

Synthesis of nanocrystalline rutile-phase titania at low temperatures

J. G. SANTOS¹, T. OGASAWARA², R. A. CORRÊA^{1*}

¹Instituto de Engenharia Nuclear IEN/CNEN Caixa Postal 68505, Cidade Universitária,
Rio de Janeiro RJ - CEP: 21941-972, Brasil

²COPPE/PEMM, Universidade Federal do Rio de Janeiro, Brasil

Anatase and rutile are the predominant phases in titanium dioxide. In many cases, rutile stable phase is the desired product material, but at low temperatures methods of synthesis (aqueous route) produce metastable anatase as a major product that reverts to rutile only when heated up to 1000 °C. Calcination for obtaining rutile phase is the greatest energy demanding step for titanium dioxide production by the sulphate process, and is responsible for almost 60% of total energy consumption. In this work, an innovative technique involving a sonication pre-treatment in acid medium was developed to change particle reactivity and accelerate the anatase-to-rutile transformation. Scanning electron micrographs and surface area measurements confirmed the alteration in texture and porosity of the powders. Results indicate that it is possible to obtain 100% of rutile phase at temperatures as low as 430 °C.

Key words: *oxides; sonication; X-ray diffraction; transition temperature*

1. Introduction

Titanium dioxide (titania) is the most widely used white pigment in the world. It has no toxicity and is chemically stable, being used mainly to achieve or improve certain properties of commercial paints. It is also used in other industrial applications like filters, catalyst supports, ceramics, paper, food, cosmetics, or fibre manufacturing. Titania exists in three fundamental crystalline phases: tetragonal rutile, tetragonal anatase and orthorhombic brookite, but the latter is not commercially produced. Each phase shows different physical properties, such as refraction, chemical or photochemical reactivity, which allow its use in particular applications usually requiring a specific particle size.

*Corresponding author, e-mail: racorrea@ien.gov.br

Several works about the anatase–rutile transition, emphasizing the temperature of the process, have been discussed [1–5]. This transformation consists in changing from a metastable to a stable phase and occurs without a well-defined temperature, as in the case of reversible transformations in equilibrium processes. This phase transformation temperature can vary from 400 to 1200 °C, being influenced by many factors such as impurities, the method employed, the atmosphere in which the transformation occurs, unreliable stoichiometry, particle size etc. [4].

Rutile is thermodynamically stable at room temperature while anatase, for kinetic reasons, remains essentially metastable. Anatase–rutile transition is very slow at room temperature, being insufficiently useful for industrial purposes. Macroscopic change from anatase to rutile occurs at appreciable rates at temperatures higher than 800 °C [6, 7]. Nanometric particles of anatase enable processes to occur at appreciable rates at temperatures higher than 400 °C [1, 8, 9].

Reports on anatase–rutile transition, with emphasis on the temperature of the transformation process, are mostly found in patent texts [10, 11]. They provide the reader with information concerning the use of seeds, conditioners or promoters of the anatase–rutile transformation used to control calcination and to reduce the temperature of the process. Other works, using inorganic precursors, indicate the beginning of the anatase–rutile transition at 600 °C by addition transition promoters, conditioners and seeds before or during calcination [12, 13] and this temperature is further decreased to 400 °C when an alkoxide is used as a precursor [14]. Commercial production of TiO₂ pigment by sulphate process or derivatives, requires higher temperatures, due to the technical requirements of achieving the crystalline transformation, namely the solid state diffusion during calcination. Thus, anatase–rutile transition is influenced by the synthesis chosen to fabricate the amorphous precursor, and by impurities, addition of stabilizers, morphology and atmosphere of the system, and has no established temperature [2]. Nevertheless, attempts to reduce this temperature are important because high temperatures of calcination generate undesirable growth of primary particles that turns white titanium dioxide pigment slightly yellow, and promotes the formation of hard agglomerations, instead of the small particles that are necessary to improve pigment quality.

The objective of this work is to develop a process to obtain rutile titanium dioxide by calcination at low temperatures of a previously sonicated material. The role of sonication is to increase the number of defects on the surface of the powder in order to improve the kinetics and diffusion processes related to the anatase–rutile transitions.

2. Experimental

Hydrothermal treatment and sonication experiments were performed on hydrated TiO₂. This compound was obtained hydrometallurgically, by leaching an ilmenite solution through several solvent extraction stages, using di(2-ethylhexyl)phosphoric acid (DEHPA) as an agent to extract Ti⁴⁺ ions selectively. Titanium was re-extracted

from organic phase with ammonium fluoride yielding a titanium fluoride solution, which was precipitated with ammonium hydroxide at room temperature and pH ranging from 8 to 10, filtered under vacuum, suspended and reduced to pulp, and finally washed to remove fluorine traces. Separation and purification of titanium from ilmenite through conventional processes yields products of limited purity. Liquid–liquid extraction processes allow the attainment of products of elevated purity and minimize generation of liquid and solid rejects. As a result, all these studies are considered as pioneering efforts, due to the innovative use of hydrated TiO_2 as precursor.

