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The size refinement of Cu crystallites under mechanical processing conditions: a phenomenological modeling approach

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Abstract A phenomenological model is developed for describing the kinetics of the crystallite size refinement process of Cu powder under mechanical treatment conditions. Based on the evidence that collisions represent the elementary events of energy transfer, the rate of crystallite size decrease is related on a statistical basis to the amount of powder trapped at each collision, to the number of collisions and to the collision energy. The mathematical approach allows for identifying the approximate functional form of the kinetic curves obtained at largely different impact energies. The values of the apparent kinetic constants and of the model parameters involved can be thus estimated by fitting the model curves to the experimental data. The results obtained provide a deeper insight into the details of the crystallite size refinement process.

Introduction

The mechanical processing of powder in ball mills combines a remarkable simplicity with a unique capability of promoting thermodynamically disfavored reactions and destabilizing equilibrium compounds [1, 2]. The production of metastable phases such as amorphous and nanostructured systems is accomplished via the excitation of unusual states of reactivity due to the direct application of mechanical forces to powder particles [2]. Repeatedly trapped between the colliding surfaces of milling tools, these undergo coalescence and fracturing events as well as plastic deformation [2]. This latter determines a gradual modification of the microstructure, with the initial formation of grain boundaries and a successive refinement of coherent crystalline domains down to the nanometer range [2].

The apparent simplicity of the mechanical treatment hides however a complex mix of intertwined processes that still represents a challenge to the scientists working in the field and an obstacle to the application of mechanochemical methodologies to the industrial production of advanced materials [2]. For example, the intimate nature of the local excited states appearing in the solid phases as a result of mechanical forces as well as the atomic-scale processes underlying the transformation mechanisms are still intensely debated questions [2, 3]. At the same time, the field also lacks a systematic investigation of the kinetic features of the various processes taking place under mechanical processing conditions [3]. This is a consequence of the undeniable intrinsic difficulties of defining a comprehensive conceptual framework as well as of the inadequate characterization of both mechanical treatment regimes and transformation degrees [3–6]. Any advance of basic knowledge in these directions could then significantly contribute to rationalize the mechanochemical reactivity and open the door to practical applications [3].

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Along this line, the present work attempts to gain deeper insight into the intimate kinetic features of the crystallite size refinement process in elemental Cu powder mechanically processed at largely different impact energies. A phenomenological description of the mechanical processing is carried out laying emphasis on its intrinsic statistical character.

Phenomenology of the mechanical processing of powder by ball milling

The processing of powder in ball mills is characterized by three fundamental features. In the first place, the transfer of significant amounts of energy to the powder takes place at the impact events in which both powder and milling tools are involved. The amount of energy transferred in collisions involving only powder particles is indeed negligible. In the second place, only a relatively small fraction of the total powder charge is trapped between the colliding surfaces of milling tools at each impact. Finally, the turbulent granular flow within the moving vial is such that powder particles are constantly remixed and the powder involved in a given collision effectively redistributed in the whole powder charge after the impact [7]. All the powder particles have then roughly the same probability of being involved in the successive collision. It follows that the mechanical treatment of powder is a discrete process with a statistical character.

Powder particles undergo fracturing and coalescence processes that continuously change their number during the course of the mechanical treatment [2]. However, being dependent on the size of the milling tools and their relative impact velocity as well as on the total amount of powder inside the vial [8, 9], the volume of powder trapped between the colliding surfaces of milling tools remains approximately constant. This is a simplifying evidence in view of a statistical description of the gradual modification of powder properties induced by the sequence of collisions.

The mechanical loading and shearing at impact underlie all the processes taking place during the course of the mechanical treatment. Coalescence and fracturing events induce a variation of the number as well as of the morphology of powder particles. Local deformations determine the decrease of the crystallite size and the accumulation of lattice disorder. This in turn can promote phase transitions and chemical transformations. The rationale for the evidence that the processes mentioned above occur at different rates [2–6] can be roughly provided by considering the ideal system schematically depicted in Fig. 1. It consists of a

