

Kinetics and Mechanisms of Phase Transformations Induced by Ball-Milling in Anatase TiO₂

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Received April 30, 1999; in revised form July 28, 1999; accepted August 27, 1999

Ball-milling is a way of inducing phase transformations, chemical reactions, and changes in the reactivity of solids. It is a complex process for which several models have been developed to predict the evolution of systems and to describe its physics. These models sometimes empirically need experimental data to be ascertained and to confirm general theories of system evolutions. In this work, we investigate the effect of two milling parameters, the powder to ball weight ratio R and the nature of the grinding media, on the kinetics of phase transformations in anatase TiO₂ powder. These experiments established that R affects only the reaction rate. The kinetics are faster with alumina than with steel grinding tools for a given R , specific injected powers being similar. It has been demonstrated that the phase transformations induced by grinding TiO₂ occur without fracturing of particles and mechanisms are commented upon. © 2000

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INTRODUCTION

Besides synthesizing crystalline materials with nanometer-sized grains, high-energy dry ball-milling is a way of inducing phase transformations in solids (1–5). Many oxide structures formed under such conditions are metastable at ambient temperature and pressure and exist at equilibrium only at high temperature and/or high pressure. In this high-energy ball-milling operation, two simultaneous processes are reported to occur mainly in metallic systems: cold welding between powders and fracturing of powders. The powders are plastically deformed under high energy between balls and the wall of the vial. Mechanical alloying and grinding of materials are thus complex processes which depend on many factors, for instance, on the type of mill and on physical and chemical parameters such as milling dynamical conditions, temperature, nature of the atmosphere, chemical composition of the powder mixtures, and chemical nature and properties of grinding tools.

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Many models are currently developed to describe the physics of the process and to predict the evolution of ground compounds (6–15). On one hand, there are “global models,” which give information on the kinematics of balls: the energy involved during collisions, the trajectory of balls in the mill, the velocity of balls V_{ball} , the shock frequency, and so forth. These models consider, for example, that milling intensities such as the specific milling intensity I_s , defined by Chen *et al.* (14) as the momentum transferred by the ball to the unit mass of powder per unit time, or the specific injected power (shock frequency multiplied by kinetic energy of the ball) defined by Abdellaoui and Gaffet (7–9) are pertinent parameters to describe the grinding process. On the other hand, “local models” based on the Hertz impact theory (6, 10, 15) consider the interaction between balls and trapped powder during a collision and allow evaluation of the trapped powder volume, the maximum contact pressure, the contact radii, the duration of contact under stress, etc.

However, a detailed understanding of the basic mechanisms at work during milling is still missing. For instance, one still lacks a realistic modeling of shearing events, as emphasized by Martin (16). Kinetic studies and their dependence on experimental milling parameters provide one way to a better understanding of the mechanisms of polymorphic transformations and mechanochemical reactions.

The present work attempts to investigate the effects of the nature of grinding media and the powder to ball weight ratio on phase transformations in anatase TiO₂ powder. Anatase TiO₂ can be transformed by high-energy ball-milling into rutile via the α -PbO₂ type high-pressure modification of TiO₂ (TiO₂ II), whatever the materials constituting the milling tools (2). This high-pressure phase TiO₂ II (orthorhombic, space group *Pbcn*, density 4.34) has also been prepared from the other titanium dioxide polymorphs—anatase, brookite, and rutile—by shock wave techniques or experiments at high temperature and under high pressure (17–23). However, the kinetic information provided in such reports is very limited if at all present and the mechanisms of phase transformation are not discussed.

The present kinetic and structural studies demonstrate that the polymorphic phase transformation of TiO_2 occurs without fracturing of particles, in contrast to most reported processes of transformation induced by grinding. Phase transformation mechanisms are further commented upon.

EXPERIMENTAL DETAILS

Continuous grinding was performed in a planetary ball mill (Fritsch Pulverisette 7) in air. In such a mill, a rotating disk bears vials which rotate in opposite directions. The rotation speed of the disk is around 710 rpm and that of the vials around 1420 rpm. The grinding tools are made either of steel (Fe-13% Cr) or of alumina, the volume of the vial is approximately 45 cm^3 , and seven balls of diameter $\phi = 15 \text{ mm}$ are used. The powder to ball weight ratios were $R = 1/40, 1/30, 1/20,$ and $1/10$ with steel and with alumina grinding tools. The starting material is TiO_2 (anatase form, origin Aldrich).

