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KINETICS OF CRYSTALLITE SIZE EVOLUTION BY BALL MILLING

One of the distinguishing features of mechanochemical treatment is crystallite size reduction. The crystallite size of the powder subjected to milling decreases to some minimal value characteristic for the given material. Two processes occur concurrently during milling: reduction of the crystallite size and grain growth, whereby the steady–state crystallite size is attained when the rates of these processes are in equilibrium. This study deals with the kinetics of crystallite size evolution by milling. Published experimental data were analyzed using three kinetic models: $dr/dt = -k_1 r^2 + k_2 r^{-1}$; $dr/dt = -k_1 r^3 + k_2 r$ and $dr/dt = -nkt^{n-1} (r - r_s)$, where r and r_s are the crystallite radius and steady–state crystallite radius, respectively, t time, k_1 and k_2 the rate constants of crystallite reduction and grain growth, respectively, k the rate constant and n the Avrami exponent. The applied kinetic relations describe the crystallite size dependence on milling time in a satisfactory manner.

Mechanochemical treatment has been recognized as a powerful tool for the synthesis of a wide range of materials. A monograph published in 1984 [1] is a good source of information about a great number of various mechanochemical reactions, as well as a basic text indicating the various aspects of mechanochemical phenomena. In addition, a number of reviews have appeared in recent years providing a general overview of mechanochemical methods [2,3], materials synthesized by mechanical alloying [3,4], as well as amorphization [5,6], the preparation of nanocrystalline materials [7,8] and displacement reactions [9] by milling.

Although the essence of the process is not fully understood, the accumulation of a large number of results published after 1984 allows several generalizations to be made for most mechanochemical reactions: (i) reactions induced by milling take place in nonequilibrium conditions whereby the final product retains the non–equilibrium state i.e., the structure is highly distorted, typically amorphous or nanocrystalline; (ii) the milling time required to attain the final products greatly depends on the milling conditions and (iii) before the chemical reaction can begin, the crystallite size needs to be decreased to the nanometer size range, typically between 5–20 nm.

Crystallite size reduction is perhaps the most distinguishing feature of mechanochemical treatment. A number of researchers have observed that the average crystallite size of either metal or ceramic powders decreases during milling. Several investigations were devoted exclusively to the preparation of nanocrystalline elemental metallic powders by ball milling [10–14]. It appears that a common feature of all the materials studied is that the crystallite size decreases with milling time to some minimal value characteristic for the given

material. With prolonged milling the crystallite size remains unchanged, therefore, further reduction seems to be difficult.

The development of nanocrystalline structures under the severe plastic deformation introduced by milling is explained by the mechanism of generating a large number of dislocations that on further deformation form grain boundaries [12]. It has been suggested [10–12] that a small grain size in itself prevents further plastic deformation via dislocation motion and, therefore, further grain size refinement by milling. However, it seems plausible, that recovery (e.g., annihilation of dislocations) and grain growth also occur during milling, thus limiting the reduction of grain size. Therefore, the final (steady–state) grain size achievable by ball milling is generally determined by the competition between heavy plastic deformation and the recovery behavior of the materials [12]. However, as already stated, due to the complexity of the phenomena occurring during milling, as well as the difficulties following them *in situ*, the mechanism of crystallite formation has remained undetermined.

It may be little bit surprising that investigation of the kinetics of crystallite size reduction by milling has been quite neglected, in spite of the fact that such a phenomenological approach may contribute to a deeper understanding of processes leading to nanocrystalline structures. To our knowledge, there are only two reports attempting to establish kinetic laws [15,16]. They both investigated iron powder subjected to milling taking into account the simultaneous processes of crystallite (grain) size reduction and grain growth occurring during milling. However, different relations for the rate of crystallite size evolution were derived. From the work of Secondi [15] it may be concluded that the process of crystallite size reduction is second order, i.e. $dr/dt \propto r^2$, while the crystallite growth rate scales with r^{-1}. On the other hand, Tian and Atzmon [16] developed a kinetic model in which the rates of crystallite size reduction and growth are third and first order, respectively. Therefore, there are

some discrepancies between those two kinetic models. Apart from that, our own research on the kinetics of mechanically induced reactions [17] reveals that they may be described by the expression widely used for solid–state reactions, namely the well–known Johnson –Mehl–Avrami equation. Therefore, it seems reasonable to apply it also to crystallite size reduction. Considering all these facts, it appears that there is a certain interest to test the proposed kinetic models to various materials milled under quite different milling conditions reported in the pertinent literature.

