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Structural Study of TiO_2 Nanopowders Obtained in a Planetary Ball Mill

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Abstract

The effects of milling time (6 and 24 hours) on the polymorphic transformation and the evolution of the powder characteristics of TiO_2 during high-energy ball milling was investigated using X-Ray diffraction accompanied of Rietveld refinement. It was found that polymorphic transformation of Anatase to Srilankite and Rutile took place during milling. Furthermore, amorphization of crystalline phases occurred during milling. Our results indicates that the crystallite size of the TiO_2 polymorphs is in the range of nanometers with a slightly decrease in the size as the milling time increases. Additionally, we perform a milling parameters analysis to interpret the mechanisms of transformation of the TiO_2 phases.

Keywords: Titanium oxide nanoparticles, Mechanical milling, X-ray diffraction, Rietveld Refinement.

INTRODUCTIÓN

TiO_2 exists in three main crystalline forms that are: Rutile, Anatase and Brookite [1]. In addition to these, there are two phases of high pressure: Srilankite and TiO_2 (B). The relative stability of rutile and Anatase under environmental conditions is a controversial topic in the literature, both from the point of view of experimentation and the theoretical one [2-3]. Rutile is considered the most stable configuration of TiO_2. Traditionally, the rutile phase has been the most widely investigated experimentally and theoretically, the former due to the availability of good monocrystals for characterization and the second due to the relatively simple crystalline structure. However, recently, experimental investigations have also focused on the other nanocrystalline polymorphs of TiO_2 due to their applications in the protection of the environment, protection against ultraviolet radiation, antibiosis, pigments, optical coatings, photoelectrochemical use, and its application in organic coatings [4-5].

The properties of TiO_2 are greatly affected by the synthesis method and the precursors employed in the preparation, these determine the physico-chemical, crystallographic, and magnetic properties of final product. Therefore, the search for proper experimental conditions to successfully prepare these materials has become an important issue of this research field. Over the past three decades, ball milling has evolved from being a standard technique in mineral dressing and powder metallurgy, used primarily for particle size reduction, to its present status as an important method for the preparation of either materials with enhanced physical and mechanical properties or, indeed, new phases, or new engineering materials. The mechanical milling uses a conventional ball mill in which the mechanical energy activates chemical reaction and induces structural changes. Repeated ball-powder collisions continually regenerate reacting interfaces, alloying chemical reactions to occur at low temperatures.

In the present work, we present our investigation to understand the effects of two different milling times (6 and 24 hours) on the crystalline phases and structural parameters of TiO_2 nanopowders. Additionally, we perform a milling parameters analysis to interpret the mechanisms of transformation and synthesis induced in TiO_2 powder by the planetary mill.

EXPERIMENTAL METHOD

Mechanical milling of TiO_2 (99,9 % purity, Sigma Aldrich) powder in a single Anatase phase was carried out in a Fritsch Pulverisette 5 classic planetary ball mill (see Fig. 1) using 2 using Cr-based stainless steel jars of 250 cc capacity, with balls of 12 mm in diameter and 7 grams of mass (each), made of the same material. Different milling times were considered (6 and 24 hours), the rotation velocity of the discs was of 250 rpm (medium energy) and the ball to powder ratio was of 20:1. The products were characterized in detail using the X-ray diffraction (XRD) technique. XRD patterns were obtained using a Cu (Kα) radiation; data were collected in the 20°-80° 2θ range with a 0.02° step and a counting time of 3 seconds per step. Quantitative XRD analysis was performed using the MAUD program, which combines the Rietveld method and a Fourier transform analysis [6]. The scale factor, incident intensity, sample displacement, three-order polynomial background, unit cells, average crystallite sizes (*D*), microstrains and volume fraction of the phases were treated as adjustable parameters during the numerical analysis. The average crystallite size and the texture were assumed isotropic and arbitrary, respectively, for all phases.

Figure 1. Planetary ball mill
(classic line Fritsch Pulverisette 5) with two jars.
Source: Authors

RESULTS AND DISCUSSIONS

Structural properties

The XRD patterns of TiO_2 for the 0, 6 and 24 hour of milling time, fitted with the MAUD program are shown in Fig. 2. It can be seen that the powder initially was in the Anatase phase. For the diffractograms of TiO_2 milled for 6 and 24 h, a coexistence of Anatase, Rutile and high pressure phase (Srilankite) was found. As the milling time increased, the intensity of the reflections corresponding to the Anatase phase decreased and the width of the peaks increased, associated with the decreasing in average crystallite sizes (*D*) and the increasing of microtensions induced by the milling process (see Table 1).

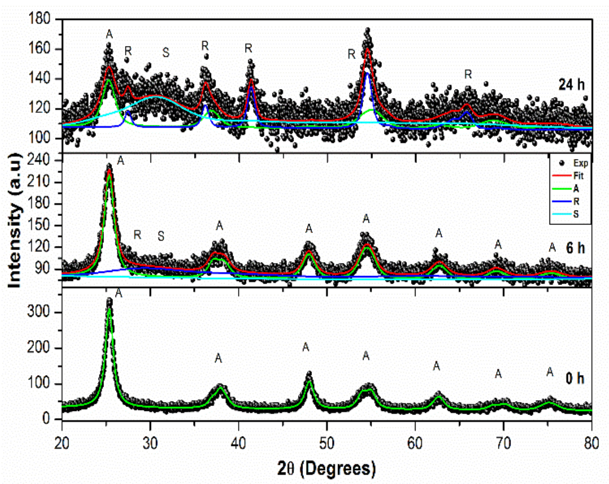

Figure 2. XRD pattern of unmilled TiO_2, and considering 6 and 24 h of milling time. A (Anatase), R (Rutile), and (Srilankite).