Three types of samples of hydrated titanium dioxide were used in the experiments performed in this work:

Original powder 01 (OP1) – hydrated TiO_2 slowly precipitated with ammonium hydroxide.

Original powder 02 (OP2) – hydrated TiO_2 quickly precipitated with ammonium hydroxide. This powder was used only in adsorption experiments for determination of the Brunauer–Emmet–Teller (BET) parameters.

Hydrated TiO_2 powder quickly precipitated after addition of ammonium hydroxide to titanium sulphate solution.

The precipitated titanium hydroxide was calcined at 600, 700, 800, 940 and 970 °C for 3 h and at 980 °C for 4 h to determine the exact temperature of the anatase–rutile transformation. The same powder was also subjected to a hydrothermal treatment in the microwave system of Provecto Analitica – DGT 100 Plus Model. The influence of various solvents on the crystallization of TiO_2 and on the kinetics of anatase–rutile transition was also investigated.

Suspensions of amorphous TiO_2 were also submitted to high power sonication in acidic medium (HCl or HNO_3) for various durations and various acid concentrations (0.1 to 1.0 M). Sonications were performed in an ultrasonic bath Thornton – INPEC Electronica S.A. 12D Model (25 kHz, 900 W).

The titania was analyzed by the X-ray diffraction (XRD) techniques to observe the progression with time of the anatase–rutile transformation. Diffraction patterns were obtained with a Rigaku model Miniflex diffractometer using CuK_α radiation (40 kV, 40 mA) and a graphite monochromator.

BET specific area measurements were performed with Micromeritics GEMINI 2375 equipment. Scanning electronic microscopy (SEM) for morphological and particle size analysis was performed with a Zeiss DMS 950 model using electron retro scattering.

3. Results and discussion

Several calcination experiments were performed in order to determine the anatase–rutile transition temperatures by analysis of the XRD of the samples obtained. Figure 1 shows the XRD patterns obtained for the anatase phase.

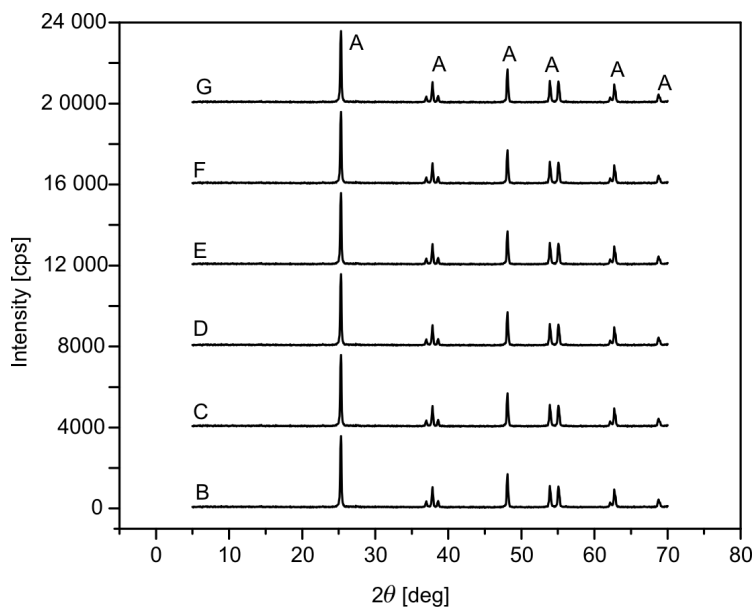


Fig. 1. XRD patterns of anatase (A). Calcinations at 600 (B), 700 (C), 800 (D), 870 (E), 940 (F), and (G) 970 °C

XRD patterns for calcinations at 980 °C and for residence times ranging from 30 min to 4 h are shown in Fig. 2.

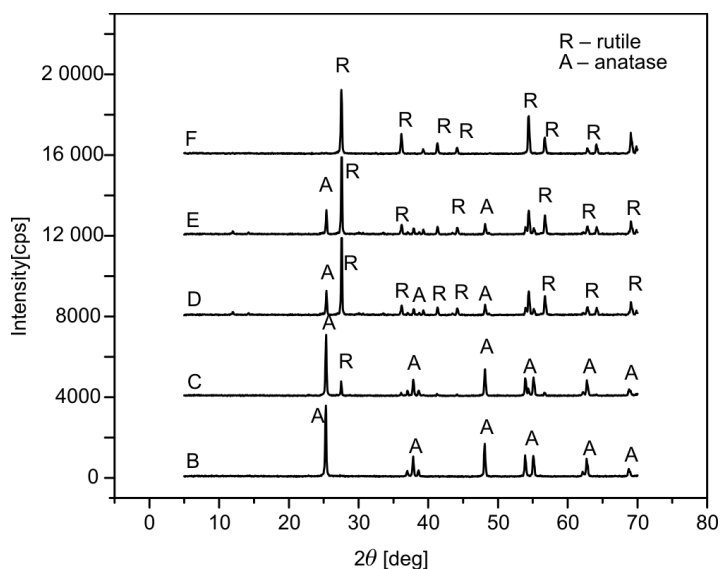


Fig. 2. XRD patterns of TiO_2 . Calcinations at 980 °C, 0.5 h (B), 1 h (C), 2 h (D), 3 h (F) and 4 h (G)

The hydroxide was also subjected to hydrothermal treatment in a microwave oven to investigate the effects of this type of synthesis on the kinetics of the anatase–rutile transformation. Water was used as a solvent.

