Variation of the rutile and anatase phase using a high energy planetary mill in a carbon dioxide atmosphere

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Abstract. Nowadays, the ball milling technique has become one of the most important owing to its ease of getting the combination of different materials in a short time thus obtaining nanostructures of different types. In the present work, the temporal evolution of the phase change of titanium dioxide from anatase to rutile is shown through the ball milling technique. The milling time was varied from 1 to 9 hours at a carbon dioxide atmosphere controlled at a pressure of 34.47 KPa and a ratio of 1:10 (gram of material: gram of balls). The results were analyzed through X-ray photoelectronic spectroscopy. A change from anatase to rutile of the titanium dioxide structure is shown for each range of the milling time. In the same way, through scanning electron microscopy, a 90% reduction in the initial size was shown, thus, getting nanostructures of approximately 20 nm.

1. Introduction
The technique of grinding by means of a planetary mill or mechanical alloy is a flexible and powerful process that is mainly used to produce new materials while found in the solid state [1]. It consists of the deformation of the powder in a repetitive, continuous and plastic way at room temperature to create new alloys and / or microstructures, as well as the reduction of the size of the particles [2]. Currently, the formation of nano crystal composed of metal oxides such as ZnO, TiO and TiO₂. Titanium dioxide is one of the polycrystalline semiconductors used in a large number of applications due to its good physical and chemical stability, its strong ultraviolet absorption in photocatalysis processes, its good resistance to corrosion [3,4]. Nowadays, the applications in the chemical industry [5], electronics [6], and biology [7] among other applications, generated a greater interest of study towards TiO₂. The different forms of presentation of titanium dioxide normally known are anatase, rutile and brookite [8]. The literature shows a large number of techniques for synthesizing Ti and TiO₂ powder nanocrystals, however; there are very few reports in the literature on the reaction of Ti grinding under different atmospheres of oxygen, hydrogen as well as nitrogen [9]. which allowed a change in the structure of TiO₂ Xiaoyan, et al. used the high-energy grinding technique with different atmospheres and found that the anatase phase increases with oxygen depletion [10]. Avar, et al. found that by increasing the grinding time the particle size changed (approximately 10 nm); In addition, the use phase can be reached at temperatures of 600 °C to 800 °C [4].

In the present work, we study the effects on the structure of TiO₂ through the ball milling process with times of 1 h, 3 h, 6 h and 9 h, at a rotation speed of 450 rpm in a CO₂ atmosphere at a constant pressure of 34.47 KPa. A structural transformation of TiO₂ anatase to rutile was obtained; in addition to obtaining 20 nm nanoparticles.
2. Experimental setup
Commercially available TiO2 powder (> 99% purity, León Laboratory), was used as starting materials. Then, the samples were calcined at 300 °C for 48 hours in a heating oven to ensure the elimination of some organic component. Narrow spectra of Ti2p and O1s were taken to observe the anatase phase, by means of the X-ray photoelectronic spectroscopy (XPS / ISS / UPS) surface characterization platform (SPECS -Germany). The platform is equipped with a PHOIBOS 150 2D-DLD energy analyzer. During the analysis of the pressure in the fuel analysis chamber approximately 1×10−9 Pa. For measurements, a monochromatized Al-Xα X-ray source (FOCUS 500) is operated at 100 W. The analyzer's passing energy hemispheric was set at 100 eV for general spectra and 30 eV for high resolution spectra. The surface load compensation is controlled using a flood gun (FG 15/40-PS FG 500) which was operated at 58 μA, 2.5 eV. At the end of each analysis, the C1s region was recorded again to verify the evolution of the surface charge of the samples during the analysis.

TiO2 powders were synthesized in the absence of CO2 through a mechanical-chemical process using a high-energy ball mill (Planetary mill PM 100 CM). Simultaneously, the grinding was carried out under atmospheric conditions of CO2 at a pressure of 34.47 KPa in a 125 ml steel container using 30 stainless steel balls with a diameter of 10 mm, maintaining the ball-to-powder ratio at approximately 10:1 throughout the experiment. The amount of powder used in each experiment was 12.4 g. The effect of the conditions of mechanochemical synthesis on the nanopowders obtained by varying the grinding time (1 h, 3 h, 6 h, and 9 h) was studied. The grinding speed was maintained at 450 rpm with rest intervals every 15 minutes in which the direction of rotation was reversed. Narrow spectra of Ti2p and O1s were taken to observe the evolution of the TiO2 phase. TiO2 nano-powder microstructures were analyzed by scanning electron microscope (SEM) TESCAN MIRA 3 FEG-SEM, with a Bruker X-ray detector for EDS and SPRIT 2.0 software. The acceleration voltage used was 30 KV.

3. Results and discussion

3.1. X-ray photoelectronic spectroscopy results
Figure 1(a) shows the bond energies of 458.1±0.3 eV, 461.6±0.3 eV and 460.0±0.3 eV for the sample without grinding; which represent TiO2 in anatase phase, TiO2 and TiO2 respectively that agree with the values reported by [10,11], and where it is initially shown that TiO2 is in anatase phase. Figure 1(b) corresponding to 1 hour of grinding, the appearance of TiO2 can be evidenced in the anatase phase for an energy of 458.4±0.3 eV as well as 459.4±0.3 eV for a rutile phase reported by [12,13]. Therefore, the grinding process has an effect on the initial phase change of the original material. Figure 1(c) correspond to three hours of grinding, the two phases of TiO2 anatase and rutile are found with values of the near peaks of 458.4±0.3 eV and 459.9±0.3 eV respectively. These values were also reported by [11,13]. The proximity of these values shows that as the process progresses, energy is gained, facilitating the appearance of the rutile phase of TiO2.