The specific shock powers P injected during the ball-milling process were obtained from powers calculated by Abdellaoui and Gaffet ((7-9) and personal communication). They are $P_s = 0.67/R \text{ W/g}$ for steel tools, with R the powder to ball weight ratio, and $P_s = 0.70/R \text{ W/g}$ for alumina tools. For a given R , the specific powers are similar for steel and alumina tools.

The resulting powders were all characterized by X-ray diffraction (XRD) using $\text{Co } K\alpha$ radiation ($\lambda = 0.17889 \text{ nm}$). The different phase amounts were quantified by the Klug-Alexander method (24).

The evolution of particle size was followed by granulometric measurements (Coulter LS 120 granulometer). The powders in hexamethylphosphate (HMP, 1 g/L) solutions were ultrasonically deagglomerated for 3 min and then granulometric measurement was performed. The particle shapes of ground with steel powders were observed with a scanning electron microscope (SEM) equipped with a field emission gun (Philips XL 30S FEG) and by transmission electron microscopy (TEM) in a Philips CM200 electron microscope at 200 kV.

RESULTS

1. Structural Characterization

Figure 1 displays the XRD patterns of anatase ground in steel grinding media with $R = 1/40$. After milling times greater than 90 min, rutile is the only phase remaining (2). After grinding for 5 min, diffraction peaks corresponding to the transient phase TiO_2 II are clearly observed. Their intensities first increase and then decrease with milling time. As previously observed (2), the diffraction peaks of TiO_2 II are broad, meaning that the TiO_2 II crystallite sizes are nanometric even for short milling times as confirmed by recent TEM observations (25). A marked broadening of

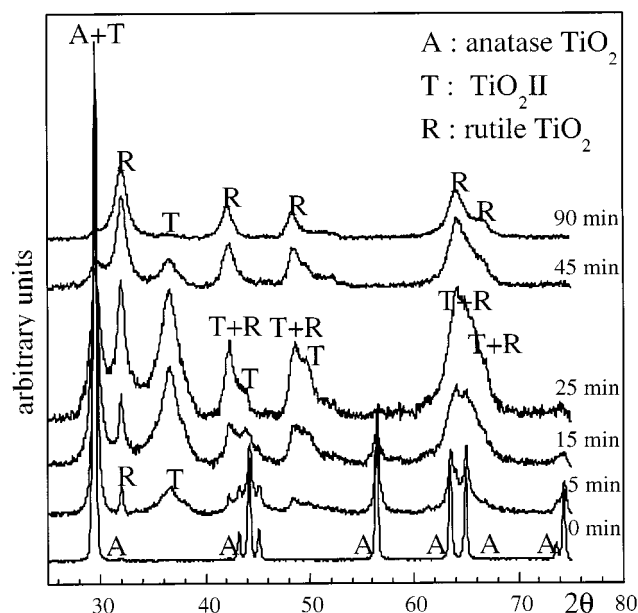


FIG. 1. XRD patterns of anatase TiO_2 as a function of milling time (steel grinding tools, $R = 1/40$).

TiO_2 II diffraction peaks have often been reported during the preparation of TiO_2 II from anatase or rutile at high temperature and under high pressure (17-19, 21) or during vibratory milling of anatase (26). This broadening was attributed to a combined effect of lattice defect distortions, stacking faults, and small crystallite sizes.

Ground powders were observed by SEM and TEM after various milling times (Fig. 2 and 3). The starting anatase powder displays monocrystalline particles (25) with a bimodal distribution of sizes (with modes around 0.15 and 0.9-1 μm , respectively) (Fig. 4). As observed in Fig. 2, particle sizes and shapes are quite stable up to 15 min of grinding, but particles tend to agglomerate with grinding time. The TEM micrographs presented in Fig. 3 reveal that after 15 min of grinding, the particle size distribution remains basically unchanged and further show that the transformed particles are now polycrystalline; $\sim 80\%$ of the anatase has been transformed. TEM observations by Girot *et al.* (25) of anatase particles ground for 5 min show that they exhibit the same particle shape as the starting anatase particles although roughness appears on faceted surfaces. Some particles are unaffected by grinding but most of them are anatase particles with TiO_2 II nanograins (10 nm) at their surface (25), which explains the previous roughness. The anatase core of some particles is strain-hardened. With grinding time (up to 15 min), the thickness of the TiO_2 II layer increased (25).