Table 1: Obtained parameters from Rietveld refinement with the MAUD program of the DRX patterns.

Time (h)	Phase	Vol. (%) Fraction	*a*(Å)	*b*(Å)	*c*(Å)	*D(nm)*
0	A	100	3,80		9,52	11
6	A	70	3,80		9,47	9
	R	22	4,59		2,97	8
	S	8	4,54	5,50	4,90	8
24	A	43	3,79		9,31	6
	R	26	4,67		2,85	5
	S	31	4,53	5,50	4,85	6

Our results are in according with the reported by Bégin-colin et al. [7-8], Dutta et al. [9], Hu [10], Bose et al.[11 and Pan [12]. They showed that high-energy milling of the TiO_2 Anatase phase induces Anatase-Rutile phase transformations via the high-pressure phase, Srilankite:

$$Anatase \rightarrow Srilankite \rightarrow Rutile \quad (1)$$

Additionally, the decrease of the integrated area of the Anatase reflections observed in the XRD patterns, caused by the transformation of crystalline TiO_2 to the amorphous phase and the appearance of integrated area of the Rutile reflections increases slightly with the milling time. These facts are related with some reflections of Anatase that disappear after milling for 24 hours, while many reflections of Srilankite and Rutile never appear (see Fig. 1), probably caused by the introduction of substantial amounts of defects in the crystalline TiO_2 phase like Oxygen vacancies generated by the milling process.

Milling parameters analysis

During the milling process, the impact pressure at the collision sites of the powder and the balls, and the increase in temperature, are important parameters that contribute to the transformation of the Anatase-Srilankite-Rutile phase. In an attempt to understand the mechanisms of transformation and synthesis induced in TiO_2 powder by the planetary mill, is assumed that collisions are the main mechanism by which energy is transferred to the powder during the process of mechanical milling, and therefore the most important parameters are [13]:

-The kinetic energy of the balls

-The kinetic energy fraction transferred to the powder

-The volume of the powder trapped in a collision.

In Table 2 some important parameters are calculated during the milling process using the model proposed by Maurice and Courtney [13-14] that does not consider the powder, that together with the model that considers the balls covered with a thin layer of powder produce similar results [15]. This model is based on the theory of Hertz impact having a ball–ball collision. Considering our milling conditions and having into account that for our mill, we have that the radius of the disc is $r_p = 0{,}126m$ and the radius of the balls $r_b = 0{,}006m$ The density of the balls $\rho = 7870Kg/m^3$ and Young's modulus $Y = 211400*10^6 Pa$. Additionally, the density, specific heat, thermal conductivity, and hardness of TiO_2 in the Anatase phase are $\rho_p = 3893Kg/m^3$, $C_p = 800J/Kg.K$, $H_v = 7870Kg/m^3$ and $k_0 = 8.4w/mK$, respectively.

Table 2: Characteristic parameters of milling carried out in a planetary mill Fritsch Pulverisette 5 with two jars.

Characteristics parameters	Obtained values
Impact velocity, $v(m/s)$	2,96
Collision energy, $\Delta E(J)$	30,27E-3
Collision time, $2\tau(s)$	4,42E-5
Contact radius, $r_h(m)$	2,94E-4
Compression of the balls, $\delta_{\max}(m)$	2,89E-5
Maximum impact pressure, $p_{\max}(Pa)$	4,94E9
Impacted powder temperature, $\Delta T(°C)$	536
Volume of the powder trapped, $V_{polvo}(m^3)$	1,98E-12

It is well known that the Anatase-Srilankite transformation occurs under high pressures and the Anatase-Rutile transformation takes place at high temperatures and high pressures [16]. According to the parameters calculated for our planetary mill shown in Table 2, the impact pressure experienced by the Anatase powders during the collision of two balls and/or ball-wall of the jar is around of 5 GPa. Now, if it is considered that the increase in the density of defects due to milling can further reduce the minimum pressure required for the transformation of Anatase phase to Srilankite (1.5 GPa) [16], it is clear that the pressure exerted on the powder of Anatase by the elements of our mill is such that it satisfies the conditions of Anatase-Srilankite transformation. It has also been established that for pure materials amorphization can be induced by high pressures and / or crystallite decrease.

Considering also that the Anatase-Rutile transformation due to the increase in temperature occurs around 425 °C [17], which compared to our obtained values, see Table 2 (536 °C) of the model described for our planetary mill, would guarantee Anatase-Rutile transformation.

CONCLUSIONS

The planetary ball mill induces phase transformations in the TiO_2 powders in the Anatase phase due to the local increase of the temperature and the collision pressure plus an additional energy due to the refinement of the crystallite size and defects induced by the milling, which satisfy the limits of the Anatase-Rutile-Srilankite transformation. Additionally, our results show that there was no total transformation to Srilankite and Rutile. We are facing a complex process of milling, where the formation of two new phases occurs simultaneously, and where the total transformation of the initial phase (Anatase) is not achieved.

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