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Development of a mathematical expression for the variation of amorphization phenomenon during intensive milling of minerals

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ABSTRACT

Attempts have been made to develop a mathematical expression on the basis of dislocation theory to describe the effect of intensive milling time on the changes of dislocation density as well as amorphization degree of a mineral substance during intensive milling process. Validity of the proposed expression was verified by the results of experiments performed on a natural chalcopyrite mineral as well as those reported in the literature. It was concluded that the expression satisfied the experimental results with a good accuracy.

1. Introduction

Mechanical activation by intensive milling is an innovative method that improves the efficiency of mineral processing via several factors, most importantly due to the formation of new surfaces and the creation of lattice defects. Its benefits include lower reaction temperatures, enhanced dissolution efficiencies and increased reaction rates. As a consequence, further processing can be performed in simpler and less expensive reactors with shorter reaction times (Baláž et al., 2005).

Different types of milling apparatus such as ball mills, planetary mills, vibratory mills, stirring ball mills, pin mills and rolling mills (Baláž, 2003) may be used for milling operations. It is believed that wet milling and/or the use of small milling balls (as in stirring ball mills) is more favorable for the generation of new surfaces, while dry milling and/or the use of larger milling balls (as in vibratory and/or planetary mills) brings about intensive bulk disorder in the milled material (Baláž et al., 2005). The primary effect of mechanical activation is comminution of mineral particles that results in changes in a great number of physicochemical properties of a particular system. This disintegration is accompanied by an increase in the number of particles and by the generation of fresh surfaces (Baláž, 2003). Mechanical activation also induces significant changes to the bulk structure of minerals. It decreases the crystallinity of the mineral components of a concentrate (Ficeriova et al., 2005).

Among the physicochemical changes in minerals, some phase transformations have also been identified. The local high pressures and temperatures at contact surfaces of mechanically activated particles as well as the presence of volume defects are responsible for the phase transformations (Baláž, 2003). To appreciate the disordering in the bulk of minerals as a consequence of mechanical activation, the method of X-ray diffractometry is frequently applied. Different parameters such as structural disorder, crystallinity, amorphization, crystallite size and lattice deformation can be calculated from the diffraction lines of mechanically activated minerals (Baláž, 2003; Xiao et al., 2004; Tkacava and Balaz, 1990; Balaz et al., 2000).

Several research works have been performed on the effect of milling parameters on the bulk structure such as the effect of intensive milling time on the line broadening of XRD pattern (Maurice and Hawk, 1999), the effect of intensive milling time on amorphization and lattice deformation (Baláž, 2000). Nevertheless the authors could not find any model or quantitative analysis regarding these effects. Hence, attempts have been made in the present study to develop a mathematical relationship based on dislocation theory to explain the changes of amorphization phenomenon during intensive milling (e.g. mechanical activation) of a mineral.

2. Experimental

2.1. Materials

A series of experiments was performed on a natural chalcopyrite mineral. The mineral originated from Mazra-e mine, south-east Iran. Some ore lumps containing high amounts of chalcopyrite were collected by hand sorting. Wet chemical analysis of the sample showed the copper content as high as 12 wt.%. The ore samples were first crushed to less than about 2 mm and then milled to less than about 300 μm. A concentrate was subsequently obtained by repeated froth flotation using xanthate collectors. XRD analysis of the concentrate (Fig. 1) showed a mineralogical

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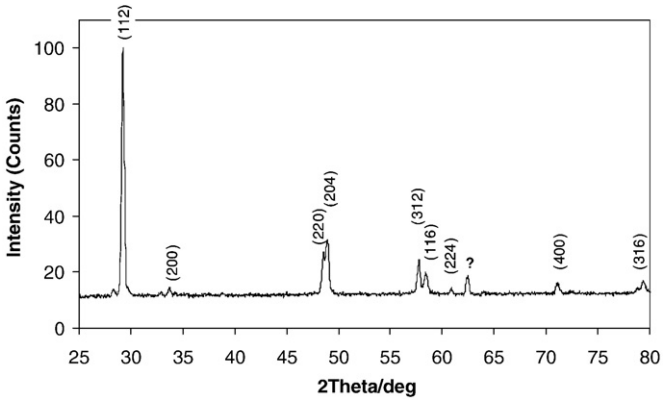

Fig. 1. X-ray diffraction pattern of natural chalcopyrite mineral.

analysis of about 96 wt.% chalcopyrite ($CuFeS_2$) together with around 4 wt.% gangue minerals. BET analysis result showed the specific surface area of the concentrate to be 0.3678 $m^2\ g^{-1}$.

