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Effect of prolonged dry grinding on size distribution, crystal structure and thermal decomposition of ultrafine particles of dolostone

Pedro L. Guzzo [a,*], Filipe B. Marinho de Barros [a], Alan A. de Arruda Tino [b]

[a] Departmentof Mining Engineering, Federal University of Pernambuco, 50740-530 Recife, PE,Brazil
[b] Department of Mining Engineering, Federal University of Western Pará, 68170-000 Juriti, PA,Brazil

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ABSTRACT

The effect of ultrafine dry grinding for up to 1920 min in a planetary ball mill at 300 rpm on size distribution, particle agglomeration and bulk structural changes in a dolomite-rich ($CaMg(CO_3)_2$) rock was studied. The size and shape of the ground particles were characterized by laser scattering and scanning electron microscopy (SEM) respectively. The uniformity index of the size distribution evaluated using the Rosin-Rammler equation showed that the apparent grinding limit was reached after 480 min. Differential- and thermo-gravimetric (DTA-TG) analyses showed that the decomposition temperature of magnesite ($MgCO_3$) was affected to a far greater extent by the input energy of grinding than that of calcite ($CaCO_3$). The activation energy of the total decomposition decreased for the aliquots ground above 480 min. This behavior was explained by the storage of extensive lattice distortions in dolomite crystal structure evaluated by X ray line profile analysis of major diffracting peaks. The infrared (IR) bands related to the bending (877 cm^{-1}) and stretching (1418 cm^{-1}) vibrations of the anionic CO_3^{2-} groups increased with the particle size decreasing as well as being sensitive to particle coarsening caused by agglomeration. Coupled to morphological and Rosin-Rammler size distribution analyses, IR data confirmed extensive agglomeration above 480 min. The transformation between calcite and aragonite polymorphs was also noticed in those aliquots ground for periods ≥480 min. The bulk structural changes documented here were useful to show that the inversion from the breakage to the agglomeration regime observed in dolostone powder system is directly associated with the change in the energy relaxation mechanism inside the dolomite grains.

1. Introduction

The manufacturing of ultrafine powders by high-energy milling is influenced by two counteracting processes: particle breakage and interparticle interaction. Particle breakage is dependent on microcracking propagation controlled at the most basic level by the Griffith criterion of brittle fracture [1,2]. This affects the kinetics of the comminution process as well as increasing the specific surface area of the ground product. Interparticle interactions are governed by interfacial and surface properties such as intermolecular forces and chemical reactivity [3–5]. This controls the kinetics of aggregation and agglomeration processes during the comminution operation and reduces the specific surface area of the grinding product. Intense mechanical action during dry grinding can also initiate significant bulk structural changes such as polymorphic transformations, amorphization and solid-state reactions in the particulate system [6–9]. The technological importance of exploring particle agglomeration and structural changes induced by high-energy milling is due to the fact that certain properties of the grinding product, such as the ability to hydrate, reactivity and solubility are negatively affected. This issue is particularly important for the ultrafine grinding of industrial minerals and rocks that are not currently processed in the presence of water. The use of dispersants in wet processes reduces the effect of interparticle interactions and bulk structural changes. Nevertheless, in industrial processes, the wet grinding is frequently followed by solid-liquid phase separation and drying which entails several practical difficulties and losses inherent to handling ultrafine particles [8,10].

Carbonate rocks such as limestone and dolostone in ultrafine size are widely used in paint, pharmaceuticals, paper making and polymer industries due to its performance in whiteness, thermal stability and rheological properties. The ultrafine grinding of carbonate rocks usually occurs in dry systems where interparticle interactions and crystal-structural alterations coexist with breakage mechanisms. Our previous studies with limestone showed that dolomite is much more affected by the mechanical action of grinding than its major constituent calcite [11,12]. Ideal dolomite has a crystal lattice consisting of alternating layers of Ca and Mg, separated by layers of CO_3^{2-} and is typically represented by a stoichiometric chemical composition of $CaMg(CO_3)_2$ where calcium and magnesium are present in equal proportions. Whilst examining structural alterations caused by high-energy milling in

* Corresponding author.
E-mail address: pguzzo@ufpe.br (P.L. Guzzo).

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different rhombohedral carbonate minerals, Kristóf and Juhász [13] have shown that the most significant changes were found in dolomite. Combining differential thermal analysis (DTA) and high-temperatureX-ray diffraction (XRD), it was shown that deformed dolomite decomposes directly into $CaCO_3$ and MgO between 650 and 750 °C, whereas undistorted dolomite decompose into CaO and MgO in a one-step process between 600 and 800 °C [14]. Further studies devoted to the investigation of the consequences of ultrafine dry grinding on size distribution and structural regularity of calcium carbonate powders reported the occurrence of agglomeration and the subsequent polymorphic calcite-aragonite transformation [15,16]. Severe structural degradation in dolomite and in its two end components, calcite and magnesite, when milled up to 172 h in a ball mill, was previously investigated by Gammage et al. [17]. However, as far as we know, an entirely investigation connecting the coarsening of finely ground particles with structural distortions induced by grinding and its consequences on the thermal decomposition has never been carried out for dolostone. This study is particularly important for the industry of cement clinker since coarsening and structural distortions caused by high-enery milling has practical consequences in the effectiveness of calcination and sintering processes in finely ground carbonate particles.