After 30 min of grinding, particles are more strongly agglomerated and their shapes are slightly modified, because

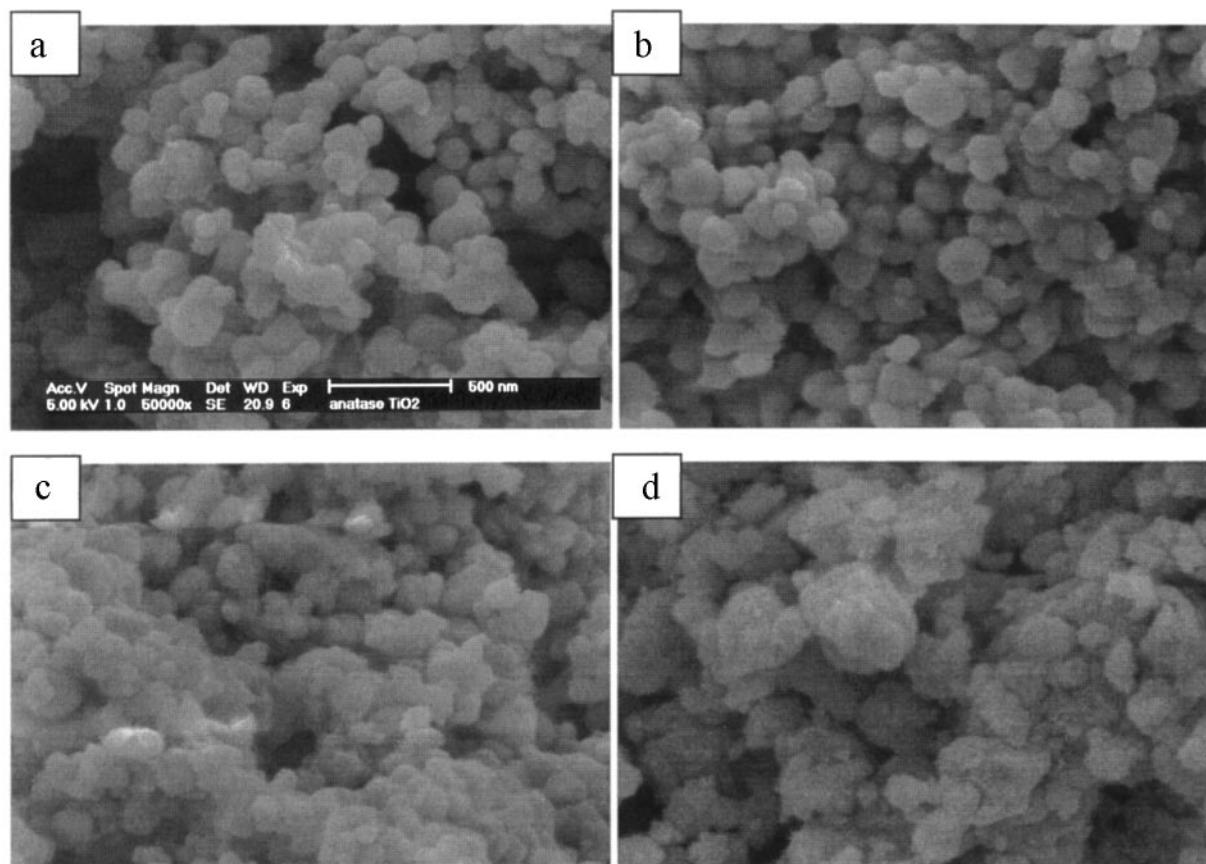


FIG. 2. SEM observations of powders after grinding with steel grinding tools for (a) 0, (b) 5, (c) 15, and (d) 30 min.

of abrasion phenomena and also because of transformation of anatase particles into very small TiO_2 II crystallites. The granulometric measurements presented in Fig. 4 show that the particle size distribution of powders ground for 30 min is quite the same after ultrasonic deagglomeration (for 2–3 min) as that of the starting anatase powder. That suggests that particles are not strongly bound in agglomerates, whose formation results more from surface interactions than from the welding of particles, and confirms that the particle size is preserved up to 30 min of grinding.