For the six-hour milling it is shown that the anatase phase disappears Figure 2(a) that is found with a value of 459.5±0.3 eV for rutile phase and 458.4±0.3 eV corresponding to TiO2 anatase phase as
reported in the literature, 456.0±0.3 eV reported by Gonbeau D, et al. corresponding to an oxide of Ti$_2$O$_3$ [11]. This result is very important because a new phase of TiO$_2$ is obtained. This as a consequence of the increase in temperature during the six hours of grinding facilitating the obtaining of different phases.

In Figure 2(b) for a grinding time of nine hours, there is a value of 458.5±0.3 eV, energy corresponding to the anatase phase as reported by Biesinger, et al. [14]. In the same way, there is a value of 460.0±0.3 eV corresponding to TiO$_2$, reported by Ocal, et al. [15,16]. The literature provides numerous examples Lowenberg, et al. [10,15] of studies involving TiO$_2$. However, these involve the adsorption of compounds on anatase or rutile surfaces specifically and focus on the chemistry that takes place in these processes, and not on the procedures for adapting or quantifying the values of BE that arise from the milling process.

![Figure 2](image2.png)

**Figure 2.** Spectral lines Ti2p for a grinding to: (a) 6 h and (b) 9 h.

Figure 3 shows the change in the spectral lines of O1s of the different titanium oxides in which there are energies of 532.5±0.3 eV, 534.8±0.3 eV, 530.6±0.3 eV without grinding also identified by Cardinaud, et al. [15,17]. For the samples of the first hour of grinding (Figure 3(b)) there are energy values of 529.7±0.3 eV, 530.5±0.3 eV, 531.5±0.3 eV corresponding to the oxidation processes of TiO$_2$ as reported by Stypula, et al. [18-21] and OH as a result of the grinding process.

![Figure 3](image3.png)

**Figure 3.** Spectral lines O1s (a) 0 h and (b) 1 h.

In the three-hour processes, see Figure 4(a), there are peaks of 529.8±0.3 eV, 531.5±0.3 eV, 533.6±0.3 eV, corresponding to oxidation states of TiO$_2$ reported by Dausher, et al. [20,22,23]. In the six-hour grinding, see Figure 4(b), energy values of 529.7±0.3 eV, 528.1±0.3 eV, 530.8±0.3 eV and 532.7±0.3 eV were obtained. These values have been reported by Ju F, et al. [18-20]. Figure 4(c) shows the spectral lines of O1s for a grinding time of 9 hours with values of 529.8±0.3 eV, 531.9±0.3 eV, 530.7±0.3 eV corresponding to TiO$_2$: link energies [20-22].

Finally, it can be said that there is a strong relationship with the time of the grinding process for the appearance of titanium oxides and their states of Ti, at a time of 9 hours only the rutile phase was found, that is, as it increased the time in the mill the anatase phase was changing to rutile. Avar, et al. found that at temperatures above 600 °C the rutile phase appears [4], it should be noted that as the grinding
time is increased, the temperature inside the container increases, making the reactions of the material with the medium allow more easily the structural change from TiO$_2$ anatase to rutile.

Figure 4. Spectral lines O1s 5 to: (a) 3 h, (b) 6 h, and (c) 9 h.

3.2. Scanning electron microscope
The SEM results show a reduction in the size of the granulated material compared to the one that did not grind. Initially the size of the particles that make up the TiO$_2$ powder is on average 170 nm - 100 nm (Figure 5(a)), there is no significant change in the material size after one hour of grinding under a CO$_2$ atmosphere (Figure 5(b)).

Figure 5. SEM images of grinding (a) 0 h, (b) 1 h, (c) 3 h and (d) 6 h.
Figure 5(c) shows an increase in particle size as evidenced after three hours of milling, possibly caused by the impact of the grinding material with the walls of the jug used, presenting a plastic deformation in the particles that make up the alloy of mixture. A hypothesis that we handle is that the chemical reaction of TiO$_2$ with oxygen of CO$_2$ influences the increase of the particle since according to B Avar and S Ozcan [4]. The oxygen begins to be absorbed from 65 minutes: value reported by [24], causing a slight modification in the crystal lattice. It would be necessary to carry out other tests to verify this premise. In contrast, after six hours of grinding the particle size is in a range of 70 nm to 46 nm (Figure 5(d)).

A significant change in the size of the nanoparticle is visible after nine hours of milling (Figure 6), where sizes of 30 nm to 17 nm are reached, reflecting one of the main purposes of this technique, because the material undergoes a severe mechanical deformation producing plastic deformations that occur inside the particles after a prolonged milling, as well as the different variations in their microstructural parameters in the different phases of TiO$_2$ anatase during the grinding process [8]. In summary, it can be said that the size of the nanoparticle formation is related to the time in the grinding exposure.

![Figure 6. SEM images 9 h of grinding.](image)

4. Conclusions
It was possible to obtain the phase change of the TiO$_2$ from anatase to rutile through the grinding process, which appears from the first hour of the process and staying throughout all the stages, which it is evident in the XPS results. The study is pending to achieve TiO$_2$ oxidation states which have not been reported by this technique, as well as having the degree of crystallinity and the formation of the network. The results of SEM, clearly shows the relationship between the grinding time and the formation of TiO$_2$ nanoparticles starting from the six hours of the process; where a change from 197 nm (0 hours) to 20 nm in (9 hours) is evidenced. It is difficult to conclude that the change in particle size as a function of time obeys to some known function.

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