KINETIC RELATIONS OF THE CRYSTALLITE SIZE CHANGE WITH MILLING TIME

Second order rate law of crystallite size reduction

The first attempt to describe crystallite size reduction by milling was made by Secondi in his PhD thesis [15]. He investigated the milling of pure Fe powder in nitrogen atmosphere using a vibratory ball mill. The energy transformed to the grain (crystallite) boundary during impact was defined as:

$$E_{GB} = \left(\frac{1}{r} - \frac{1}{r_i}\right)3\gamma \tag{1}$$

where r and r_i are the crystallite size before and after impact respectively and γ the surface energy.

The power transferred to the grain boundary, W_{GB}, is given as $W_{GB} = -E_{GB}/\tau$, where τ is the time of impact. If $\Delta t = \tau$ then the rate of crystallite size reduction in incremental form is:

$$\frac{\Delta r}{\Delta t} = \frac{-W_{GB}r^2}{3\gamma} \tag{2}$$

The role of grain growth was also taken into account. Presumably, the steady–state crystallite size would be characterized by the equilibrium between the rates of crystallite site reduction and the grain growth. For the thermal process, the grain growth may be expressed as [18]:

$$r^m - r_i^m = Dt \tag{3}$$

or in incremental form as:

$$\frac{\Delta r}{\Delta t} = \frac{D}{mr^{m-1}} \tag{4}$$

where D is the coefficient of diffusion, t time and m a coefficient having a theoretical value of 2.

Hence, considering both phenomena the following equation was obtained:

$$\frac{\Delta r}{\Delta t} = \frac{-W_{GB}r^2}{3\gamma} + \frac{D}{mr^{m-1}} \tag{5}$$

Good agreement was obtained between experimentally obtained values and those predicted by eq. 5, taking the physical constants of pure Fe for the

calculation: $D \approx 1 \times 10^{-12}$ cm^2 s^{-1}, $W_{GB} \approx 6$ W mm^{-3} and $\gamma \approx 1.14$ J m^{-2}.

In order to apply eq. 5 to other materials, $W_{GB}/3\gamma$ may be replaced by k_1 and D by k_2, where k_1 and k_2 are the rate constants of crystallite size reduction and grain (crystallite) growth, respectively.

Thus, the generalized expression of overall crystallite size change with milling time may be given as:

$$\frac{dr}{dt} = -k_1 r^2 + \frac{k_2}{2r} \tag{6}$$

or in the integral form:

$$\frac{1}{k_1} \int \frac{r dr}{\frac{k_2}{2k_1} - r^3} = dt \tag{7}$$

Replacing $a = \sqrt[3]{k_2 / 2k_1}$ and $X = a^3 - r^3$, integration yields t as a function of r:

$$t = \frac{1}{k_1}\left[\frac{1}{6a}\ln\frac{a^2 + ar + r^2}{(a-r)^2} - \frac{1}{a\sqrt{3}}arctg\left(\frac{2r+a}{a\sqrt{3}}\right)\right] + C \tag{8}$$

The constant of integration, C, is determined from the initial conditions, $t = 0$, $r = r_0$.

The rate constant of grain growth, k_2 (m^2 s^{-1}) may be estimated assuming that in the stationary state, where $\dot{r}_1 = \dot{r}_2$, hence $k_1 r_r^2 = k_2/2r_g$, the crystallite size for both reactions is equal, thus $r_r = r_g = r_s$, where the subscripts r, g and s denote reduction, growth and steady–state, respectively.

The steady–state crystallite size was takes as the average of the values in the stationary state and are given in Table 1. Hence, the rate constant of grain growth was estimated from the relation $k_2 \approx 2k_1 r_s^3$.

The following expression is suitable for the analysis of kinetic data:

$$\frac{1}{r} = \frac{1}{r_0} + k_1 t \tag{9}$$

which shows that the reaction is second order, if a plot of $1/r$ against t gives a straight line. The slope of the line is equal to the rate konstant k_1.