2.2. Procedure

Sampling was performed by coning and quartering method. Intensive milling experiments were carried out in a FP2 four milling jar planetary ball mill (Fara-pajouhesh, Iran). Milling jars were made of tempered chromium steel (11.5%Cr, 2.1%C, 0.7%W) having a volume of 125 ml. Milling balls were made of stainless steel (0.45%C, 13%Cr). Each jar was loaded with 3 balls of 20 mm diameter and 2 balls of 10 mm diameter. Milling time was varied from 15 min to 10 h and ball to powder weight ratio from 2.5 to 40. The rotation speed of the supporting disc was set at 600 rpm with a direction reversal after every 15 min. Intensive milling experiments were carried out at ambient temperature and under air atmosphere.

2.3. Characterization

The specific surface area was determined by the low temperature nitrogen adsorption technique (BET method) by means of a Gemini 2375 sorption apparatus (Micromeritics, USA). X-ray diffraction analysis was performed by a D8-ADVANCE diffractometer (Bruker, Germany) using Cu-K_α radiation with 0.5° s^{-1} goniometer rate.

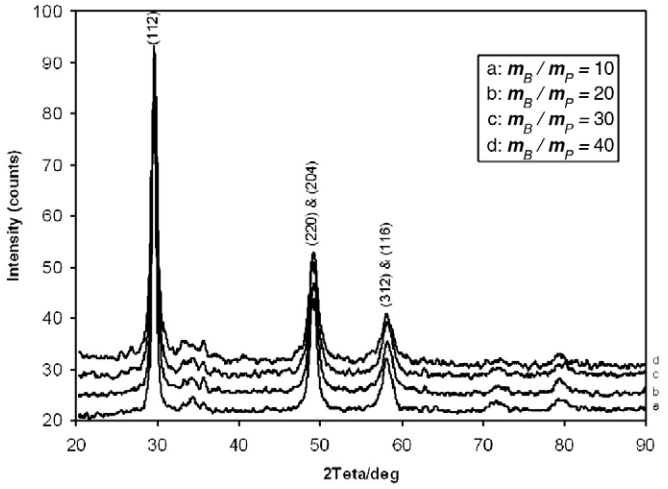

Fig. 2. X-ray diffraction patterns of mechanically activated chalcopyrite for 1 h milling time and different ball to powder weight ratios (m_B/m_P).

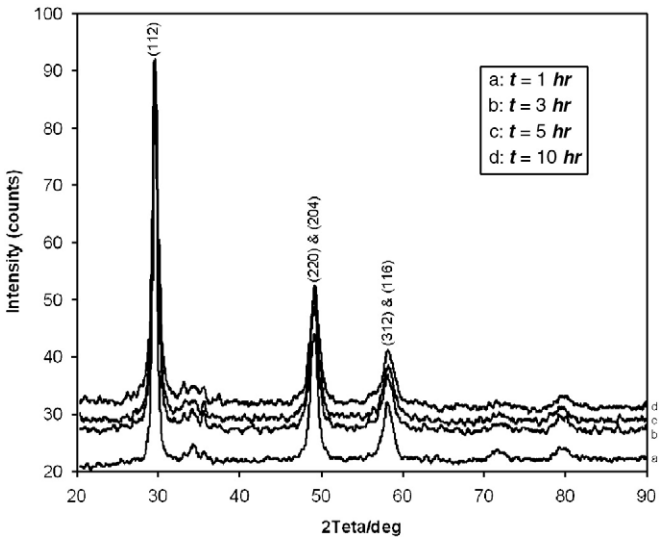

Fig. 3. X-ray diffraction patterns of mechanically activated chalcopyrite for ball to powder weight ratio of 10 and different milling time (t).