Thus, we can conclude that contrary to the case of metal-based systems (27–28) and of other oxide systems (4, 5, 29–31), apparently the fracturing and welding of particles is not the predominant mechanism of powder evolution in our experimental conditions. In oxides, the transformations are reported to occur generally in two consecutive stages: a preliminary stage during which the average crystal size decreases with increasing distortions followed by the polymorphic transformation stage. The stored strain energy is released during the phase transformation, at constant crystallite size (4, 5, 29–31). In our case, the observed nanosized

grains of TiO_2 II do not result from mechanical size reduction: TiO_2 II is formed at the surface of anatase particles (25) and should result from the local force applied at the contact point between two particles during a collision. The presence of unaffected and transformed particles at the beginning of grinding, after milling for 5 min, suggests, as discussed in detail in (25), that there is a threshold value above which TiO_2 II grains form at the surface of anatase particles. Most untransformed particles are indeed expected to have been trapped at least once after milling for 5 min since the typical time interval between two trapping events for a given particle is estimated to be of the order of a few tens of seconds in our experimental conditions (25). Heterogeneous distributions of contact forces in a trapped powder volume, typical of stressed granular media (32), would then suffice to explain the presence of untransformed particles at that milling time (25). The phase transformation threshold value is smaller than the critical stress for fracture, which is known to be very high for oxide materials and is expected to be still larger for the small particle size of starting anatase (33).

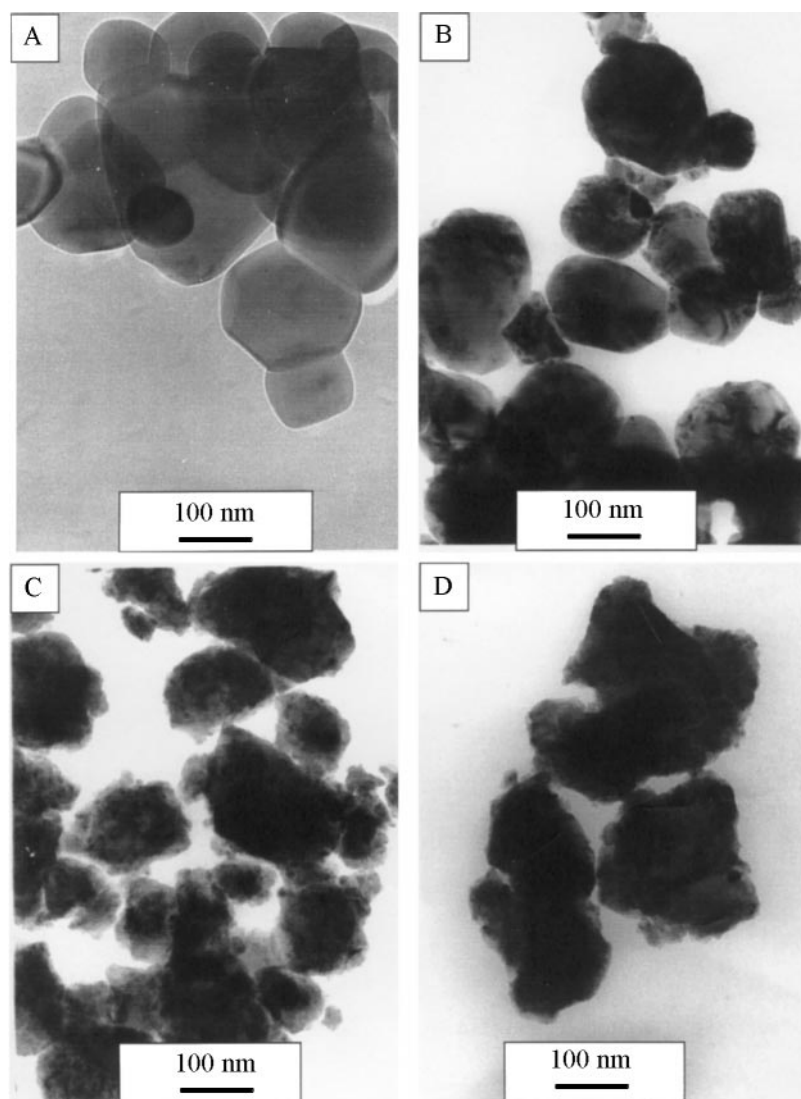


FIG. 3. Transmission electron micrographs of anatase powders ground with steel tools for (A) 0, (B) 5, (C) 15, and (D) 30 min.

In a previous study (22), we suggested that the TiO_2 II phase can be formed as a result of stresses applied to anatase during grinding. The macroscopic morphology of the powders, which remains more or less the same during milling, supports this idea. However, the detailed TEM observations (Fig. 3, Ref. (25)) evidence polycrystalline particles which are constituted of TiO_2 II grains at the surface of anatase particles whose core is either strain-hardened or not. We are thus led to conclude that the transformation is primarily strain-induced. Alternatively, the occurrence of plastic strain in the anatase core may result from the volume variation ($\approx 9\%$) due to an anatase- TiO_2 II stress-induced phase transformation. We are therefore unable to divide from the present experimental evidence if the transformation is stress- or strain-induced.