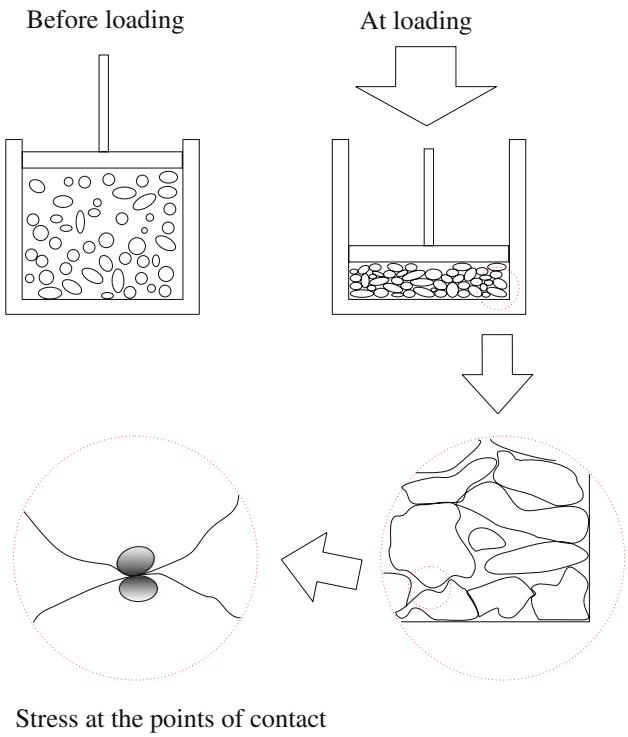

Fig. 1 A two-dimensional schematic representation of the special case of the processing by BM in which all the powder is always involved in each impact event. The powder particles are located within a cylindrical chamber closed by a piston sliding without attrition. The piston periodically exerts a mechanical load on the powder particles at a given rate. As roughly shown in the circle at the bottom on the right, during the compression stage the particles come into intimate contact establishing a so-called force network. The circle at the bottom on the left shows the mechanical stress developing at the points of contact between two particles

set of powder particles located within a cylindrical container closed by a mobile piston free to slide without attrition. The powder particles have different size but the same chemical nature. The piston periodically loads the volume of powder at a certain rate, reproducing the conditions experienced by the powder at impact. In order that the system could represent the special case of powder processing by ball milling in which all the powder charge is involved in each collision event, the loadings are assumed to take place on random configurations of particles. The mechanical load, which brings the particles into intimate contact and determines their plastic deformation, is not uniformly distributed within the powder. On the contrary, it is sustained by the force network formed by the points of contact between the particles [10–12]. Thus, even though all the particles are likely to undergo morphological modifications, only at the points involved in the force network severe plastic deformation occurs. This means that not all the volume

of a given particle undergoes the decrease of the crystallite size, but only a fraction. The rate of crystallite size decrease is therefore proportional to the volume of powder in which the necessary degree of deformation is attained.

Various questions arise in connection with the observations above concerning the ideal system. Among the others, how large is the fraction of loaded powder involved in deformation processes severe enough to induce a decrease of the crystallite size? How many loading events are necessary to attain a given average crystallite size? A further question arises in the real case of mechanical treatment, given that not the entire powder charge is trapped at each collision. The number of loading events experienced by a given fraction of powder does not generally correspond thus to the total number of collisions. Which is therefore the relationship between the number of loading events experienced by a given fraction of the powder charge and the total number of collisions? Under certain assumptions, an approximate answer to the questions above can be found.

Kinetic modeling of the crystallite size refinement process

For sake of both simplicity and comparison with apposite experimental data, the model is referred to the case in which the processing of powder is carried out with a single milling ball.

Let us assume that the volume v_{imp} and the average density ρ of the powder trapped at each collision remain constant during the processing, so that the mass $m_{\mathrm{imp}} = v_{\mathrm{imp}}\rho$ of powder involved on the average at each collision is also constant. The rate at which the crystallite size decreases will be necessarily proportional to the volume fraction $x_{\mathrm{imp}} = v_{\mathrm{imp}}/v_{\mathrm{p}}$ of impacted powder, v_{p} being the volume of the total powder charge. Let us assume in addition that the crystallite size will decrease only in the fraction of powder that experiences critical loading conditions (CLCs), i.e. a mechanical stress σ higher than a threshold value σ_0. This quantity corresponds then to the lowest mechanical stress necessary to induce a decrease of the crystallite size. For the reasons previously explained, the volume fraction k of the powder charge experiencing CLCs at each impact is expected to be smaller than x_{imp}. Finally, let us consider the powder as perfectly remixed after each impact, so that the powder charge is kept homogeneous. It follows that all the volume fractions k in which the powder charge can be ideally subdivided have the same probability of being involved in a collision.