Third order rate law of crystallite size reduction

Tian and Atzmon [16] investigated grain size evolution in Fe powder as a function of milling temperature and the amplitude of the vibratory ball mill in argon atmosphere. The data were analyzed by a model considering simultaneous grain refinement by plastic deformation and normal grain growth. The following expression for the rate of crystallite size, r was obtained:

$$\frac{dr}{dt} = -k_1 r^3 + k_2 r \tag{10}$$

The first term in eq. 10 is due to grain refinement by deformation. The second term is based on normal

Table 1. Initial, r_0 and steady–state, r_s crystallite radius and kinetic constants for crystallite size reduction by ball milling various materials

Material	r_0 $(10^{-9}$ m)	r_s $(10^{-9}$ m)	Second–order rate law, k_1 $(m^{-1} s^{-1})$	Third–order rate law, k_1 $(m^{-2} s^{-1})$	Avrami equation, k (s^{-n})	n	Mill type	Reference
Al	20*	12.5	147	9.65×10^9	1.73×10^{-9}	1.77	horizontal ball mill	13
Ag	20*	11.5	69	5.45×10^9	8.92×10^{-6}	0.89	horizontal ball mill	13
Cu	20*	10	205	1.56×10^{10}	3.95×10^{-5}	0.87	horizontal ball mill	13
Ni	20*	5.4	278	3.13×10^{10}	4.7×10^{-3}	0.48	horizontal ball mill	13
Fe	28*	4.3	173	1.64×10^{10}	6.06×10^{-3}	0.45	horizontal ball mill	13
W	12	2.5	356	8×10^{10}	4.42×10^{10}	0.99	horizontal ball mill	13
Mo	20	2.5	680	3.11×10^{11}	3.23×10^{-4}	0.71	horizontal ball mill	20
Fe	37*	5.5	107	1.19×10^{10}	1.8×10^{-5}	0.87	vibratory ball mill	15
Fe	40*	3.9	2107	2.54×10^{11}	3.49×10^{-2}	0.40	vibratory ball mill	16
Al	83	11	6422	2.59×10^{11}	7.7×10^{-1}	0.15	shaker ball mill	12
Ni	25	5.5	7800	7.6×10^{11}	7.83×10^{-3}	0.59	shaker ball mill	12
Pd	14	3	3700	3.72×10^{11}	9.76×10^{-4}	0.73	shaker ball mill	12
Ni	60	8.3	7605	3.08×10^{11}	5.63×10^{-2}	0.42	shaker ball mill	22
Ti	75	6.5	7405	2.11×10^{11}	3.29×10^{-2}	0.46	shaker ball mill	23
Ru	24*	6.5	3763	4.72×10^{11}	2.6×10^{-2}	0.43	shaker ball mill	10
AlRu	20	4	6028	6.8×10^{11}	4.88×10^{-3}	0.33	shaker ball mill	10
Fe_2O_3	117*	10	32839	2.18×10^{12}	1.89×10^{-4}	1.37	planetary ball mill	21
$MgFe_2O_4$	65	8	514	3.51×10^{10}	8.63×10^{-6}	1.05	planetary ball mill	24
$NiFe_2O_4$	50	9.5	561	3.44×10^{10}	5.27×10^{-6}	1.14	planetary ball mill	24

*Estimated value

grain growth. The authors claimed that the power of r differs from -1 for grain growth (compare eq. 6) because the vacancy sink density, which affects the diffusion coefficient, depends on the grain size. The model assumptions predict $k_2 \propto A^{1/2}$ and $k_1 \propto A^{3/2}$, where A is the amplitude of the vibratory ball mill, yielding for the steady–state grain size: $r = (k_2/k_1)^{1/2} \propto A^{-1/2}$. If the temperature dependence of the rate of vacancy production and that of grain refinement is ignored, k_2 and k_1 are predicted to be temperature independent. Equation 10 may be easily integrated to yield:

$$r = \sqrt{\frac{1}{\frac{1}{r_s^2} + \left(\frac{1}{r_0^2} + \frac{1}{r_s^2}\right) e^{-2k_2 t}}} \qquad (11)$$

where r_0 and r_s are the initial and steady–state crystallite radius respectively, k_2 the rate constant for the grain growth and t time. The rate constant, k_2 (s^{-1}) is estimated from the relation $k_2 = k_1 r_s^2$.