This paper reports the effect of the prolonged dry grinding of millimeter size dolostone particles in a planetary ball mill and the consequences on particle size distribution, particle aggregation and the loss of crystal regularity in dolomite, the major constituent of this rock. Besides the determination of nominal diameters and specific surface area as a function of the grinding time, the size distribution curves were further interpreted with the Rosin-Rammler function. This procedure, together with scanning electron microscopy (SEM) and particle size analysis carried out with dispersant, was employed to identify the apparent limit of grinding and the growth of agglomerates. The second part of this study investigated the alterations in the crystalline structure of dolomite occurring in dolostone particles which were ground for up to 32 h. In order to achieve this, X ray diffraction (XRD) and attenuated total reflectance infrared (ATR-IR) spectroscopy techniques were adopted. Finally, the ground product was systematically characterized by thermal analysis (DTA-TG) in order to investigate the alterations induced by the grinding process on the thermal decomposition of dolostone. The discussion of the results allowed us to find out a correlation between the apparent grinding limit and the loss of crystal regularity with the onset of agglomeration and the changes in the activation energy required for the thermal decomposition of finely ground dolostone. The transition from breakage to plastic flow mechanisms was also considered.

2. Experimental

2.1. Sample and grinding tests

This study was carried out with dolostone blocks collected from the Jandaíra district; one of the cretaceous terrestrial formations of the Potiguar sedimentary basin located in the state of Rio Grande do Norte (RN), Brazil [18]. The blocks (~ 9 kg) were crushed until all particles had been passed to the 850 μm screen aperture. The crushed material classified between 850 and 450 μm was used to prepare 30 aliquots of 40 ml (~ 60 g). The composition of the material studied was estimated by the refinement of the X-ray diffracting pattern using the Bruker-Diffract.Topas software (version 4.2), which is based on the Rietveld method to quantify multiphase materials [19]. The experimental XRD patterns were obtained using two distinct feed aliquots. The aliquots were carefully comminuted with an agate mortar and pestle to adjust particle size for measurement. As a result, it was found that the dolomite content in Jandaira dolostone is approximately 95%. The other main constituents are calcite and muscovite. Quartz probably occur in very low concentration.

The grinding experiments were carried out in dry with a planetary ball mill, model *Fritsch Pulverisette 5* (revolution radius: 123 mm; rotation/revolution ratio (relative): 2.19; nominal power: 1300 W), with zirconia bowls (inner diameter: 70.6 mm; volume: 250 ml) rotating in the counter direction against the revolution disc. The grinding media was composed of 25 balls of zirconia with diameter equal to 10 mm. The charge volume in each bowl was fixed at 21 ml. The experiments were carried out with 12 grinding times from 1 to 1920 min with a revolution speed equal to 300 rpm. For grinding times ≥60 min, a break of 2 min was adopted after each 15 min of grinding followed by the reversal in the direction of the revolution. For grinding time ≥ 480 min, a substantial amount of ground material became aggregated on the ball and bowl surfaces. The disaggregation was carried out manually with the aid of a screwdriver. This procedure affected the dimensions of large-sized agglomerates (> 1 mm) that were not included in the particle size analysis. Grinding experiments were completely repeated once, for 30 and 480 min periods.

2.2. Particle size analysis and electron microscopy

Particle size distributions were measured by laser scattering using the *Malvern Matersizer 2000* equipment. The measurements were carried out in distilled water using the *Hydro 2000* accessory. Each ground aliquot was measured three times with the same dispersed sample. For aliquots ground at 1, 4, 60, 240, 480, 960 and 1920 min, this procedure was repeated five times with different dispersed aliquots. The nominal diameters d_{10}, d_{50} and d_{90} were calculated averaging the mean values of each measurement. The nominal diameters d_{10}, d_{50} and d_{90}, correspond to the apertures related to 10, 50 and 90% of passing material, respectively. The specific surface area (S) of each size distribution was calculated by the equipment as follows: $S = 6/(\rho.D$ [2,3]), where D [2,3] is the surface weighted mean diameter and ρ is the specific mass of dolomite (2.87 g/cm^3). For aliquots ground for periods ≥30 min, the size distribution was also measured after dispersing the ground product in a saturated solution (0.3 g/mol) of sodium silicate (Na_2SiO_3).

The particle morphology was analyzed by scanning electron microscopy (SEM) using the FEGQuanta-200 microscope. The images were obtained with secondary (SE) or back-scattering (BSE) electrons in vacuum with 18 kV. The particles were coated with a gold layer. The analyses were carried out with magnifications varying from 20 to 20,000 X.

2.3. XRD and IR spectroscopy

The effect of the grinding conditions on the crystalline structure of the dolostone particles was analyzed by X-ray powder diffraction (XRD) and infrared (IR) spectroscopy. The XRD patterns were obtained with a *Bruker D2-Phaser* diffractometer equipped with a *Lynxeye*one-dimensional detector; Cu-Kα radiation (30 kV, 10 mA; Kα wavelength: 0.154060 nm); goniometer step of 0.0202°/s; counting time 2.5 s and 2θ scanning from 4° to 80°. Aback-loadingsample-holder was used to reduce the effect of preferential orientation of the crystalline grains over the diffracting intensities. The diffracting peaks were indexed using the *Bruker-AXS Diffrac.Eva* software and the *COD*-2013 data base. The full-width at half-maximum (FWHM) of four diffracting peaks of dolomite was adopted to evaluate the peak line broadening with the aid of the *Bruker-AXS Diffrac.Eva* software. The FWHM was measured after removing the background and the contribution of the $K\alpha_2$ radiation. As already known, the broadening of the diffracting peaks is a measure for the deviation from the ideal crystal structure such as finite crystallite size, lattice strains and the increase of dislocations and two-dimensional lattice defects [20,21].

The effect of the prolonged grinding in the short range scale of the crystalline structure was investigated by the analysis of the infrared (IR) vibration modes of the CO_3^{2-} groups of dolomite. The IR spectra were obtained with a Bruker Vertex-70FT-IR spectrometer using the