3. Results and discussion

3.1. Intensive milling

Selected XRD patterns of the mechanically activated chalcopyrite are shown in Figs. 2 and 3. It can be seen that chalcopyrite sample did not undergo any sensible changes in crystal structure during high-energy milling as no shift happened to the XRD peaks. Nevertheless, some line broadening and reduction in height of the diffraction peaks due to disordering of crystal structure and plastic deformation as well as some rising of the background owing to the formation of amorphous material can be manifested.

The effect of mechanical activation may be evaluated using the degree of broadening of the diffraction peaks, or measurement of the full width at half maximum (FWHM). Results of such calculation for (112) peak are shown in Figs. 4 and 5. It appears from these figures that the ultimate changes on the chalcopyrite mineral due to mechanical activation can be obtained by about 3 h of milling in the planetary mill using ball to powder weight ratio of 30.

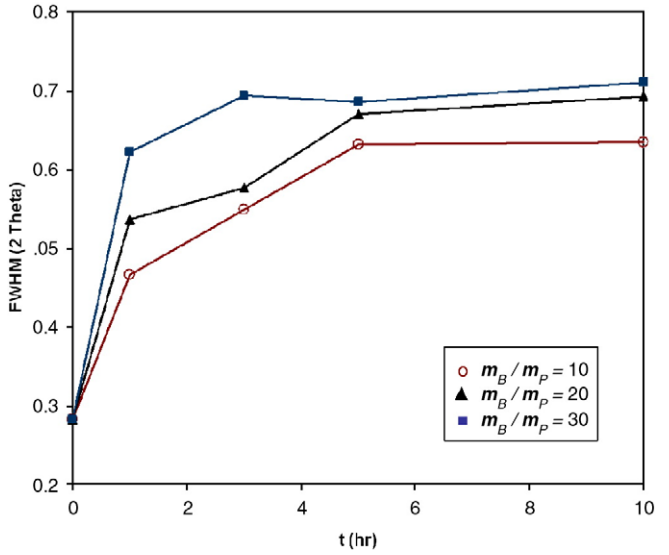

Fig. 4. The changes of the FWHM of (112) peak against milling time at constant ball to powder weight ratios.

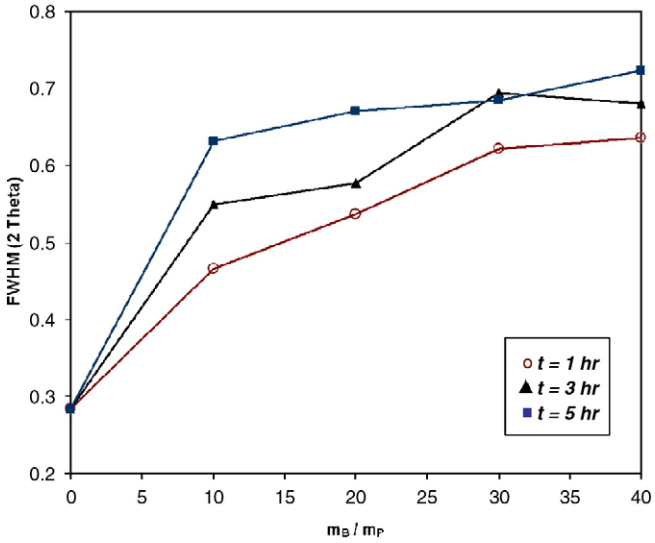

Fig. 5. The changes of the FWHM of (112) peak against ball to powder weight ratio for constant milling times.

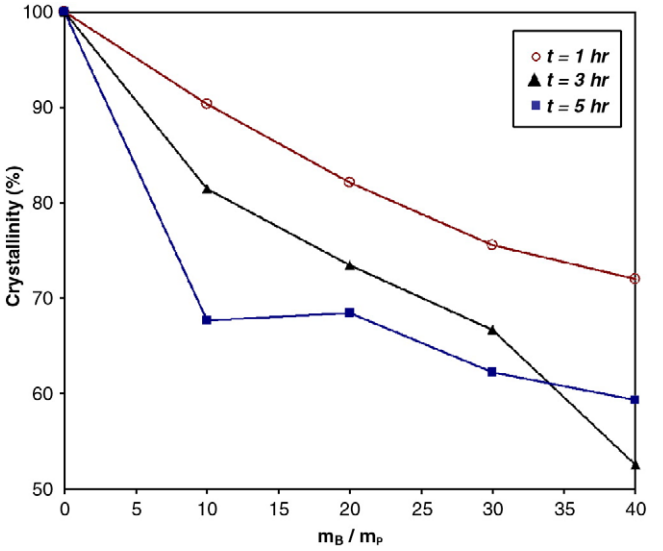

Fig. 7. Variation of crystallinity (X) of (112) peak against ball to powder weight ratio at constant milling times (t).

