Ultrafine grinding of powder oxides aqueous slurries with a controlled viscosity

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I . ABSTRACT:

Previous studies[3] have shown the importance of controlling rheological behaviors of slurries during the attrition milling in aqueous medium. Indeed, during grinding, the creation of new surfaces that react with the aqueous dispersing medium has for consequence to modify the slurries properties, in particular their pH and their rheological behavior. The slurry can then flocculate and its viscosity increases. Thus grinding efficiency can very quickly become null and a "setting" of the slurry in the grinder is sometimes noted.

Our approach of the problem is in two steps. First, we determine the optimum dispersion conditions to obtain deflocculated slurries. It's possible by the control of the solid load, of the pH, or by addition of dispersant in order to enhance electrostatic and/or steric repulsion between particles. The characterization of the dispersion state is also possible with tools as zetametry and rheology. The second step is to preserve during the whole milling process this deflocculated state of dispersion. This is possible, for example, by maintaining relatively constant the pH optimized value of slurry.

We applied this concept for the grinding of classically used powder oxides TiO_2 and Al_2O_3. We implemented with this intention a horizontal attrition mill (dyno-mill), using different kind of balls: zircon or stabilized yttrium-zirconia with diameters ranging from 0,4 to 1,6 mm. We have appreciated the grinding efficiency by powder BET specific area measurements, by DRX and TEM observations. So, powder areas about 10 m²/g have reached higher than 40 m²/g that is to said average grains diameter lower than 50 nm.

II . INTRODUCTION

Many efforts are devoted today to the synthesis of ultra fine powders, which grains have sizes that can be estimated with the nanometers unit: they range typically from 10 or 20 to less than 100 nm. Most of the technologies therefore explored deal with chemical processes or sol-gel processes allowing a fine control of the size of grains, but being mostly highly costly to be set up. One way permitting the size reduction of particles is to grind them. Yet, up to now, classically used grinding processes lead only to relatively large grain powders: it seems difficult, using classical grinding processes, to break the grains of an oxide powder to a size lower than some hundreds nanometers[1].
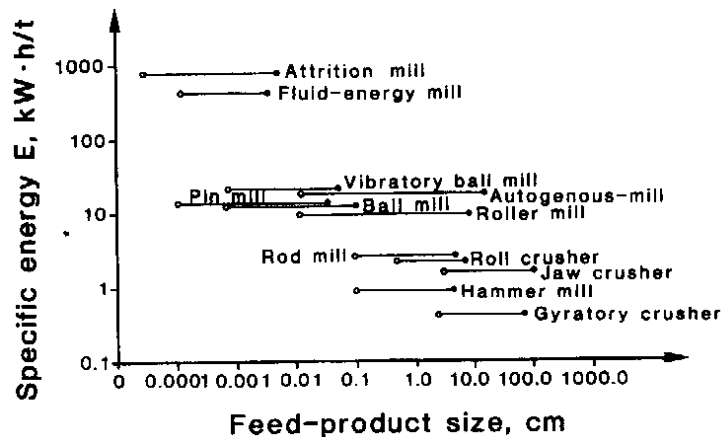
Figure 1: Average energy required for size-reduction equipment (from [2]).
○ is typical product size; ✳ is typical feed size.

Both of these operations, grinding or mixing of powders, are processed using a mill in which the powders are submitted to shear and tensile stresses that make them break and, thus, reduce size. Considering the different types of mills, one can consider the average energy required for size-reduction as illustrated Figure 1 reporting the energy required to grind a metric ton of material with the different types of mills. For the very smallest grind, the energy required can reach for the most efficient mills values as high as 1000 kWhr.ton[-1]. This energy is the sum of the energy required to move the machine, to move the material and to assume its plastic and elastic deformation and internal friction and, at last, to break the material into smaller particles. This last part is often less than 1% of the total energy needed to run the mill[2]. So, any progress permitting this "useful" energy ratio to be improved will allow breaking smaller and smaller grains. The aim of this paper is to present our first experimental results obtained when applying this philosophy that, as presented further, allowed us to get crushed alumina oxides with a mean diameter much lower than 50 nm.

