\mathrm{d}W}{\mathrm{d}\varepsilon} = kW^n \tag{3}$$

where k – the rate constant; n – the order of a reaction.

By the way, the same equation can be easily derived from a widely reported generalized equation of the Energy Laws of Comminution (Walker *et al.*, 1937; cited by Perry [5], p. 8–12): $\mathrm{d}E = -K\,\mathrm{d}d/d^n$ (E – the energy consumption; d – the particle size).

For an illustration, let us assume that the process is described by the simplest first order reaction of conversion of an initial reagent A into a product B:

$$A \rightarrow B.$$

The concentration of product

$$W_B = W_{Ao} - W_A \tag{4}$$

where W_{Ao} – the initial concentration of reagent A.

For the current concentration of reagent A we have:

$$-\frac{\mathrm{d}W_A}{\mathrm{d}\varepsilon} = kW_A \tag{5}$$

and

$$W_A = W_{A0}\exp(-k\varepsilon) \qquad (6)$$

Correspondingly, denoting the current concentration of the product of a reaction $W_B=W$, and the initial concentration value $W_{A0}=W_0$, one can yield:

$$W = W_0[1 - \exp(-k\varepsilon)]. \qquad (7)$$

Assuming the initial reagent being completely converted into the product of reaction, W_0 takes on an obvious meaning of the maximum magnitude of concentration attainable under the given conditions of treatment.

The energy taken up in the substance ε, contained in Eq. (7), is hardly measurable. So, it is worthy to substitute it by another quantity – the net energy input E_{net}. As applied to the so called drum mills with loose ball media, E_{net} is defined as the energy transferred directly into the ball media. Those mills represent a majority of machines being used for both mechanical activation and comminution, and comprise tumbling, vibratory, stirred, and planetary mills.

The ratio of the energy taken up in the substance to the net energy input (that is a characteristic of the energy transfer from ball media to a treated substance) can be defined as the factor of energetic efficiency η:

$$\eta = \frac{\varepsilon}{E_{net}}. \qquad (8)$$

(This definition is equivalent to the thermodynamic criterion of efficiency proposed by Tkacova [6].) Certainly, the factor η is dimensionless.

In classical chemical kinetics the law of mass action had to be modified by consideration of the rate constant as a function of the reactants' temperature. This dependence is expressed by the Arrhenius equation.

However, in the treatment of particulate solids the rate of transformation is determined by energetic conditions other than the temperature which sometimes does not affect the process at all [7].

The rate constant k contained in Eq. (7) has been introduced by Eq. (3) as a quantity energetic in nature and, consequently, needs no such modification. (Of course, if the temperature does affect the process, the common Arrhenius dependence $k=k(T)$ should be considered.)

However, the energy transfer from grinding balls to a treated substance depends on conditions of treatment, so a similar modification should be done for the factor η.

It is appropriate at this point to discuss an analog of 'temperature' in mechanical treatment of particulate solids.

In chemistry, the measure of kinetic energy of molecules (that is the energy of molecules collisions, which are the reason of a chemical transformation), called temperature, is used as the parameter of a chemical process (with the universal gas constant as a factor of transition to the dimensions of energy). So it is acceptable to use the measure of kinetic energy of loose ball media (that is the energy of balls collisions, which are the reason of a mechanochemical transformation) as the parameter of a mechanochemical process. This measure, usually referred to as an intensity of treatment would be the appropriate analog.

The question of which quantity in the mechanical treatment of particulate solids corresponds to 'intensity' is reviewed below.

A selection of experiments describing the efficiency of particulate solids treatment (in terms of rate of reaction, time and energy consumption, etc.) as a function of some intensity parameters (height of balls fall, amplitude of vibration, rate of stress, etc.) has been reported in the literature [6–8]. The common conlusions are:

(i) the greater the intensity, the less the energy consumption that is greater energetic efficiency;

(ii) the critical value of intensity was reported, below which the energy is not taken up in the substance at all, and the net energy consumption tends to infinity.

Unfortunately, each author in the mentioned experiments utilizes his own parameter characterizing the actual intensity of treatment, causing the data to be essentially incomparable. It is necessary to introduce a generally accepted definition of intensity; the relevant proposal is discussed in the next section.

Using the exponential form of the indicated dependence of the energetic efficiency on the intensity, and continuing the analogy with classical chemical kinetics, one may propose a general form of this dependence as the Arrhenius-like equation:

$$\eta = \eta_o \exp\left[\frac{-E_a}{I - I_o}\right] \tag{9}$$

where I – the actual intensity of treatment; E_a – the activation energy (with the dimensions either J mol^{-1} or J kg^{-1}; η_o – the maximum energetic efficiency, and I_o – the critical (threshold) intensity.