The assumptions above permit an exact analytical description of the statistic underlying the kinetics of mechanically induced processes. Define χ_0 as the volume fraction of powder charge that never experienced CLCs. Of course, χ_0 is equal to 1 before the first impact. After the first impact has taken place, a volume fraction $\chi_1(1) = k$ of the impacted powder has experienced for the first time CLCs. The fraction of powder charge that never experienced CLCs is then equal to $\chi_0(1) = 1 - k$. After the second impact, the fraction of powder that never experienced CLCs becomes equal to $\chi_0(2) = (1 - k)^2$. The fractions of powder that experienced CLCs one and two times are instead equal respectively to $\chi_1(2) = 2k(1 - k)$ and $\chi_2(2) = k^2$. The fraction of powder $\chi_0(n)$ that never experienced CLCs after n impacts can only decrease as the number n of collisions increases, so that

$$\chi_0(n+1) = \chi_0(n) - k\chi_0(n). \tag{1}$$

The amount of powder that experienced CLCs for i times after n impacts depends instead on two contributions. The first one is related to the fact that at the nth collision a fraction $k\chi_i(n)$ experiences CLCs for the $(i + 1)$th time, becoming part of the fraction $\chi_{i+1}(n)$. The second contribution is due to the fraction $k\chi_{i-1}(n)$ experiencing CLCs for the i-th time, which contributes to the fraction $\chi_i(n)$. It then follows that

$$\chi_i(n+1) = \chi_i(n) - k\chi_i(n) + k\chi_{i-1}(n). \tag{2}$$

The experimental evidence that the decrease of the average crystallite size L requires a relatively large number n of collisions suggests that the fraction k of powder experiencing CLCs at each impact is small [2–9]. Under such circumstances, the discrete equations above can be written in continuous form. Correspondingly,

$$\mathrm{d}\chi_0(n) = -k\chi_0(n)\mathrm{d}n \tag{3}$$

and

$$\mathrm{d}\chi_0(n) = -k\chi_i(n)\mathrm{d}n + k\chi_{i-1}(n)\mathrm{d}n. \tag{4}$$

Eq. 3 is solved by

$$\chi_0(n) = \mathrm{e}^{-kn}, \tag{5}$$

whereas the solution to Eq. 4 is [13]

$$\chi_i(n) = \frac{(kn)^i}{i!}\mathrm{e}^{-kn}. \tag{6}$$

$\sum_{i=0}^{\infty} \chi_i(n) = 1$ given that the total amount of powders does not change during the course of the mechanical processing.

The curves in Eqs. 5 and 6 are at the basis of a rough description of the kinetics of the crystallite size refinement process under mechanical processing conditions. Let us assume that the powder that experienced CLCs for i times has a characteristic average crystallite size L_i. The average crystallite size L of the whole powder charge is therefore equal to

$$L = \sum_{i=0}^{n} \chi_i(n)\, L_i = \left[L_0 + kn\, L_1 + \frac{(kn)^2}{2}\, L_2 + \cdots \right] \mathrm{e}^{-kn}. \tag{7}$$

The quantity k represents the apparent rate constant of the process of crystallite size decrease, whereas L_0, L_1, L_2, ..., L_i, ... are the crystallite sizes pertaining to the powder fractions that experienced CLCs for 0, 1, 2, ..., i, ... times, respectively. Given that the decrease of the crystallite size is expected to be progressive, $L_0 > L_1 > L_2 > \ldots\ L_i > \ldots$. The relationship between successive L_0, L_1, L_2, ..., L_i, ... values is however completely lacking. Given a certain volume fraction of powder, which is the L_i value attained after the ith critical loading event? How many critical loading events are necessary for a given volume fraction to attain the final asymptotic L_f value of crystallite size? It is evident that the relationship between the L_0, L_1, L_2, ..., L_i, ..., L_f values represents one of the fundamental questions underlying the process of crystallite size decrease.

According to Eq. 7, the complete characterization of the curve describing the gradual decrease of the average crystallite size L requires the estimation of all the L_0, L_1, L_2, ..., L_i, ... ,L_f values. Although possible in principle, the quantification of such values is not permitted by the currently available experimental methods. In spite of this, the comparison between experimental data and theoretical curves could however provide a first, though limited, insight.