It can be seen on Figure 1 that the smallest particles can be obtained using attrition milling. An attritor consists of a batch of small hard balls enclosed in a

volume, that are mixed by arms moving into the batch. So, particles to be crushed are slicked between two adjacent balls during their movement if the diameter of these balls is large enough and, therefore, crushed. On the other hand, if the balls are too small comparatively to the diameter of the particles, they don't stick them and only erosion occurs (see Figure 2). Of course, if the milling balls are too large, crushing occurs but with only fewer "crushing points" and, thus, the frequency of collisions is lowered with the consequence of only poor milling efficiency and, again, erosion that occurs between the milling balls. So, it seems evident that, for a correct attrition milling process, a careful choice of the diameter of the milling balls has to be made taking into account the size of the particles to be grounded.
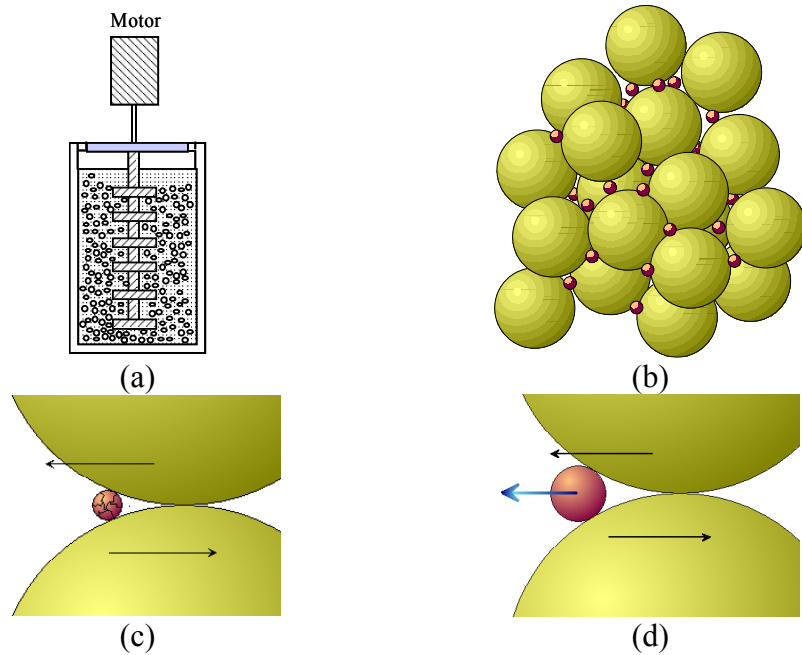

Figure 2: (a) Principle of attrition milling; (b) grinding balls that are brassed will crush the little powder grains
(c) grinding balls large enough: powder grains are stucked between the grinding balls and crushed
(d) grinding balls not large enough: powder grains are not stucked and will not be crushed

The powders to be crushed are dispersed into slurry generally composed of water with 20 to 60 volume % of powder dispersed in it. We consider here only fine grain powders that are well known to gather into flocs or agglomerates. **When agglomerates are present:** a part of the « grinding energy » is devoted to the destruction of the agglomerates. **When the slurry is viscous:** a part of the « grinding energy » is devoted to the liquid deformation and movement. **When the slurry is fluid and the particles well dispersed:** a maximum of the « grinding energy » is devoted to the crushing of the particles.

So, after some recalling on dispersion of powders in liquids and rheological behavior, we shall expose how we determine the correct dispersion conditions and

keep them all the grinding process long. We shall then present our first results concerning the grinding of titanium oxide TiO_2, and alumina Al_2O_3.