2. Kinetic Study

The general evolution of volume fractions of TiO_2 as a function of milling time is presented in Figs. 5 and 6. Similar curves are obtained whatever the milling conditions. To analyze these results, two phase transformations have been considered as taking place sequentially,



For both grinding media and both phase transformations, the higher the powder to ball weight ratio R , the slower the kinetics (Fig. 5). R does not affect the yields of the reactions. We observe that the curves relative to both phase transitions with $R = 1/20$ and $R = 1/30$ can be

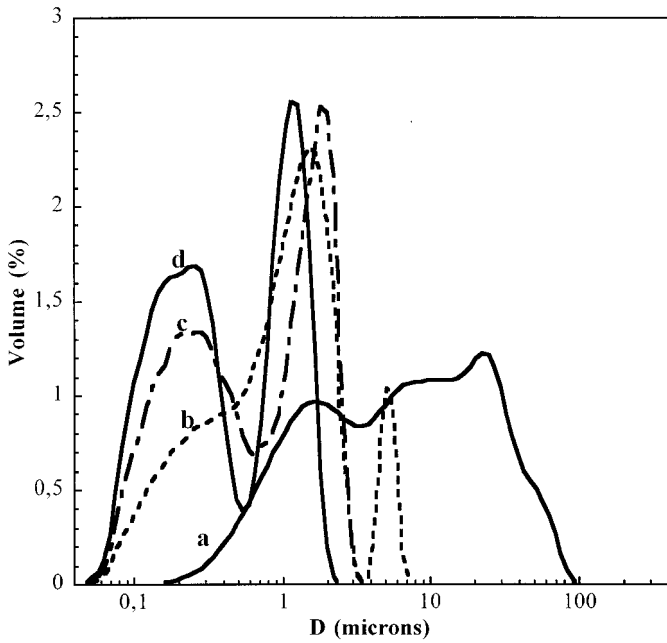


FIG. 4. Granulometric measurements of (a) the anataze powders ground for 30 min, (b) the anataze powders ground for 30 min and after 3 min of ultrasonification, and (c) the anataze powders ground for 30 min and after 3 + 3 min of ultrasonification, and (d) the starting anataze powder.

superimposed on the curves measured for $R = 1/40$ by multiplying the time data by 2.8 and 1.4, respectively (Fig. 7). For the R higher than $1/20$, the amount of powder inside the vial is greater and some powders stick to the vial walls and to the bottom of the vial so that the grinding process is no longer homogeneous for all powder particles (34).

Figure 6 shows the effect of the nature of grinding tools on the kinetics of both phase transitions. The formation rate of TiO_2 II is slower with steel than with alumina grinding tools but the yield in TiO_2 II is greater for the former

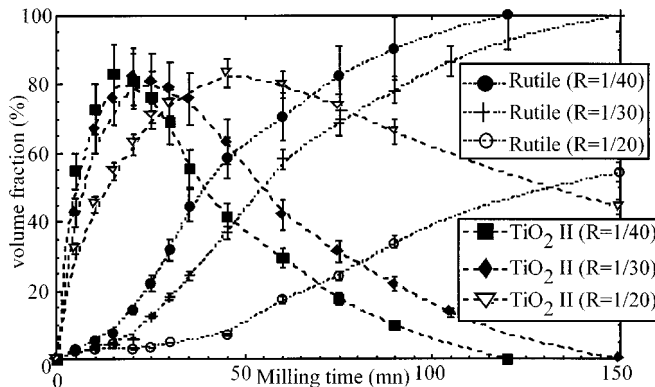


FIG. 5. Evolution of the volume fraction of TiO_2 II and rutile as a function of milling time and of R in steel grinding media.

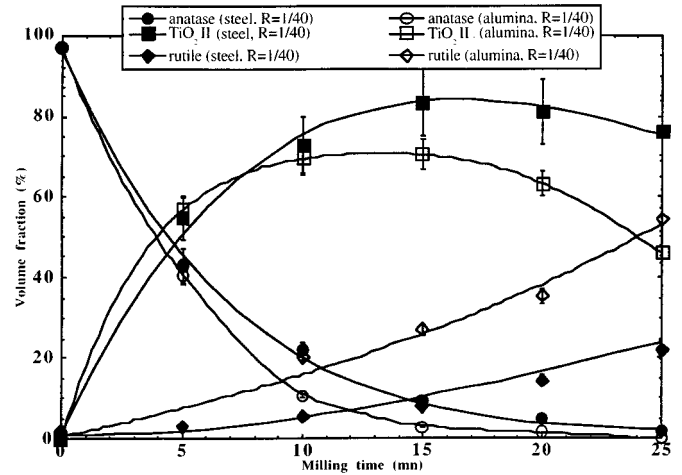


FIG. 6. Comparison of the evolution of volume fractions as a function of the nature of grinding media with $R = 1/40$.