Let us consider some possible relationships between the L_0, L_1 ,L_2, ..., L_i, ..., L_f values. The simplest situation is the one in which the final asymptotic L_f value is attained already after the first critical loading event. Under such circumstances, $L_0 \neq L_1 = L_2 = \ldots = L_i = \ldots = L_f$ and Eq. 7 can be re-written as

$$L = L_0 \mathrm{e}^{-kn} + L_f(1 - \mathrm{e}^{-kn}). \tag{8}$$

If $L_0 \neq L_1 \neq L_2 = \ldots = L_i = \ldots = L_f$, i.e. the final asymptotic L_f value is attained after two critical loading events, the average crystallite size L is instead equal to

$$L = L_0 \mathrm{e}^{-kn} + L_1 kn \mathrm{e}^{-kn} + L_f\left[1 - (1 + kn)\mathrm{e}^{-kn}\right]. \tag{9}$$

Along the same line, if $L_0 \neq L_1 \neq L_2 \neq L_3 = \ldots = L_i = \ldots = L_f$, i.e. the final asymptotic L_f value is attained after three critical loading events, the average crystallite size L amounts to

$$L = L_0 \mathrm{e}^{-kn} + L_1 kn \mathrm{e}^{-kn} + \frac{(kn)^2}{2}\mathrm{e}^{-kn} + L_f\left[1 - (1 + kn + \frac{(kn)^2}{2})\mathrm{e}^{-kn}\right]. \tag{10}$$

The previous Eqs. 8–10 and the ones that can be similarly obtained can be readjusted in order to work out the logarithm of the ratio between the quantities $(L–L_f)$ and $(L_0 –L_f)$. Accordingly, when $L_0 \neq L_1 = L_2 = \ldots = L_i = \ldots = L_f$

$$\ln\frac{(L - L_f)}{(L_0 - L_f)} = -kn, \tag{11}$$

when $L_0 \neq L_1 \neq L_2 = \ldots = L_i = \ldots = L_f$

$$\ln\frac{(L - L_f)}{(L_0 - L_f)} = -kn + \ln\left[1 + \frac{(L_1 - L_f)}{(L_0 - L_f)}kn\right] \tag{12}$$

and when $L_0 \neq L_1 \neq L_2 \neq L_3 = \ldots = L_i = \ldots = L_f$

$$\ln\frac{(L - L_f)}{(L_0 - L_f)} = -kn + \ln\left[1 + \frac{(L_1 - L_f)}{(L_0 - L_f)}kn + \frac{(L_2 - L_f)}{(L_0 - L_f)}\frac{(kn)^2}{2}\right]. \tag{13}$$

In the following, we show that a detailed characterization of the experimental curves of crystallite size decrease as a function of the number n of collisions and a proper fitting procedure can provide indications on the values of the crystallite sizes L_0 ,L_1,L_2,..., L_i,... as well as an estimate of the value of the apparent rate constant k.

Experimental methodologies

The experimental procedures and the related protocols employed to characterize the milling dynamics have been extensively presented in previous papers [4]. It is however worth remembering that the methodologies developed allow for evaluating the number n of collisions during the processing provided that a single ball and a powder amount large enough to determine inelastic impact conditions are used. Under such circumstances, the identification of single

impacts also permits the estimation of the average frequency N of the collisions as well as the average impact energy E [4, 5]. The number n of collisions should be used instead of the time t to quantify the rate of the crystallite size refinement process, given that a large separation exists between the characteristic time scales of macroscopic collision events and atomic-scale processes [2–5, 8, 9].

Experiments were performed on Cu powder with nominal purity level of 99.99%. The experimental trials were carried out in a commercial Spex/Mixer Mill mod. 8000 equipped with a variable speed electrical motor controlled by a frequency inverter [6]. The milling device worked at 750, 850 and 1,300 rpm, thus determining collision frequencies equal to about 25, 28 and 43 Hz. Amounts of powder equal to 8 g were mechanically treated under Ar atmosphere in a stainless steel vial with a single ball at impact energies roughly equal to 0.03, 0.10 and 0.25 J. The lowest impact energy at the lowest mill frequency was obtained by using a SiN ball with diameter and mass of about 14 mm and 4.5 g, respectively. In all the other cases, a stainless steel ball with the same diameter but a mass of 12 g was used. The use of milling balls with the same diameter permits to avoid any undesired effect due to the different amount of powder trapped at each impact.

Handling procedures were performed inside a glovebox under inert atmosphere with a controlled content of moisture and oxygen below 2 ppm.