The following expression is suitable for the analysis of kinetic data:

$$\frac{1}{r^2} = \frac{1}{r_0^2} + 2k_1 t \qquad (12)$$

which shows that the reaction is third order, if a plot of $1/r^2$ against t gives a straight line. The rate constant is calculated from $k_1 = $ slope/2.

The Johnson–Mehl–Avrami equation

One of the most frequently used kinetic models applied to various solid–state reactions is the Johnson–Mehl–Avrami equation, for example [19]:

$$X = 1 - e^{-kt^n} \qquad (13)$$

where X is the volume fraction transformed at time t, k is the rate constant and n is the Avrami exponent which reflects the nucleation and growth morphology. Therefore, it seems reasonable to test it for the dependence of crystallite size evolution on milling time. For this case, X may be expressed as $X = (r_0 - r) / (r_0 - r_s)$, where r_0 and r_s are the initial and steady–state crystallite radius, respectively. Thus, eq. 13 may be expressed in differential form as:

$$\frac{dr}{dt} = -nkt^{n-1}(r - r_s) \qquad (14)$$

yielding after integration:

$$r = r_s + (r_0 - r_s) e^{-kt^n} \qquad (15)$$

The kinetic data are analyses from the linear plot $\ln(-\ln(X))$ vs. $\ln t$.

ANALYSIS OF THE EXPERIMENTAL DATA

Selected experimental data of crystallite size reduction due to milling reported in the literature were analyzed by the kinetic models presented in the previous section. Regarding all the analyzed experimental data, the plots of either $1/r$ or $1/r^2$ against t revealed, in general, three regions. The first was a linear dependence corresponding to either the second– or third–order rate dependence. The second was deviation from a straight line indicating that some other processes also occurred besides crystallite size reduction. The third region might be attributed to the steady state in which the data were scattered around a straight line parallel to the abscissa. Characteristic examples of the plot of $1/r$ and $1/r^2$ against t, are given in Figs. 1 and 2.

The rate constant of crystallite size reduction, k_1 was determined for various materials from the linear part of the plot of either $1/r$ or $1/r^2$ vs. t and are given in Tab. 1. As may be seen, the rate constant depends remarkably on the material properties, as well as on the type of the mill, i.e. the rate of energy transfer to the powder. For the pure metal powders Al, Ag, Cu, Ni, Fe and W, milled under the same milling conditions [13], as may be expected, k_1 roughly scales with the melting point (and surface energy as well), with the exception of Al. The
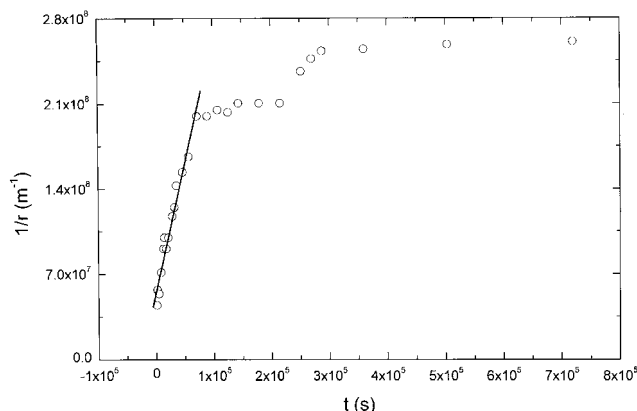

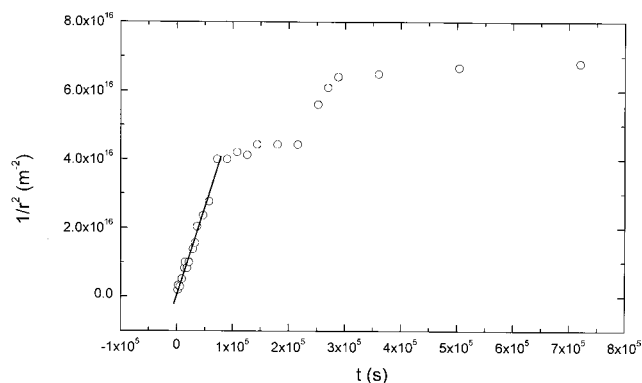Figure 1. A plot of $1/r$ against t for the data of Fe powder milled in a vibratory ball mill [16]

Figure 2. A plot of $1/r^2$ against t for the data of Fe powder milled in a vibratory ball mill [16].