grinding media than for the latter. The influence of grinding tools is more pronounced during the second transformation: indeed, with steel tools, the kinetics of rutile formation are slower than with alumina tools. These observations are confirmed by data given in Table 1. The highest yield in TiO_2 II is obtained with the following experimental conditions: milling for 45 min with steel grinding tools and $R = 1/20$.

The high-pressure and high-temperature form of TiO_2 is usually synthesized by shock wave methods or by experiments under hydrostatic pressure (17–23). It is also known to form as a finely crystalline intermediate phase when

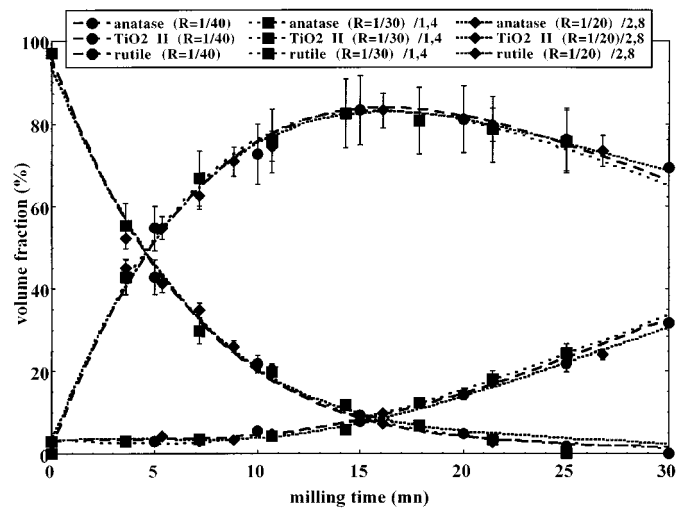


FIG. 7. Superimposition of curves relative to both transitions with $R = 1/20$ and $R = 1/30$ to curves measured for $R = 1/40$ by multiplying the time data by 2.8 and 1.4 respectively.

TABLE 1
Volume Fraction of Different Phases as a Function of Grinding Parameters and When the Maximal Fraction in TiO₂ II is reached

	<i>R</i>	Time in (mm)	Maximal volume fraction (%) in TiO ₂ II	Volume fraction (%) in anatase	Volume fraction (%) in rutile
Steel	1/40	15	83.1	9.2	7.7
	1/30	20	82.4	11.8	5.8
	1/20	45	83.1	9.7	7.2
Al ₂ O ₃	1/40	15	70.3	2.9	26.8
	1/30	20	74.1	4.0	21.9

Ti₃O₅ is dissolved in sulfuric acid at elevated temperatures (35). Yields greater than 70% are reached by grinding whereas they range in general between 10 and 30% with the previous methods. Higher yields are, however, obtained for experiments in which a shock wave propagates in some particular directions of a single crystal. Yields of about 90% have been obtained, for instance, from [001] - and [111]-oriented rutile crystals shocked to 45 GPa (21, 36).

The kinetic analysis has been focused on the first transformation of anatase into TiO₂ II. The second transformation has not been considered yet because of difficulties in the precise determination of the transformed fraction of TiO₂ II and because of the increased contamination by grinding tools, notably in the case of alumina tools, with grinding time, which involves the presence of intense diffraction peaks overlapping those of TiO₂ phases. The kinetics of the anatase-TiO₂ II transformation is described by the following law: $-\ln(1 - \alpha) = kt$, where k is the rate constant and α is the transformed fraction of anatase. The values of the rate constant, calculated for the first transformation, are given in Table 2 as a function of milling conditions. They confirm observations deduced from Figs. 5 and 6 that the kinetics is slower with steel than with alumina grinding tools. A phenomenological power relation between k and R is found for both grinding media for R ranging between 1/40 and 1/10:

$$k_{\text{steel}}(\text{s}^{-1}) = 10^{-5} R^{-1.5}$$

$$k_{\text{alumina}}(\text{s}^{-1}) = 3.9 \times 10^{-5} R^{-1.2}$$

DISCUSSION

Milling is known to generate accumulations of defects, particle size reduction, and local temperature increases which contribute to the activation of solid compounds so that they store an additional energy which facilitates chem-