The decrease of the average crystallite size was quantified by X-ray diffraction (XRD) analyses on powders sampled at given milling times. A Rigaku Diffractometer D/Max equipped with a Cu K_{alpha} radiation tube and a graphite monochromator in the diffracted beam was used. The profiles of the crystalline peaks were fitted with the Rietveld procedure [14]. The two contributions to the line broadening, connected respectively with the decrease of the crystallite size and the accumulation of lattice strain, were separated by correlating the half-height widths of the various diffraction peaks with their angular position [15, 16]. The average size L of coherent diffraction domains and the strain content ε were then estimated according to the Williamson–Hall method [17], implemented in the Rietveld procedure under the assumption of isotropic strain content and size [14].

Comparison with experimental data

The experimental data obtained at the impact energies of about 0.03, 0.10 and 0.25 J are quoted respectively in Fig. 2a, b, c as a function of the number n of collisions. As expected, the average size L of the crystallites undergoes a monotonic decrease at rates depending on the impact energy E. More specifically, the rate of the refinement process increases as the impact energy E increases. The initial crystallite size value L_0 is the same for all the curves and amounts to about 58± 9 nm. Different final values L_f are instead found depending on the impact energy with which the powders are mechanically processed. In particular, L_f amounts approximately to 20 ± 4, 17 ± 5 and 15 ± 3 nm for the powders treated respectively at 0.03, 0.10 and 0.25 J. The L_f value therefore decreases as the energy E of collisions increases.

Even though the curves in Fig. 2a, b, c have apparently the same shape, with the slope decreasing steadily as the number n of collisions increases, a careful look at their initial portions reveals the presence of small shoulders. The differences can be better appreciated when the Neperian logarithm of the ratio $(L–L_f)/(L_0 –L_f)$ is quoted as a function of the number n of collisions as in Fig. 3a, b, c. The points in Fig. 3a, b

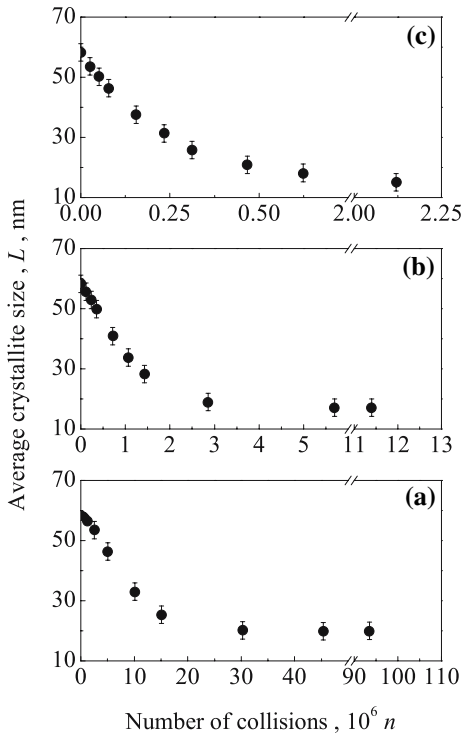

Fig. 2 The average crystallite size L as a function of the number n of collisions for the experimental trials carried out at the impact energies equal to (**a**) 0.03, (**b**) 0.10 and (**c**) 0.25 J. The rate of the crystallite size refinement process decreases as the impact energy E decreases. Small differences in the first portions of the monotonic decreasing trends are observed. Error bars are included. The bars of the first points in (**a**) have been eliminated for sake of clarity

arrange indeed according to curved trends, whereas the points in Fig. 3c define a linear trend.

The data in Fig. 3a are fitted by Eq. 13. Any other equation determines a worsening of the fit. The fitting parameters are the apparent rate constant k and the crystallite sizes L_1 and L_2, intermediate between the initial and the final ones L_0 and L_f. The quantity k is found to amount approximately to $2.8\pm\ 0.5 \times 10^{-7}$, whereas L_1 and L_2, are found to be roughly equal to $54\pm\ 6$ and $42\ \pm\ 5$ nm, respectively. As indicated in Fig. 4, three critical loading events with an impact energy of 0.03 J are then necessary for the crystallite size of a given powder fraction to decrease from about 58 to about 20 nm.