influence of the milling conditions is also obvious. Thus, by comparing the rate constants of Ni milled in different mills, it may be seen that it is an order of magnitude higher for a shaker mill [12] than for a horizontal ball mill [13]: about 7800 and 278 m^{-1} s^{-1} (or 7.6 x 10^{11} and 3.13 x 10^{10} m^{-2} s^{-1}), respectively. It may be of interest to note that the values of the rate constant for Ni powder of 7800 and 7605 m^{-1} s^{-1} (or 7.60 x 10^{11} and 3.08 x 10^{11} m^{-2} s^{-1}), determined in two independent experimental studies [12,22], are similar suggesting that the experiments were conducted under similar milling conditions.

To test the third kinetic model a plot of $\ln(-\ln(1-X)$ against lnt, where X is defined as $X = (r_0-r)/(r_0-r_s)$ was applied. An approximately linear dependence was obtained for all data revealing that crystallite size evolution could be described by the kinetic equation expressed by eq. 15. A characteristic example is given in Fig. 3. The derived kinetic data are given in Table I. The empirical exponent n may be roughly classified into two groups: $0.3 < n < 0.5$ and $0.7 < n < 1$, except Al and perhaps Fe_2O_3, which exhibit unusual behavior. Tentatively, the physical meaning may be attributed to these values: new crystallites were formed by either one– $(0.3 < n < 0.5)$ or two–dimensional $(0.7 < n < 1)$ growth of the grain boundaries. In comparison, it may be noted that $n > 2$ for mechanochemical treatment in which a chemica reaction occurs i.e. $Ni + CuO \rightarrow Cu + NiO$ [17].

The three theoretical curves given by eqs. 8, 11 and 15, compared to the experimental data for iron powder milled in a vibratory mill (amplitude: 1.5 mm, temperature: 298 K), are given in Fig. 4. As may be seen, eqs. 11 and 15 fit the experimental data very well (the curves almost overlap) while eq. 8 overestimates the experimental data in the region of intensive crystallite change (milling time up to 1 x 10^5 s). In general, all the analyzed materials exhibit similar features during milling. Plausibly, the phenomenological laws are a consequence of identical or similar mechanisms of crystallite size reduction being inherent to all the
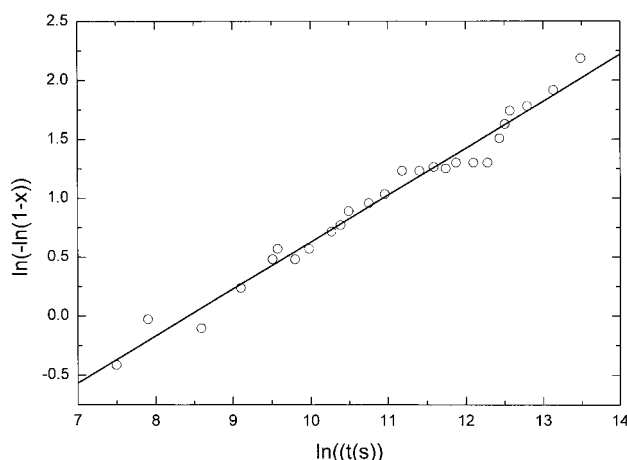