III . CONSIDERATIONS ON THE DISPERSION OF POWDERS AND ON RHEOLOGICAL BEHAVIOR OF SLURRIES[3]

Most solid surfaces are electrically charged. All of the links of a crystal are unsaturated, resulting in chemisorption, which entails the capture of foreign atoms, ions, or molecules on the surface. The surface electrical charge of particles dispersed in water or an electrolyte solution can be much more significant than that of particles in air. The electrical charges result from either dissolution of the solid into the liquid, ionization of surface groups (particularly OH^-), or substitution of ions belonging to the lattice of the solid. The charges are compensated by opposite-sign charges from the ions of the liquid, resulting in the formation of the so-called Helmholtz's double layer[4]. The potential at the Outer Helmholtz's Plane (OHP), which indicates the closest distance of approach of the hydrated ions in the solution, is assimilated into the zeta potential, ζ [5].
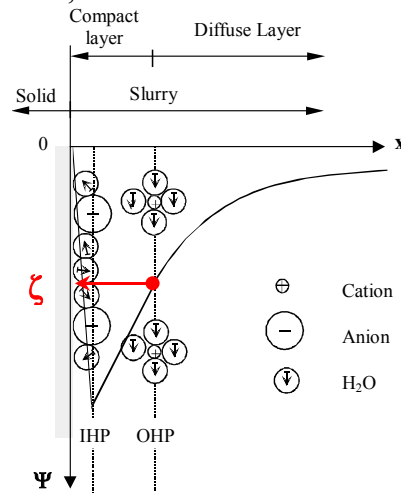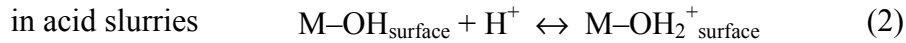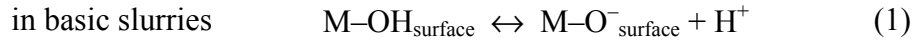

Figure 3: Concept of zeta potential

The principle of stabilization by electrostatic repulsion is described by the DLVO theory. Stabilization is possible only when repulsion forces are higher than attraction forces. The stabilization of electrostatic repulsion depends on both the radius of the particles and their surface potential, ψ_0. This latter parameter depends directly on the surface charges and is independent of the grain size of the powders. Consequently, the pH of the slurry, the concentration of the adsorbed ions and their nature are the main parameters to be taken into account. The value of the ζ potential depends directly on the concentration, in the slurry, of the ions determining the potential. As a consequence, it depends on the pH of the slurry and on the nature of these ions. **The ζ potential 0** is the IsoElectric Point (IEP) (that is the same as the Zero Point of Charge, ZPC as we assume that there is not any specific adsorption here). Table I gives as an example some typical values of isoelectric points of ceramic materials. As only low electrostatic repulsion forces

are present, flocculation occurs. **When $|\zeta|$ is high,** higher electrostatic repulsion forces occur and the best dispersion state can then be obtained. It is generally admitted that the minimum value of $|\zeta|$ for a good dispersion to occur is to be higher than 20 mV, and, when mixing different powders, that the zeta potentials of all the mixed powders are to have the same sign.

Table I. typical values of isoelectric points of ceramic materials

Material	IEP
α-Al_2O_3	8–9
$3Al_2O_3 \cdot 2SiO_2$	6–8
$BaTiO_3$	5–6
CeO_2	6.7
Cr_2O_3	7
CuO	9.5
Fe_3O_4	6.5
La_2O_3	10.4
MgO	12.4
MnO_2	4–4.5
NiO	10–11
SiO_2 (amorphous)	2–3
Si_3N_4	9
SnO_2	7.3
TiO_2	4–6
ZnO	9
ZrO_2	4–6

In the case of aqueous slurries of oxides, a surface reaction results in the formation of amphoteric hydroxide groups, such as M–OH, which can dissociate as weak acids or bases:

in basic slurries $\qquad$ $M\text{–}OH_{surface} \leftrightarrow M\text{–}O^-_{surface} + H^+$ $\qquad$ (1)

in acid slurries $\qquad$ $M\text{–}OH_{surface} + H^+ \leftrightarrow M\text{–}OH_2^+{}_{surface}$ $\qquad$ (2)

It seems evident that, when grinding powders, new surfaces are created as a consequence of the breaking of particles and that they react with the liquid and thus make the value of pH change with a concomitant evolution of the Van der Waals forces. This is well-known for years by traditional ceramics engineers who generally control the flocculation or deflocculation of clay slurries by regulating the amounts of basic compounds[1,6,7]. Recent studies have also been prompted by such considerations[8 to 12].