Certainly, the domain of the factor η is between zero and unity (or 100%); in fact, the maximum is about 25 to 30% [9] due to inevitable heat evolution.

Substitution Eq. (8) into (7) yields:

$$W = W_o[1 - \exp(-k\eta E_{net})] \tag{10}$$

where the product which includes both the conventional (i.e. temperature dependent) rate constant and the energetic efficiency:

$$\varepsilon = k\eta = k(T)\eta(I) = k\eta_o \exp\left[\frac{-E_a}{I - I_o}\right] \tag{11}$$

represents the 'general rate constant' in the form looking somewhat like the Butyagin's formula for the conventional rate constant (cited by Heinicke [7], p. 187), but differing in essence in that it contains the quantity of threshold intensity I_o.

For some substances, due to the small value of E_a , the intensity dependence of the energetic efficiency is not experimentally observed. Specifically, this case was mentioned in the introduction for the comminution of graphite (Fig. 1a).

A remark should be done. Everything set forth above concerns a specific single outcome of the process. However, one must bear in mind that if a competing process takes place (e.g., size reduction – agglomeration), the relationships may change. For example, the higher intensity may lead to the reduced rate of size reduction (due to shift of equilibrium to the agglomeration). In such a case one has to use the equilibrium constant rather than the isolated rate constant. (This consideration is beyond the scope of the given paper.)

The foregoing reasoning shows that the mechanochemical process can be readily described with well known equations of classical chemical kinetics with the following substitutions: 'energy' and 'intensity' should be used instead of 'time' and 'temperature', respectively.

Intensity of treatment

Complexity of physical processes accompanied by chemical conversions occurring in particulate solids in the course of mechanical treatment leads to an empirical approach to modeling; a dimensionless group as the scaling parameter is worthy of consideration.

The ratio contained in Eq. (9) of the activation energy to the difference of the actual intensity of treatment and the critical intensity – as including parameters of both substance being treated and a machine – is proposed to be such a group. It seems to be more convenient to consider an inverse ratio which may be termed the dimensionless intensity number:

$$In = \frac{I - I_o}{E_a}. \tag{12}$$

It is the measure of relation of the energetic potentials of the ball media of a machine and a substance being treated.

Thus, Eq. (9) can be rewritten as

$$\eta = \eta_o \exp\left(-\frac{1}{In}\right). \tag{13}$$

Obviously, the quantity of actual intensity I should have the dimensions of energy (more precisely – the activation energy).

The quantity of power transferred directly into the mill load (the net power input) is the actual characteristic of treatment. However, it is not appropriate to characterize its intensity, since it comprises the dimensions of time.

Therefore, it is logical to combine the net power input with some characteristic time; a product obtained would be the desired intensity.

A choice of what specific quantity would be the said 'characteristic time' is to a large extent arbitrary.

For the machine with some definite working cycle it makes sense to choose the duration of the cycle as the characteristic time.

The cycle of the drum mills with loose ball media is characterized by the angular frequency

$$f=\frac{w}{2\pi}\ \mathrm{Hz}$$

where w, rad s^{-1} – the angular velocity of a chamber rotation.

To meet the requirement of the same dimensions of intensity and activation energy, the net power input must be related either to a number of moles of a treated substance or to its mass. Let us designate both of the quantities as m_s. Hence it follows that the quantity given by:

$$I=\frac{P_{\mathrm{net}}}{m_s f},\ \mathrm{J\ kg^{-1}} \qquad (14)$$

should be defined as the actual intensity of treatment for a machine with the cyclic working process.

A similar quantity, also called intensity, has been proposed for the vibratory mills [10]. The power was related not to the amount of a treated substance, but to the volume of a mill's chamber:

$$I_v=\frac{P_{\mathrm{net}}}{Vf} \qquad (15)$$

where V – the chamber volume.

Correspondingly this quantity can be termed 'volumetric intensity'. Its dimensions J m^{-3}=Pa , that is the volumetric intensity characterizes to some extent the pressure exerted by balls collisions.

The use of volumetric intensity is also legitimate if the activation energy takes the dimensions J m^{-3} (instead of J mol^{-1} or J kg^{-1}). To do this the activation energy should be multiplied by the apparent density of the treated substance given by:

$$\rho^*=\frac{m_s}{V}. \qquad (16)$$

Hence, the volumetric activation energy is given by:

$$E_{av}=E_a\rho^* \qquad (17)$$

and the dimensionless intensity number (12) is kept the same for both mass and volumetric quantities of activation energy and intensity.