Figure 3. A plot of $\ln(-\ln(1-X)$ against lnt for the data of Fe powder milled in a vibratory ball mill; $X = (r_0 - r)/(r_0 - r_s)$ [16].
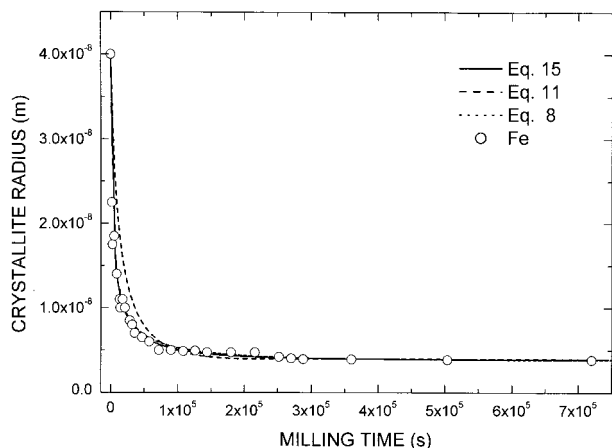
Figure 4. Comparison of the theoretical curves (full line, eq. 15; dashed line, eq. 11; dotted line, eq. 8) with the experimental data for Fe powder [16].
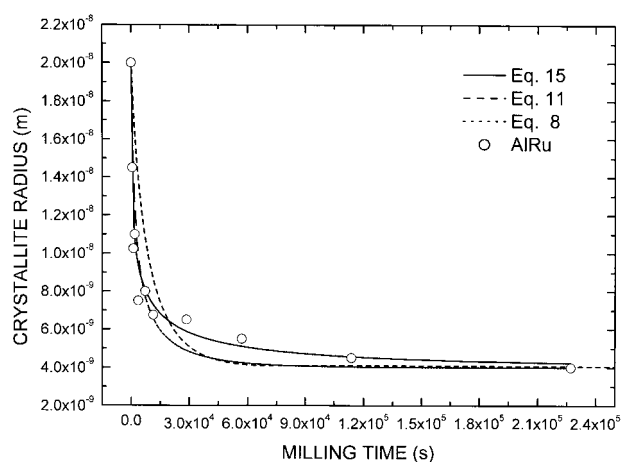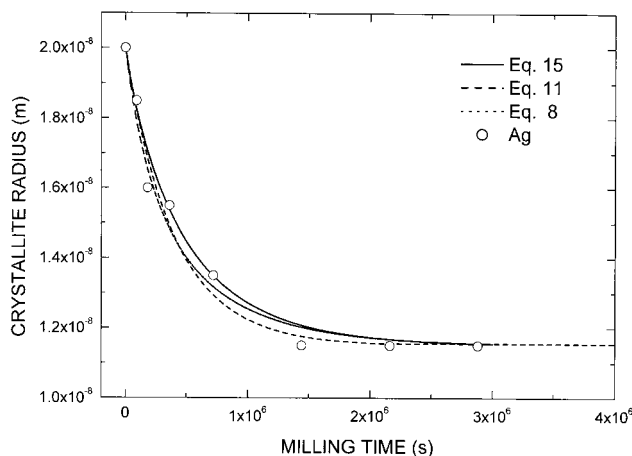

Figure 5. Comparison of the theoretical curves (full line, eq. 15; dashed line, eq. 11; dotted line, eq. 8) with the experimental data for Ag powder [13].
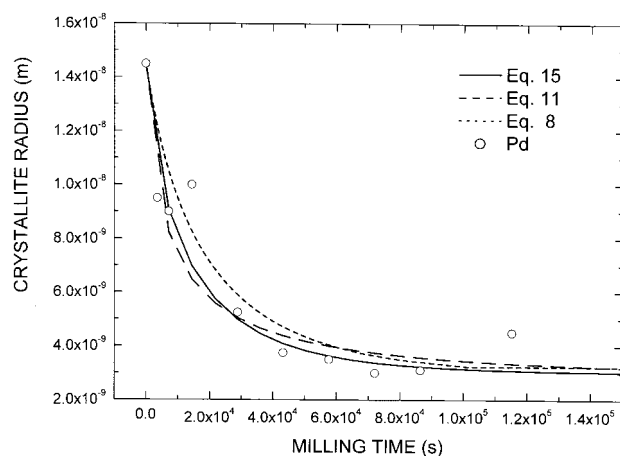

Figure 6. Comparison of the theoretical curves (full line, eq. 15; dashed line, eq. 11; dotted line, eq. 8) with the experimental data for Pd powder [12].

Figure 7. Comparison of the theoretical curves (full line, eq. 15; dashed line, eq. 11; dotted line, eq. 8) with the experimental data for AlRu powder [10].

analyzed materials. As an illustration, the theoretical prediction in comparison with the experimental data of pure Ag [13] and Pd [12] metals and the intermetallic compound AlRu [10], chosen to represent various materials milled under different milling conditions, are also presented in Figs. 5–7.