Newtonian liquids, such as water or most solvents and oils, are characterized by a viscosity independent of shear rate. A viscosity that increases with shear rate characterizes shear-thickening fluids. This seems to be characteristic of high-solid concentration suspensions[1,13,14]: they show shear thinning behavior at low shear rates and dilatant rheologies at high shear rates, typically higher than 50 s^{-1}. This behavior has been extensively studied. Although it is not yet completely understood, two different mechanisms have been proposed: the order to disorder transition and hydrodynamic clustering[15,16]. On the other side, viscosity that decreases with shear rate characterizes shear-thinning liquids. For flocculated slurries, this behavior can be related to the breaking of the links between particles

gathered in the flocculates[1,7]. Thus, rheological measurements performed on slurries can reflect the flocculated or deflocculated state of the slurries.

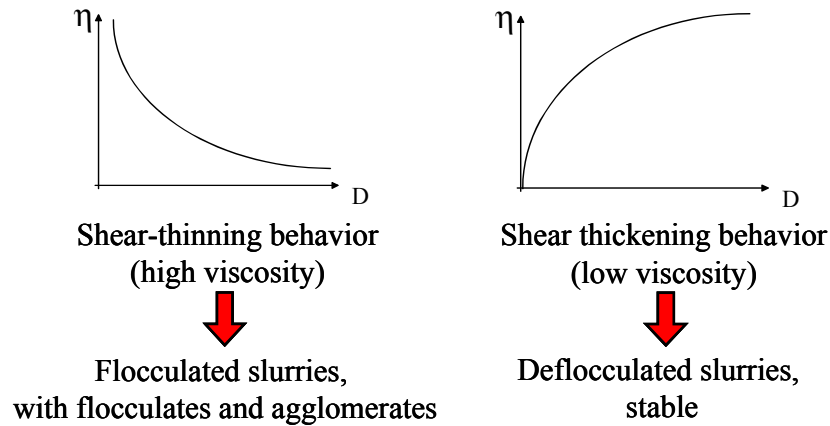| Shear-thinning behavior (high viscosity)	Shear thickening behavior (low viscosity)
↓	↓
Flocculated slurries, with flocculates and agglomerates	Deflocculated slurries, stable

Figure 4: Rheological behavior of slurries

So, we can present now the process we set to work when grinding and or mixing fine particles. The first problem to be considered is to determine the accurate dispersion parameters of the particular powders to be processed. The absolute value of the zeta potential of each powder is supposed to be higher to 20 mV with all potentials having the same sign. So, the first characterization to be done is to determine for each powder to be processed its zeta potential versus pH in order to conclude, if possible, the optimum pH of the slurry allowing a good dispersion of all the species. If pH control is not possible, good dispersion may be as an alternative obtained by an adequate dispersant addition, but we shall not develop on this here.

During the dispersion and/or grinding process, as the surfaces of the materials increase due to the break-up of the different grains, surface reactions with the dispersion liquid occur and pH and/or dispersant rate have to be continuously adjusted to be maintained at an adequate value. These characterizations of the optimal processing conditions are closely correlated with the rheological behavior of the slurries, thus providing an analysis of the flocculated or deflocculated state. If zeta potential evolution consequence of the grinding process is not controlled, flocculation can occur and, consequently, viscosity increases. The danger is thus that the grinding efficiency should shrink. The slurry may then become as consistent as a solid. The target is thus to be able to keep the deflocculated state of the slurries. So, after determination of the optimum dispersion parameters of powders in aqueous slurries by zeta potential measurements and rheological behavior determinations, the idea is to keep constant the pH value (and/or the rate of dispersant addition) high enough during the whole grinding time to be coherent with a dispersed deflocculated state.