Thus, the quantity of actual intensity characteristic of the machines with cyclic working process, particularly of the mills with loose ball media, has been formulated. The dimensionless intensity number is proposed to be a scaling parameter. This requires, of course, an experimental verification.

Experimental illustration

Unfortunately, the kinetic data against the energy consumption under various intensities are rarely available in the literature. One example – comminution of graphite shown in the introduction (Fig. 1), which can be obviously described with the energy-scaled kinetics of zero order within the experimental range.

The following example should be considered as an illustration of the relationships proposed rather than a proof, since the experiment was intended for another purpose, and the data are insufficient.

The carbonile iron powder (CIP) was treated in vibratory mill SVM-2 [11]. The main technical description of the mill is as follows: maximum gross power (variable) – 2.2 kW; chamber volume – 10 l; angular velocity – 155 rad s^{-1}; maximum volumetric intensity (variable) 8.9 kPa. Steel balls charge – 36 kg; CIP charge – 3 kg.

The treatment allowed to reduce the temperature factor of magnetic permeance (TFMP) of CIP [12, 13]. The dependence of TFMP on the specific energy input under three different intensities is presented in Fig. 2 as experimental

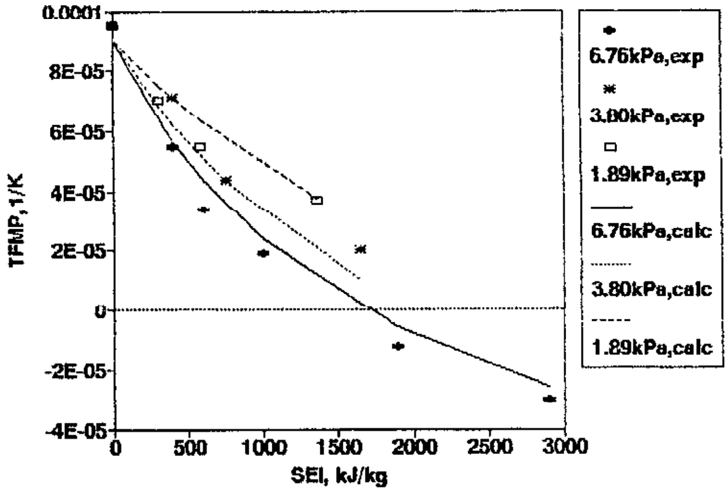

Fig. 2 Temperature factor of magnetic permeance (TFMP) *vs.* gross specific energy input (SEI) under various volumetric intensities (experimental and calculated data)

points. The gross energy input was measured and plotted instead of the net one. The temperature of the mill charge has been kept constant by means of a cooling jacket.

The process can be satisfactorily described with the second order equation, that is linearized in the coordinates of Fig. 3. A value of 100E-6 was added to the

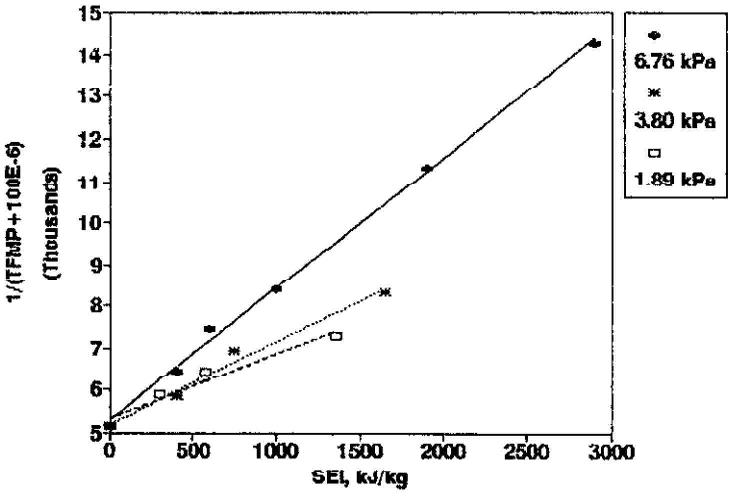

Fig. 3 Inverse temperature factor of magnetic permeance (TFMP) *vs.* gross specific energy input (SEI) under various volumetric intensities