As a remark, it should be stressed that the purpose of analyzing the literature experimental data was to test the presented kinetic models. Therefore, the determined kinetic data may not be completely accurate. For a more precise determination, experiments should be performed under well–defined milling conditions (e.g. control of mill velocity and ball–to–powder mass ratio) and samples should be taken more frequently. The only exception is the evolution of Fe crystallite size for which experimental data were obtained from carefully performed experiments [16]. Figure 8 gives agreement between the experimental [16] and calculated crystallite size using the three kinetic models. As may be seen, there is very good agreement for the second (Fig. 8b) and the third (Fig. 8c) model, with regression coefficients of 0.9905 and 0.9952, respectively. For the first model (Fig. 8a), the agreement is not quite as good (regression coefficient 0.9249). In general, it seems likely that eq. 11 and eq. 15 fit the experimental data better than eq. 8. However, a firm conclusion which kinetic model describes the experimental data the best should be avoided at this stage of the investigation.

CONCLUSION

Considering the importance of crystallite size evolution during mechanochemical treatment by milling, this study was an attempt to investigate the kinetics of such a process. The three applied kinetic models describe the experimental data considered well regardless of the notably different physical properties of the materials subjected to milling under various milling conditions (which influence the different time scales required to reach steady–state crystallite size).
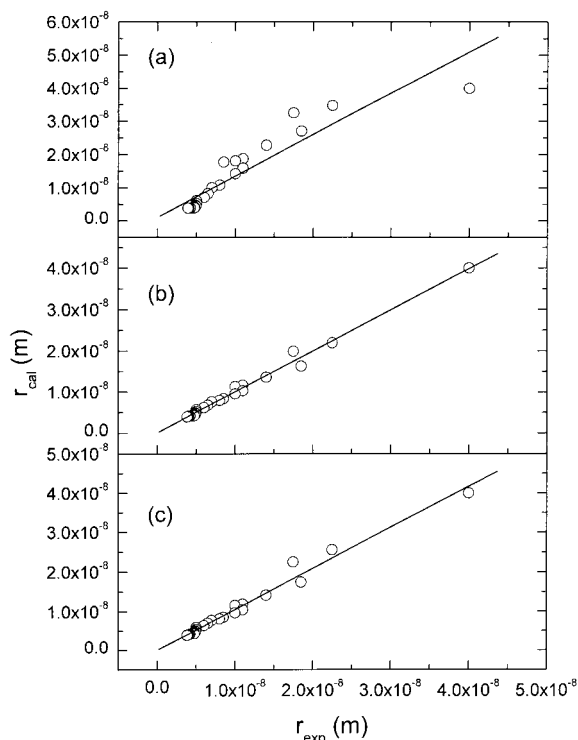
Figure 8. Agreement between the values of the experimental and calculated crystallite radius of Fe powder [16]; (a) eq. 8; (b) eq. 11; (c) eq. 15.

Regarding the incompleteness of the experimental data, firm conclusions on the most reliable model should be avoided at this stage of the investigation.

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IZVOD

KINETIKA STVARANJA KRISTALITA U PROCESU MEHANIČKOG MLEVENJA

(Naučni rad)

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Smanjenje veličine kristalita je jedna od od prepoznatljivih osobina mehano-hemijskog tretmana. Veličina kristalita praha podvrgnutog mlevenju se smanjuje do neke minimalne veličine karakteristične za dati materijal. Tokom mlevenja dva procesa se odvijaju istovremeno: smanjenje veličine kristalita i rast zrna, pri čemu se postojana veličina kristalita (minimalna veličina kristalita u stacionarnom stanju) dostiže kada su brzine ova dva procesa u ravnoteži. Predmet ovoga rada je kinetika promene veličine kristalita sa vremenom mlevenja. Publikovani eksperimentalni podaci su analizirani pomoću tri kinetička modela: $dr/dt = -k_1 r^2 + k_2 r^{-1}$; $dr/dt = -k_1 r^3 + k_2 r$ i $dr/dt = -nkt^{n-1} (r-r_s)$, gde je r poluprečnik kristalita, r_s postojani poluprečnik kristalita, k_1 konstanta brzine reakcije smanjenja veličine kristalita, k_2 konstanta brzine reakcije rasta zrna, k konstanta brzine reakcije i n Avramijev koeficijent. Pokazano je da primenjene kinetičke jednačine zadovoljavajuće opisuju zavisnost veličine kristalita od vremena mlevenja.

Ključne reči: Mehanohemijski tretman • Mlevenje • Veličina kristalita • Reakcije u čvrstom stanju •

Key words: Mechanochemical treatment • Ball milling • Crystallite size • Solid–state reactions •