ical reactions or transformations. The effect of the nature of grinding media and of R on the kinetics of phase transformation of anatase into TiO₂ II has been investigated. The powder to ball weight ratio only influences the reaction rates for given grinding tools. The smaller the value of R , the lesser is the amount of powder inside the vial and consequently the lesser is the powder volume trapped between two balls or between a ball and the vial wall. The volume of powder trapped in our experimental conditions has been calculated by adapting the value defined and experimentally confirmed by Maurice and Courtney (6) in the case of a vibratory mill. In their calculation of the trapped volume, Maurice and Courtney (6) considered the movement of the ball across the height of the vial. In a planetary ball mill, the ball movement is mainly across the diameter of the vial. Thus we have substituted the height of the vial in a vibratory mill with the diameter of the vial in a planetary ball mill and the following relationship is obtained,

$$V_{\text{powder}} = \frac{2RM_b r_h^2 (R_{\text{vial}} - R_b)}{3\rho_p (R_{\text{vial}}^2 h_{\text{vial}} - \frac{4}{3}n_b R_b^3)},$$

where R_{vial} and R_b are the vial and ball radii, respectively, h_{vial} is the height of the vial, n_b is the number of balls, M_b is the weight of ball, ρ_p is the density of powder, R is the powder to ball weight ratio, and r_h is the contact radius calculated from models based on the Hertz impact theory (6, 15). The parameters related to the mill configuration do not vary with experimental conditions,

$$V_{\text{powder}} = K M_b r_h^2 R$$

and

$$r_h = g_r v^{0.4} \left(\frac{\rho_b}{E_{\text{eff}}} \right)^{0.2} R_b,$$

where g_r is a parameter related to the surface curvature of contacts, v is the impact velocity (which is the same for both grinding media), and E_{eff} is the effective Young's modulus (Young's moduli are 340 and 203 GPa for alumina and

TABLE 2
Rate Constant of the Anatase-TiO₂ II Transformation as a Function of Milling Conditions

<i>R</i>	Steel (s ⁻¹)	Alumina (s ⁻¹)
1/40	2.55 × 10 ⁻³	3.33 × 10 ⁻³
1/30	1.82 × 10 ⁻³	2.37 × 10 ⁻³
1/20	0.86 × 10 ⁻³	1.65 × 10 ⁻³
1/10	0.33 × 10 ⁻³	0.61 × 10 ⁻³

steel, respectively); thus the trapped volume depends on the properties of grinding media and R . Therefore

$$V_{\text{powder}} = K M_b r_h^2 R = K' R.$$

For a given grinding material, the trapped volume depends thus only on the powder to ball weight ratio. Thus if we consider that the energy injected to the trapped powder volume during a collision is of the same order whatever R , at least in our experimental range of R , then the average energy transferred to a powder particle in the trapped volume during a collision is inversely proportional to R . Thus the reaction rate increases when R decreases for a given grinding media. However, the reaction rate is expected to vary with the impacted volume in a way that depends further on the nature of grinding materials, which determine the force intensities that are actually applied to trapped particles.

The nature of grinding media with different densities implies changes of the trapped volume and of the average energy injected to powder per shock. To explain further the different kinetics for both types of grinding media, we consider the specific power injected P_s , as defined by Abdellaoui and Gaffet (7–9), or P_v , the power injected per unit volume of trapped powder, which may also be a relevant and physically meaningful parameter. The latter parameter depends on the nature of the grinding media, which influences the trapped volume as discussed previously. Milling intensities such as P_s and P_v or the specific milling intensity I_s , defined by Chen *et al.* (14) as the momentum transferred by the ball to the unit mass of powder per unit time, all vary as $1/R$ in usual experimental conditions of such high-energy mills. In our case, the ratio $P_s(\text{steel})/P_s(\text{alumina}) \approx 1$ for a given R . A similar ratio, ≈ 1.2 , is found with the model of Magini *et al.* (10, 11). As observed in Fig. 8, the rate constants vary indeed fairly linearly with P_v and P_s (and so $1/R$) in the investigated ratio of R . However, the alumina line lies above the steel line when P_s or I_s is considered as the relevant intensity whereas the reverse holds when P_v is used instead (Fig. 8). The fact that the two sets of rate constants are not fitted by a unique curve, even when P_v is considered, indicates that the transformation rate does not depend solely on an intensity parameter. We have to conclude that there is also a supplementary effect related to the nature of grinding materials. It may be related to differences in their mechanical characteristics and/or to mechanisms of the phase transformation.