IV . EXPERIMENTAL PROCEDURE

Measurements of ζ versus the pH of the dispersion medium were performed using a ZetaSizer 3000 (Malvern Instruments, Malvern, U.K.) coupled with an automatic titrator. Powders were first dispersed using an impeller mixer in desonized water and a drop of the upper part of this mixture was taken after some minutes of sedimentation and diluted into the zetasizer in such a concentration that the analyzed signal is correct. The pH of the dispersion was adjusted from this initial conditions by hydrochloric acid or ammonia additions and measurements performed. When used later to adjust the pH value of the mixed slurries, these particular acid and base will not introduce any undesirable cations detrimental to the microwave characteristics of the ceramics. No inert electrolyte was used to fix the ionic strength, in order to be as close as possible to the dispersion conditions in the ground slurries.

Rheograms were performed with a rheometer (Model No. Rheolab MC10, Physica Messtechnik, Stuttgart, Germany) using the Couette geometry (cell dimensions: $\phi = 48$ mm; height $= 116$ mm. cylinder dimensions: $\phi = 45$ mm; height $= 68$ mm. gap $= 1.5$ mm). Before any experimental evaluation of the rheological behavior, the time needed for the shear stress to stabilize under each shear must be determined. The time necessary for stabilization, independent of the shear rate, is for this particular rheometer ~ 2 s. Thus, when the rheograms of the different slurries were made, the shear rate was varied between 0 and 1000 s^{-1}, either increasing or decreasing with 50 measurements in each direction, and was applied 4 s before every measurement. Rheograms were immediately performed on samples just taken from the batches being ground.

Grinding and dispersion/mixing of the present powders were performed by attrition milling. The present dispersion medium was deionized water, the pH of which was adjusted by hydrochloric acid or ammonia additions. Fairly high-density slurries with a powder weight amount equal to 20wt%, 40wt%, 50wt% and 60wt% (that is to say ranging from approximatively 5 to 25 volume % of solids in water, depending on the grounded powders), were ground. Prior to grinding, the powders were pre-mixed in this dispersion medium using an impeller mixer. Balls (0.4 to 2.5 mm in diameter) of either zircon or Y-zirconia were used in a horizontal attrition mill (Dyno-Mill$^\circledR$, CB Mills, Gurnee, IL), which allowed high-energy grinding in a continuous process and recycling of the slurry. Batches of 1 kg were ground in this manner. The normalized grinding time, t_N, which represents the real grinding time, is defined as

$$t_N = \frac{t_A . V_S}{V_T} \tag{3}$$

where t_A is the total attrition time, V_S the volume of slurry ground in the attrition chamber, and V_T the total volume of the batch.

We characterized the powders during and after grinding by measuring their specific surfaces with the Brunauer–Emmet–Teller (BET) method using a Flowsorb II 2300 (Micromeritics Instrument Corp., Norcross, GA) using Heliofuit (mix of helium and 30 mol % nitrogen) as adsorption gas. Samples have been desorbed at 250°C for 1 hour before measurements. The equivalent diameter of powders θ_{eq} is then deduced using the formula $\theta_{eq} = \dfrac{6}{S_{BET}.\rho}$ where ρ is the specific weight, assuming that all particles are spherical and have the same diameter.

The equivalent diameter of powders has as well been estimated by X-ray diffraction: the shape of each diffraction peak depends on a convolution of the experimental peak (effect of the material) together with the « real » peak (effect of the material)[17]. So, after experimental correction using a quartz monocristal, we have analyzed the shapes of the peaks that depend on both the size of the crystallites and the rate of distortion. Two methods have been developed, the choice depending on the shape factor of the peaks: Williamson and Hall method and Halder and Wagner one. In our case, we used the Halder and Wagner method, making the estimation on five diffraction peaks with highly good correlation coefficients (see Figure 5 in the example of the TiO_2 powders). X-ray diffraction patterns were performed using a Siemens D5005 diffractometer and Cu $k_{\alpha1}$ with the following recording conditions: 0.02° 2θ steps, 0.05 mm analysis slit and 100 s count time for each step.
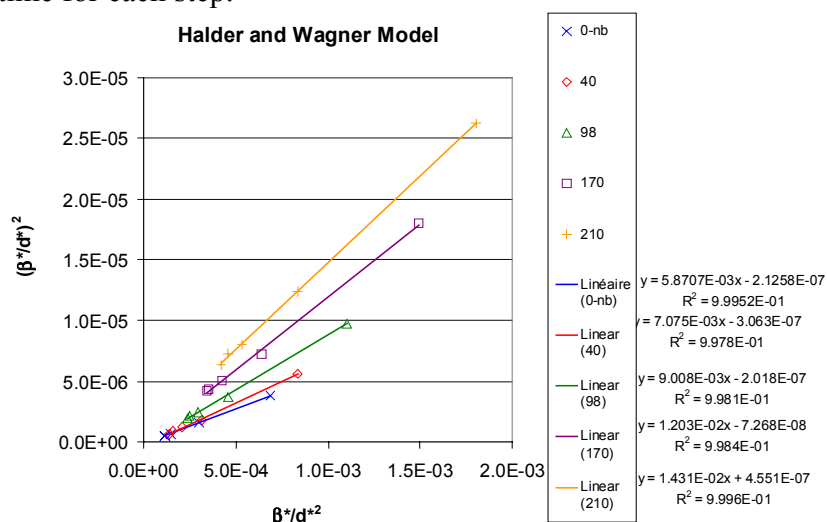