Another method for the evaluation of the mechanical activation process can be achieved by comparing the extent of crystalline portion in the X-ray patterns of the mechanically activated samples to that of the reference material (as-received sample) that is assumed to be 100% crystalline. Degree of crystallinity, X, is therefore defined as (Baláž, 2000):

$$X = \frac{U_0}{I_0} \cdot \frac{I_X}{U_X} \cdot 100\ (\%) \tag{1}$$

where U_0 and U_X denote the background of the as-received and milled samples, while I_0 and I_X are integral intensities of diffraction lines of the as-received and activated samples, correspondingly. The variation of crystallinity of (112) peak against intensive milling time and ball to powder weight ratio are respectively plotted in Figs. 6 and 7. The figures show that the degree of crystallinity of chalcopyrite mineral diminishes with the time of ball milling. The rate is initially high but gradually diminishes and tends to be negligibly small at elevated milling times. It can be concluded that, in the most severe milling conditions, the degree of crystallinity of the activated chalcopyrite is reduced to about 60%.

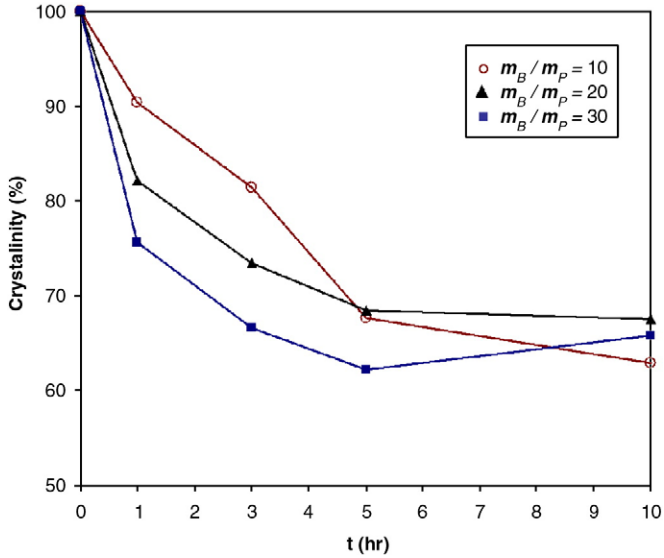

Fig. 6. Variation of crystallinity (X) of (112) peak against milling time at constant ball to powder weight ratios (m_B/m_P).

3.2. Development of mathematical expression

The value of amorphization, A, has been calculated for the determination of the degree of mineral disordering (Baláž, 2000):

$$A = 100 - X\ (\%). \tag{2}$$

The development of large numbers of dislocations during an extended milling process, and their associated strain fields, leads to an overall decrease in long-range lattice periodicity. This may be interpreted as the formation of a metastable amorphous phase, because of the line broadening and disappearance of diffraction peaks on the X-ray pattern after extended milling (Baláž, 2000). Hence, it can be assumed that there is a direct relationship between dislocation density ρ and amorphization A.

$$\rho = \alpha A \tag{3}$$

where α is a proportionality constant and is equal to 0.01ρ when the substance is completely amorphous ($A = 100$). Eq. (3) provides a basis for the development of a mathematical expression to describe the temporal evolution of dislocation density of a mineral substance during an intensive milling process.

Increase of dislocation density is related to the strain according to the following equation (Tegart, 1966):

$$\rho = \rho_0 + a\gamma^{\beta} \tag{4}$$

where ρ and ρ_0 are dislocation density after and before introducing stress, respectively. γ is shear strain and a and β are constants. Compressive stress reaches several GPa during intensive milling and hence, dislocation density increases several times (for example, over 100 times for chalcopyrite) (Tromans and Meech, 2001). Therefore, for the sake of simplicity, we may ignore ρ_0 against ρ during intensive milling and rewrite Eq. (4) as:

$$\rho \approx a\gamma^{\beta}. \tag{5}$$

Measurements of the velocity of dislocation motion, v_D, in a number of ionic crystals and metals have shown that the velocity is a

very strong function of the produced shear stress, τ, in the slip plane. This is given by the equation:

$$v_D = \left(\frac{\tau}{\tau_0}\right)^m \tag{6}$$

where τ_0 (shear stress corresponding to unit velocity) and m are constants related to material properties (Dieter, 1986). There is a direct relationship between produced shear stress in the slip plane τ and the applied vertical stress σ and also between shear strain in the slip plane γ and the applied vertical strain ε (Hertzberg, 1983):

$$\sigma = \overline{M}\tau \tag{7}$$

$$\varepsilon = \frac{\gamma}{\overline{M}} \tag{8}$$

where $\overline{M}$ denotes Taylor factor. On the other hand, there is a power law relationship between stress σ and strain ε, the so-called Hollomon relation (Dieter, 1986):

$$\sigma = K\varepsilon^n \tag{9}$$

where K is the stress at $\varepsilon = 1.0$ and n the strain-hardening coefficient. Substituting Eqs. (7)–(9) gives:

$$\tau = K'\gamma^n \tag{10}$$

where K' is the shear stress at $\gamma = 1.0$. By combining Eqs. (6) and (10):

$$v_D = A\gamma^{m\cdot n} \tag{11}$$

where A is the dislocation velocity at $\gamma = 1.0$. Shear strain rate, $\dot{\gamma}$, is a function of dislocation density ρ and dislocation velocity according to the following equation (Dieter, 1986):

$$\dot{\gamma} = \frac{d\gamma}{dt} = b\rho v_D \tag{12}$$

where b is the Burger's vector. Substituting Eqs. (5) and (11) to Eq. (12) leads to:

$$\frac{d\gamma}{dt} = b\left(a\gamma^{\beta}\right)\left(A\gamma^{m\cdot n}\right). \tag{13}$$

Therefore:

$$\frac{d\gamma}{dt} = D\gamma^p \tag{14}$$

where D (shear strain rate at $\gamma = 1.0$) and p are constants. By integration:

$$\int_0^{\gamma} \frac{d\gamma}{\gamma^p} = D\int_0^t dt \tag{15}$$

then:

$$\gamma^{1-p} = D(1-p)t \tag{16}$$

or:

$$\gamma = [D(1-p)t]^{\frac{1}{1-p}}. \tag{17}$$

Substituting Eqs. (17) to Eq. (5) leads to Eq. (14):

$$\rho = k_1 t^{n_1} \tag{18}$$

where k_1 and n_1 are constants. Taking Eq. (3) into account, Eq. (18) gives:

$$A = k_2 t^{n_2} \tag{19}$$

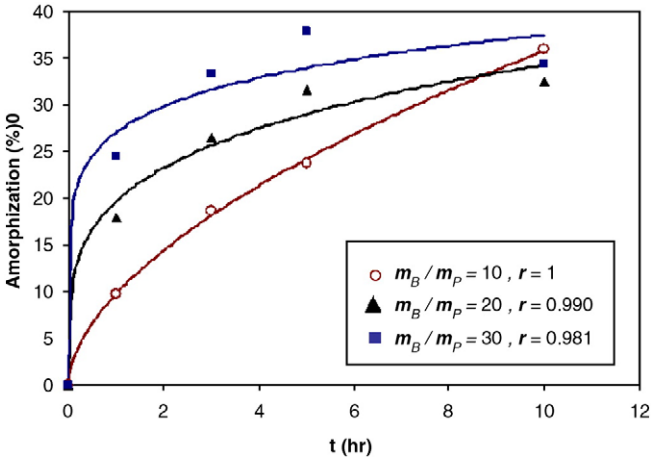

Fig. 8. Fitness of the proposed equation to the data of amorphization of chalcopyrite for different milling times and ball to powder weight ratios (data points from the present study).

where k_2 and n_2 are constants that depend on both the feed material and intensive milling condition. Eq. (19) represents a simple mathematical relationship (a power function) that describes the change in the value of amorphization of a mechanically activated mineral with intensive milling time.