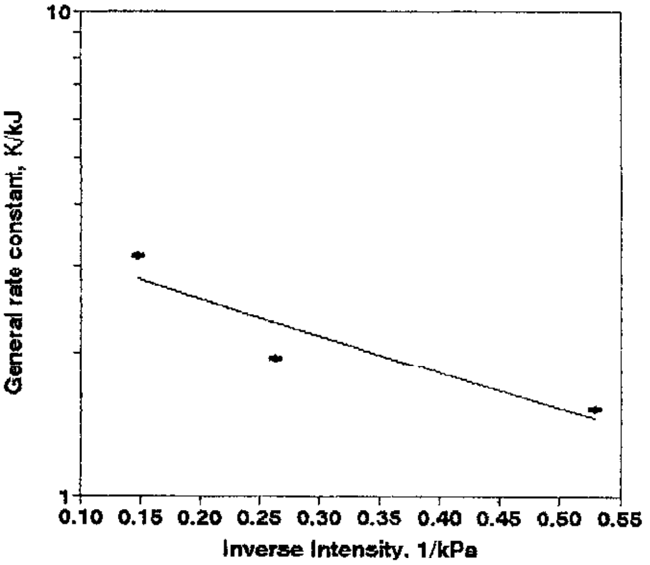

Fig. 4 General rate constant *vs.* inverse volumetric intensity

value of TFMP to avoid a function discontinuity at TFMP=0. The general rate constant was calculated as a tangent of the lines. Its dependence on the volumetric intensity (in the routine coordinates of the Arrhenius-like equation) is shown in Fig. 4.

The data should be admitted insufficient for determination of the critical intensity, so it was assumed $I_o=0$.

TFMP calculated by the equation

$$\frac{1}{Z}=\frac{1}{Z_o}+\varepsilon E_{gr}=\frac{1}{Z_o}+k\eta_o\exp\left(-\frac{E_{av}}{I_v}\right)E_{gr}$$

where Z=TFMP+100E-6, is presented as curves in Fig. 2. The values of pre-exponent $k\eta_o=3.6$ K kJ^{-1} and volumetric activation energy $E_{av}=1.7$ kJ m^{-3} were determined from Fig. 4.

The agreement of the experimental data with the calculated data is believed to be good enough for the first attempt of such a calculation. (The process has been successfully scaled up to the industry.)

Conclusions

Energetic approach to kinetics of a mechanochemical process has been developed. The mathematical apparatus of classical chemical kinetics has been proposed to describe the process quantitatively with the substitution of time by energy and of temperature by intensity.

The definition of the actual intensity of mechanical treatment of particulate solids for the machines with cyclic working process, particularly for drum mills with loose ball media, has been proposed. The dimensionless intensity number has been introduced and proposed to be a scaling parameter.

* * *

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References

1 P. Yu. Butyagin, Kinetics of Mechanochemical Transformations in Solids, lst Int. Conf. on Mechanochemistry Kosice, 1993, Cambridge Interscience Publishing, Cambridge 1993, p. 27.
2 P. Yu. Butyagin and I. K. Pavlichev, Reactivity of Solids, 1 (1986) 361.
3 P. Yu. Butyagin, Energy aspects of Mechanochemistry, in: Transaction of Siberian Branch of Academy of Science of the USSR, Chemical Science ser., 5 (1987) 48 (in Russian).

4 A. S. Kheifets, Energetic considerations in a planetary grinding mill, M. Sc. Thesis, Technion – Israel Institute of Technology, 1994.

5 R. H. Perry (Late Editor), Perry's Chemical Engineer's Handbook, McGraw-Hill, Sixth Edition, 1984.

6 K. Tkacova, Mechanical Activation of Minerals, Elsevier, Amsterdam 1989.

7 G. Heinicke, Tribochemistry, Carl Hanser Verlag, München 1984.

8 Mintek Bulletin, 56 (December), 1992.

9 A. S. Kolosov, in: Transaction of Siberian Branch of Academy of Science of the USSR, Chemical Science ser., 1 (1985) 26 (in Russian).

10 A. D. Lesin, Vibratory Mills, in: Vibrations in Technique, Handbook in 6 Volumes; Vol. 4 Moscow, Mashinostroyeniye, 1986 (in Russian).

11 A. D. Lesin and A. S Kheifets, Vibratory mill SVM-2, VNIIESM, ser. 7, vyp. 11 (1986), p. 3 (in Russian).

12 I. S. Tolmasski, V. G. Syrkin, G. G. Alekseyev, Yu. A.Chernov, A. I. Sazonov, A. S. Kheifets and A. D. Lesin, Method of manufacturing of carbonile iron powder. Inventor's Certificate of the USSR (1985) (in Russian).

13 I. S. Tolmasski, V. G. Syrkin, G. G. Alekseyev, Yu. A. Chernov, Yu. N. Maslov, A. V. Fedyay, A. D. Lesin and A. S. Kheifets, Method of treatment of carbonile iron powder. Inventor's Certificate of the USSR (1988) (in Russian).