Figure 5: X-ray diffraction peaks analysis using the Halder and Wagner model

V. RESULTS AND DISCUSSION

V - 1 Titanium oxide TiO_2

We have grounded anatase TiO_2 with a 8.6 m².g^{-1} BET specific area (189 nm calculated equivalent diameter). The IEP of this particular TiO_2 powder is at pH =

3, and ζ is equal to -30 mV for pH 10. The density of the slurries that have been attrition milled was 50w% (20.7 volume % of powder) and the pH value maintained at 10 all the process long in order to keep, as shown Figure 6, the rheological behavior unchanged during the whole grinding process. In an attempt to evaluate the influence of the attrition balls diameter on the grinding efficiency, we used four different materials described Table II.

Table II. Attrition balls used for the different grindings

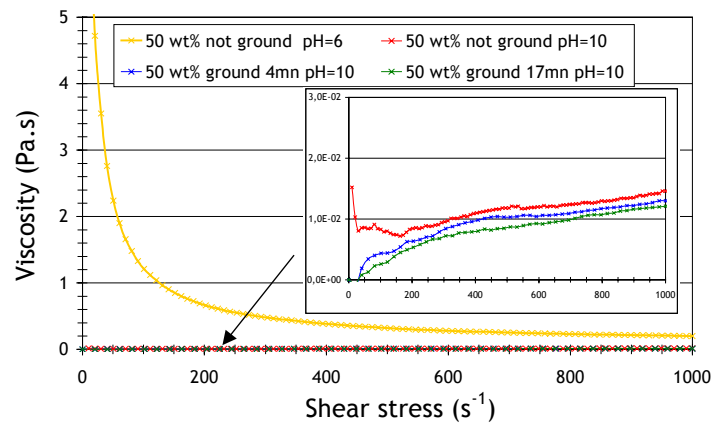| SEPR ER120S Zircon		TOSOH YTZ Y-zirconia	
1.25-1.6 mm	0.8-1 mm	0.8 mm	0.4 mm

Figure 6: Rheological behavior of flocculated (pH = 6) and deflocculated (pH = 10) TiO$_2$ slurries

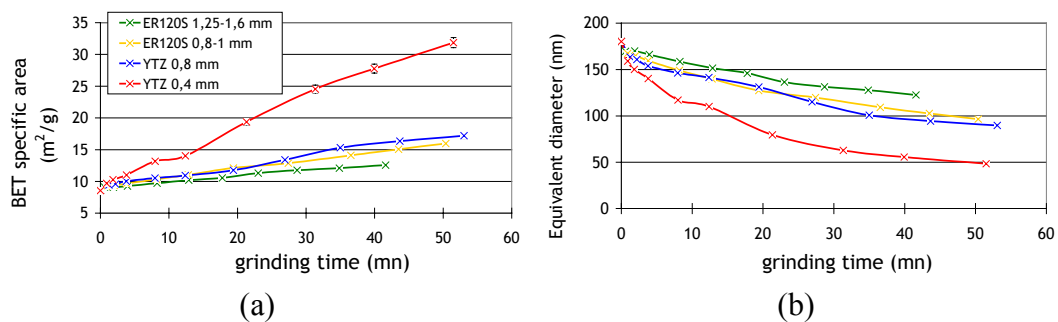(a)   (b)