The situation changes at the intermediate impact energy of about 0.10 J. The curved plot in Fig. 3b is no longer fitted by Eq. 13, but by Eq. 12. The fitting parameters are in this case the apparent rate constant k and the intermediate crystallite size L_1. For these two quantities the fitting procedure yields the values of about $1.57\ \pm\ 0.3 \times 10^{-6}$ and $45\ \pm\ 4$ nm, respectively. The kinetic model indicates that two critical loading events are necessary to induce a decrease of the crystallite size from about 58 to about 17 nm.

Finally, the linear plot in Fig. 3c obtained at the highest impact energy of about 0.25 J is fitted by Eq. 11. The only fitting parameter is the apparent rate constant k, the value of which is found to be approximately equal to $4.49\pm\ 0.2 \times 10^{-6}$. In this case, a single critical loading event is sufficient for the crystallite size to decrease from about 58 to 15 nm.

The results obtained form the fitting procedure have been summarized in Table 1 together with the relative conditions of mechanical processing.

The L_i values are reported as a function of the number i of critical loading events in Fig. 4. It appears that the impact energy E determines the number of critical loading events necessary to decrease the crystallite size of a given powder volume from the initial to the final value. At high impact energy, the mechanical stress is so high that the powder volume experiencing CLCs is deformed to a large extent. Correspondingly, the size of coherent diffraction domains decreases suddenly from the initial value to the lowest one possible under such loading conditions. As the impact energy and then the mechanical stress at impact decrease, the decrease of the crystallite size become more gradual. Therefore, two or more critical loading events are necessary for a given powder volume to

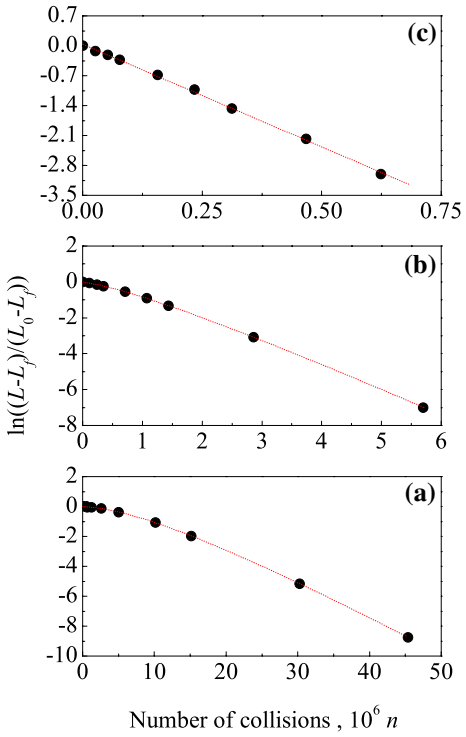

Fig. 3 The Neperian logarithm of the ratio $(L–L_f)/(L_0 –L_f)$ as a function of the number n of collisions for the experimental trials carried out at the impact energies equal to (**a**) 0.03, (**b**) 0.10 and (**c**) 0.25 J. The arrangements of experimental points in (**a**), (**b**) and (**c**) can be best fitted with Eqs. 11, 12 and 13, respectively. Best-fitted curves are also shown. Correspondingly, the kinetic model indicates that between the initial L_0 to the final L_f values two intermediate L_1 and L_2 sizes, one intermediate L_1 size and no intermediate size exist

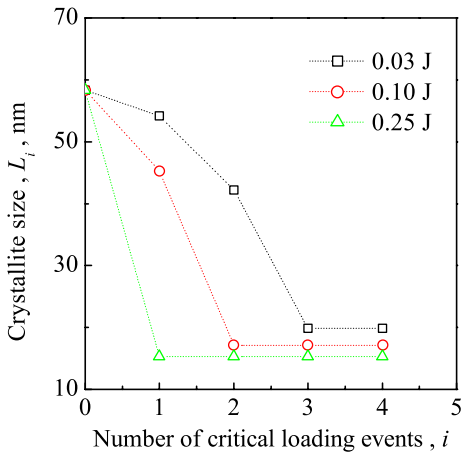

Fig. 4 The crystallite size L_i of a given volume of powders experiencing CLCs for i times. The data refer to the experimental trials carried out at the three impact energies indicated. The decrease from the initial L_0 to the final L_f values requires two intermediate L_1 and L_2 sizes at the lowest impact energy. At the intermediate energy value, a single intermediate crystallite size L_1 is found. Finally, the kinetic model suggests that at the highest impact energy the crystallite size changes abruptly from L_0 to L_f at the first critical loading event. The final L_f value is affected by the impact energy E, decreasing as the latter increases