3.3. Verification of the mathematical expression

In order to validate the proposed expression, experimental data of the present study as well as those reported in the literature are examined. Fig. 8 illustrates the effect of intensive milling time on the amorphization of the chalcopyrite mineral in the planetary ball mill of the present investigation for various ball to powder weight ratios. Good fits are observed between the proposed expression (solid lines) and experimental data points. Coefficients of the expression (k_2 and n_2 in Eq. (19)) were calculated by nonlinear regression method and goodness of fits are expressed by values of the correlation coefficient, r.

Published data may be employed for further verification of the derived expression. Data on the mechanically activated hematite in

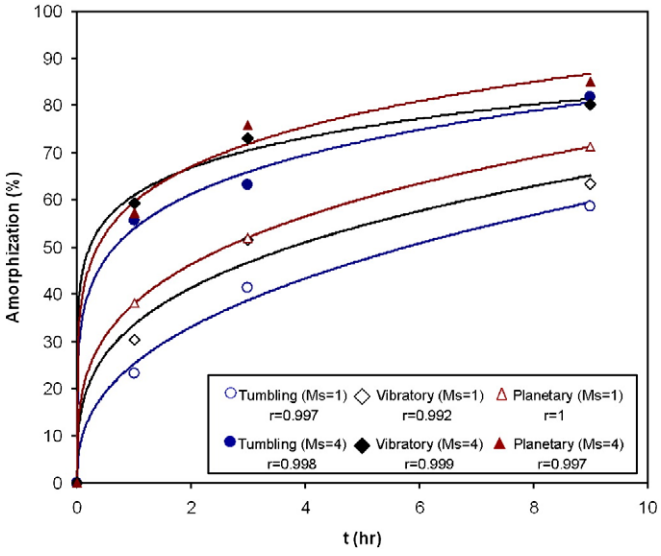

Fig. 9. Fitness of the proposed equation to the data of amorphization of hematite with the time of mechanical activation and milling media surface (m^2/kg of material) in different milling devices (data points from Pourghahramani and Forssberg, 2006).