Figure 7: Evolution of TiO$_2$ powder versus grinding time. (a): BET specific area; (b): equivalent diameter

The evolution versus grinding time of the BET specific area of the powders issued from these four batches is reported on Figure 7 (a). It is noteworthy that both grinding balls diameter and viscosity value effects are confirmed:

➢ Grinding efficiency remains constant all the process long while the slurry was kept deflocculated by continuous adjustments of the pH value;

➢ The smaller the balls are, the more efficient the grinding process is.

Figure 7 (b) shows the evolution of the calculated equivalent diameter. The most significant effect is obtained with the 0.4 mm YZT balls that allow to obtain after 50 minutes grinding time a 32 m²g^{-1} BET specific area. That corresponds to a

calculated grain diameter equal to 48 nanometers. This is confirmed by the X-ray diffraction evaluation of the particles diameter as shown Figure 8.
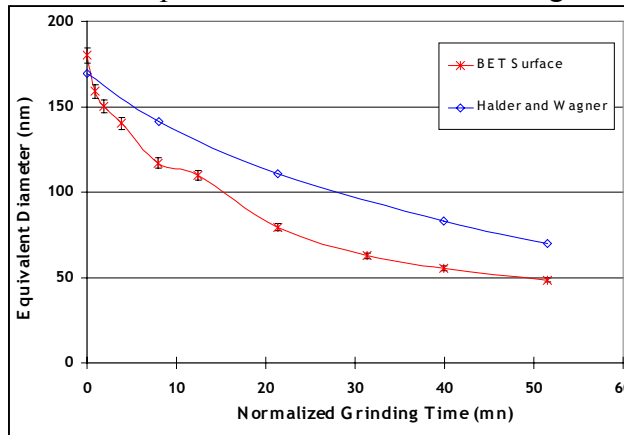

Figure 8: Evolution of the diameter of the particles versus grinding time evaluated by BET specific area measurements and by X-ray diffraction with the Halder and Wagner method
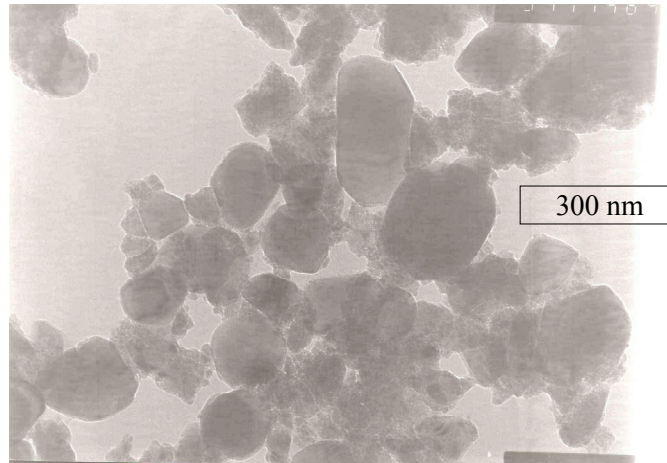

*Figure 9: TEM observation of the 32m².g⁻¹ TiO₂ powder**

TEM observations of the powders* confirm these evaluations, as the diameter of most of the grains lies between 50 and 80 nm. Some large grains remain. their presence could be explained by the fact we have ground this particular powder directly with the 0.4 mm balls that were too small to crush these large grains. Thus, a correct schedule could be to process following grinding using balls with decreasing diameters. On the other hand, grinding with larger balls (1.25 to 1.6 mm in the present case) seems much less efficient when considering the BET specific area evolution versus time, but is necessary as a first operation to reduce the diameter of the largest grains.