Table 1 Mechanical processing conditions and results obtained form the fitting procedure of theoretical curves to experimental data for the different trials carried out

	N (Hz)	E (J)	L_0 (nm)	L_1 (nm)	L_2 (nm)	L_f (nm)	k ($\times 10^{-7}$)
1	25	0.03	58 ± 9	54 ± 6	42 ± 5	20 ± 4	2.8 ± 0.5
2	28	0.10	58 ± 9	45 ± 4	–	17 ± 5	15.7 ± 3
3	43	0.25	58 ± 9	–	–	15 ± 3	44.9 ± 2

The average collision frequency N and the impact energy E are reported together with the initial L_0, intermediate L_1 and L_2 and final L_f crystallite sizes and the apparent kinetic constants k of the crystallite size refinement process

decrease its crystallite size from the initial value to the final one.

As already pointed out in previous work [4–6], the impact energy E also determines the rate of crystallite size decrease. It can be seen in Fig. 5 that the apparent rate constant k decreases linearly as the impact energy E decreases. The best-fitted line crosses the abscissa axis at a small positive value E_0, thus indicating the existence of a threshold impact energy below which no crystallite size refinement takes place. Previous studies have shown that such threshold should be related to the mechanical properties [6]. In the present case, the threshold value determined by the linear plot in Fig. 5 is larger than the one previously obtained [6]. It is however worth noting that a different batch of Cu powders has been used in the previous experiments. It is therefore probable that the slightly different properties of the commercial Cu powder used in the two series of experiments could have determined the different result.

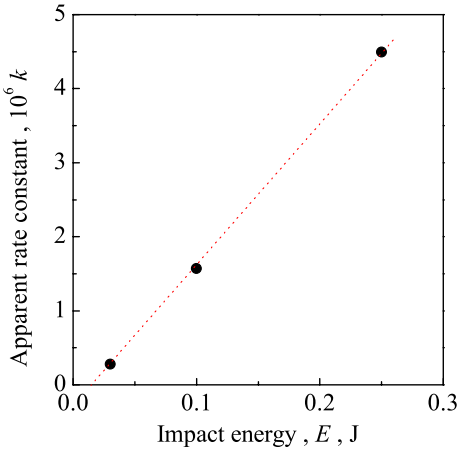

Fig. 5 The apparent rate constant k of the crystallite size refinement process as a function of the impact energy E. The k values obtained from the best-fitting procedure arrange according to a linear increasing trend. The best-fitted line, also shown, crosses the abscissa axis at a positive value, thus indicating the existence of a threshold impact energy E_0

Conclusions

A phenomenological model has been developed to provide novel insight into the kinetics of the crystallite size refinement process taking place under mechanical processing conditions. Despite its crudeness, the model is able to catch some fundamental aspects of the powder processing by ball milling. Taking into account its statistical character, the modeling approach provides equations useful for a phenomenological rationalization of the experimental data. The comparison between experimental findings and theoretical curves indicates that the crystallite size refinement process is intimately connected with the loading conditions that the powders experience when trapped between the colliding surfaces of milling tools. Provided that the minimum stress necessary to induce a decrease of the crystallite size is overcome, the extent to which such process occurs within a given powder fraction depends on the impact energy and on the number of times that such fraction experienced a critical mechanical loading. At high impact energies, the crystallite size can attain the final value after a single critical loading event. Conversely, at low impact energies the number of critical loading events necessary to attain the final crystallite size is larger.

The phenomenological interpretation of the experimental data permitted for the first time to distinguish between the statistical character of the mechanical processing and the intrinsic kinetics of crystallite size decrease related to the number of loading events experienced by the powder. At the basis of such distinction lies the application of refined experimental methodologies for the estimation of both average energy and number of collisions as well as of the average crystallite size. This is a sine qua non condition for a satisfactory characterization of the kinetics of the crystallite size refinement process.

A systematic application of the phenomenological model to the study of crystallite size refinement processes in pure phases could hopefully contribute to further progress in the field and to address future research. Various points needs however significant

improvement. One of the most important ones concerns the concept of critical loading event. Although reasonable from an intuitive point of view, it certainly requires a definite understanding. The most important advances are expected in this direction from numerical simulations, able to reproduce in detail the atomic-scale behavior of large ensembles of atoms undergoing shearing and loading events.

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