We have shown previously that the force at the contact point between two particles during a collision plays a key role in the anatase–TiO₂ II transformation. However, the actual distribution of contact forces is presently difficult to calculate in a 3D granular medium loaded for very short time (Table 3). In a first approach, we have used the model of Maurice and Courtney (6) based on the Hertz impact

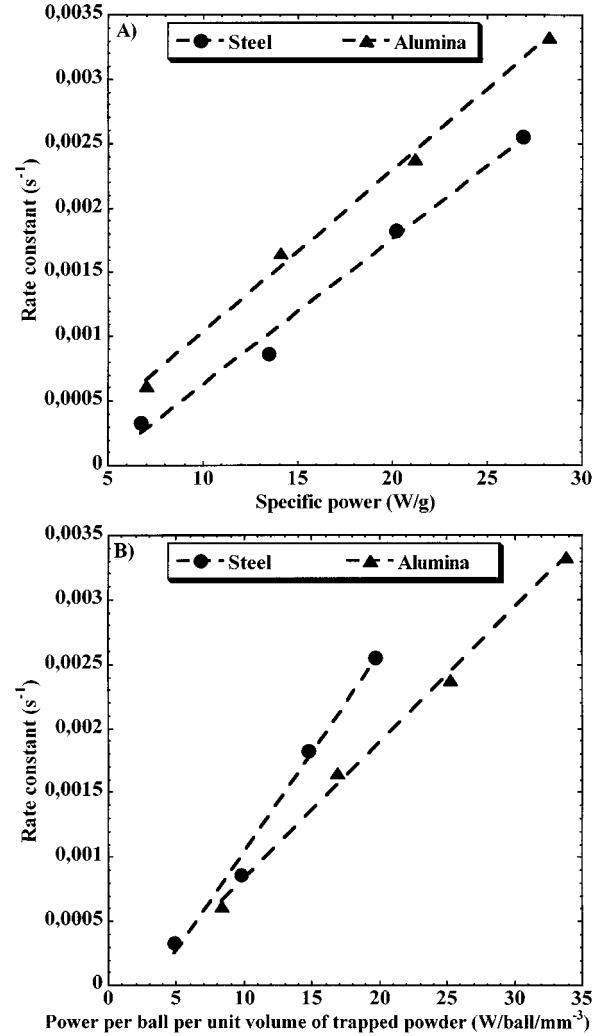


FIG. 8. Rate constants as a function of (a) the specific power and (b) the power per ball per unit of trapped volume injected during ball-milling.

theory to evaluate local parameters other than the trapped powder volume V_{shock} and the contact radius r_h ; the maximal contact pressure P_{max} , the stress contact life 2τ , and so on. These parameters are defined for collisions not involving powders. However, Maurice and Courtney (37) have proposed a more advanced model which considers collisions of powder-coated balls and they have shown that for copper powders, it gave similar results (37, 38). The comparison of contact radii, maximum contact pressures, and stress life values for alumina and steel tools (39) agrees with the calculated results of Schaeffer and Forester (15). These “local” models show that the maximal contact pressure, on a volume of powder trapped between a ball and the wall of the vial, is higher and the trapped volume is smaller with alumina than with steel grinding tools for a given R (39) (Table 3). These results indicate that the contact pressure

TABLE 3
Maximum Contact Pressure, Contact Radii, Stress Lifetime,
and Injected Power Calculated for Our Experimental Conditions

	P (GPa)	r_h (10^{-3} m)	2τ (μ s)	P (W/ball)
Steel	3.8	0.97	32	9.7
Alumina	5.1	0.75	20	4.8

and the trapped volume, which depend on the nature of the milling tools, are supplementary pertinent parameters to describe the transformations of milled powders which occur only above some threshold value. This is in agreement with works of Huang *et al.* (40), who report that the impact force (which is the product of the contact pressure times the contact area) is a relevant parameter for characterizing the impact event due to its sensitivity to milling conditions.

CONCLUSION

The influence of the nature of grinding media and of the powder to ball weight ratio (R) on the transformation of anatase in TiO_2 II and of TiO_2 II in rutile by grinding has been studied. The ratio R acts only on the reaction rate, all other parameters being kept constant. The kinetics are faster with alumina than with steel grinding tools for a given R . The specific injected power is a relevant parameter to describe the kinetics evolution but the mechanical properties of grinding materials must also be considered to explain the observed differences in transformation rates. In our experimental conditions of high-energy milling, the phase transformations induced by grinding in TiO_2 occur without fracturing of particles.

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