V - 2 Alumina Al_2O_3

The isoelectric point of α-alumina is known to be around pH 8 or 9, and alumina slurries are known for a long time to be highly viscous for pH values ranging from 6 to 10. This behavior is confirmed Figure 10, shear-thickening deflocculated being only obtained for highly basic pH ≥ 11 or acid pH ≤ 5.7.
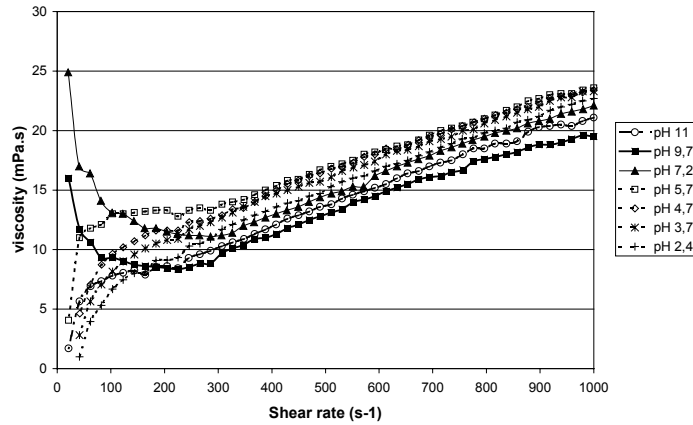

Figure 10: Rheological behavior of Al_2O_3 50wt% versus pH

The α-alumina to be ground was characterized by a 15 m².g^{-1} BET specific area. We chose to grind it with 0.4 mm balls in an acid slurry, maintaining the pH equal to 4 all the process long. Figure 11 shows together the evolution of the BET specific area versus grinding time and the calculated equivalent diameter. After 50 minutes grinding time, BET specific area was as high as 44 m².g^{-1} that corresponds to a 34 nm calculated equivalent particles diameter.
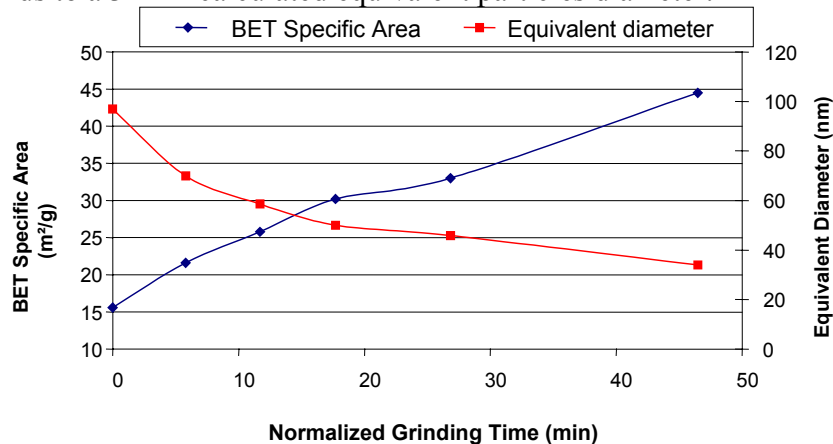

Figure 11: Evolution versus time of the BET specific area and of the equivalent calculated diameter of particles for Al_2O_3 grounded with 0.4 mm grinding balls

VI . CONCLUSIONS

The experimental results presented here show that it is possible, using a classical attrition milling material, to get nanometric powders. There are some conditions to be respected that allow this performance:

- ➢ Importance to keep at any moment a low value of the viscosity of the slurry;
- ➢ That is closely correlated to the keeping of a deflocculated state that can be characterized with a shear-thickening rheological comportment;
- ➢ These conditions have to be maintained during the whole grinding process, any flocculation of the slurry being impossible to be salvaged;
- ➢ Importance of the diameter of the balls: large enough to allow the grinding of large grains, small enough to permit a good efficiency. A "string of milling" using grinding balls with decreasing diameters may be implemented.

Much work has yet to be made to go further in that direction. It includes first a careful investigation of the rheological properties of slurries under different shear conditions and a modeling of the shear stresses occurring during the grinding process. Automatic regulation of the optimum grinding parameters will be also studied. And, at least, similar prospective studies will be devoted to slurries deflocculated with steric dispersants.

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