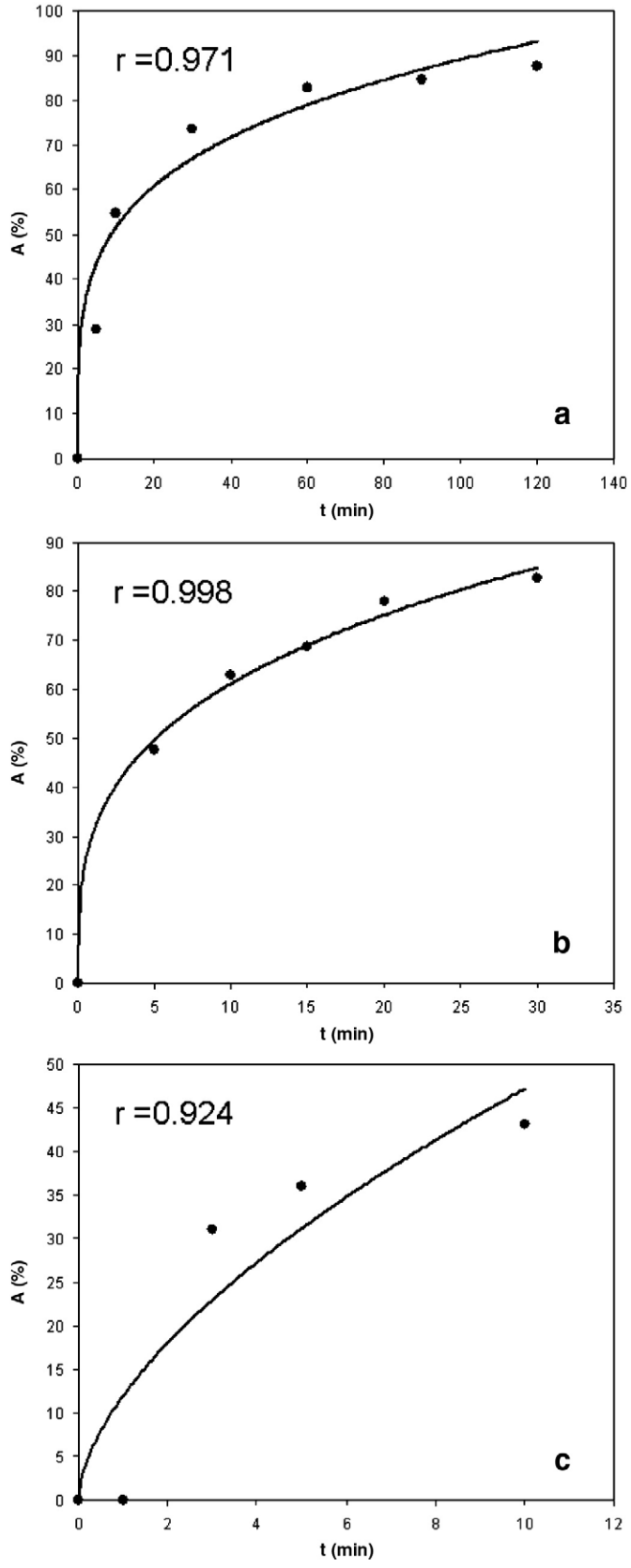

Fig. 10. Fitness of the proposed equation to the data of amorphization with the milling time for olivine in a) an attritor, b) a planetary and c) a nutating mill (data points extracted from Baláž et al., 2008).

Table 1
k_2 values for different experimental data.

Chalcopyrite	$m_B/m_P=10$	$m_B/m_P=20$	$m_B/m_P=30$
	9.73	19.61	26.98
Hematite	Tumbling	Vibratory	Planetary
Ms = 1	25.23	33.56	38.00
Ms = 4	53.91	60.96	59.52
Olivine	Attritor	Planetary	Nutating
	29.91	30.8	11.92

Table 2
n_2 values for different experimental data.

Chalcopyrite	$m_B/m_P=10$	$m_B/m_P=20$	$m_B/m_P=30$
	0.56	0.24	0.14
Hematite	Tumbling	Vibratory	Planetary
Ms = 1	0.39	0.30	0.29
Ms = 4	0.18	0.13	0.17
Olivine	Attritor	Planetary	Nutating
	0.24	0.30	0.60

different milling environments, i.e. tumbling, vibratory and planetary mills (Pourghahramani and Forssberg, 2006) are depicted in Fig. 9. The trend lines based on Eq. (19) exhibit excellent agreement with these data having r (correlation coefficient) values of 0.992 and above.

High intensity milling of olivine $(Mg, Fe)_2SiO_4$ in an attritor and a planetary mill as well as in an industrial nutating mill was investigated and degrees of crystallinity for different milling times have been reported (Baláž et al., 2008). The results can be reproduced in the form of amorphization vs. milling time data as depicted in Fig. 10. Again, a very good agreement between the mathematical expression and experimental data is observed for high-energy mills (attritor and planetary mill). These examinations show that the equation developed in the present study can predict very well the effect of intensive milling time on the amorphization of different minerals (e.g. chalcopyrite, hematite and olivine) processed in various high-energy mills (e.g. planetary, tumbling, vibratory, attritor) and conditions. The coefficients k_2 and n_2 determined for all available sets of experimental data are summarized in Tables 1 and 2. An immediate inspection of these tables suggest that for a given mineral, a more intense milling condition (higher energy mills or higher m_B/m_P ratios), provides a relatively higher and lower values for k_2 and n_2, respectively. However, consistent experimental data are needed to examine how k_2 and n_2 parameters would change with the milled material itself.

Considering the extraordinary performances of mechanically activated minerals, the equation presented here would be helpful from a practical point of view. It would be possible to determine the parameters of the equation for a given set of experimental condition by a few experiments in order to predict the amorphization values after extended milling time. It is reported that the rate of leaching increases with the degree of crystal disordering (Godocikova et al., 2002) or dislocation density (Tromans and Meech, 2001) as a result of intensive milling. Therefore, the equation developed in the present study can be integrated into the current understanding of the behavior of a mechanically activated mineral in extraction and processing operations.

4. Conclusions

- A mathematical expression has been developed to describe the changes in crystal disordering of a mineral substance as a result of intensive milling process.
- It was shown that the value of amorphization could be a power function of the intensive milling time.

- Validity of the proposed expression has been verified using the results of experiments performed on a natural chalcopyrite mineral as well as the relevant experimental data in the literature.
- It was concluded that the mathematical expression fits the experimental data of different materials, milling devices and conditions with a good accuracy.

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