Figure 3 shows the XRD patterns of the sample subjected to a hydrothermal synthesis in a microwave field, using water as solvent, and calcined to verify if the hydrothermal treatment would allow the formation of rutile in temperatures below those usually required by the anatase–rutile transformation. Although the diagrams indicate that this treatment can lead to increased reactivity, the transformation of anatase to rutile at low temperatures was not observed.

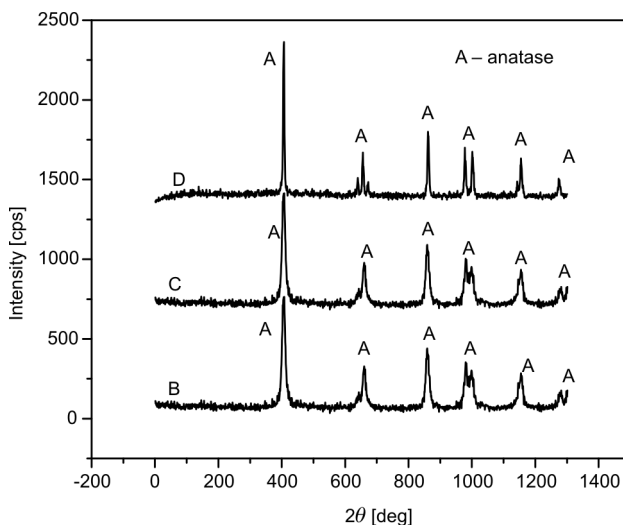


Fig. 3. XRD pattern. Hydrothermal synthesis of hydrated TiO_2 in microwaves in water; no calcinations (B), calcinations at 800 °C (C) and 960 °C (D)

The behaviour of the sample subjected to a hydrothermal synthesis using 1 M HCl as a solvent, instead of water, is shown in Fig. 4. The XRD patterns show that the powders became slightly more reactive than when treated in water, but not reactive enough to advance significantly the anatase conversion to rutile or even any important observable change in the transition phenomena.

Hydrothermal synthesis was also performed using precipitation of titanium fluoride with urea followed by hydrolysis of the latter, which provides OH^- ions during precipitation. The XRD patterns in Fig. 5 show the complete conversion of the product to rutile at 960 °C what indicates an increase in the rate of the transformation anatase–rutile. This observed increase, however, is not significant since the calcined material maintained an anatase structure both at 800 and at 900 °C.

The variation of the specific surface area BET with the calcination temperature is shown in Fig. 6 for the two main powders used in this research, labelled powder 1 and powder 2, respectively. It can be seen that the specific surface area of the original powder 02, which was quickly precipitated, reached larger values compared with

those for OP1. A severe decrease in the BET values is observed with the increase in the calcination temperature. At rutile conversion, the specific surface areas fall significantly, reaching values below $1\text{ m}^2/\text{g}$.

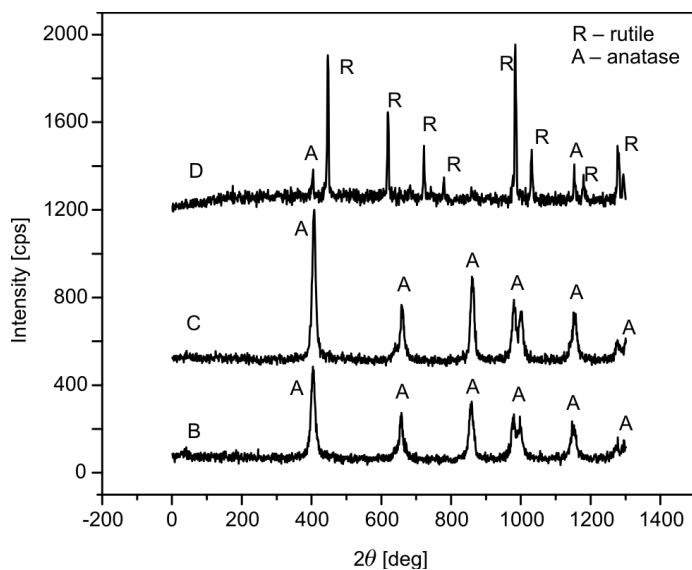


Fig. 4. XRD patterns. Hydrothermal synthesis in microwaves in 1 M HCl; no calcinations (B), calcinations at 800 °C (C) and 900 °C (D)

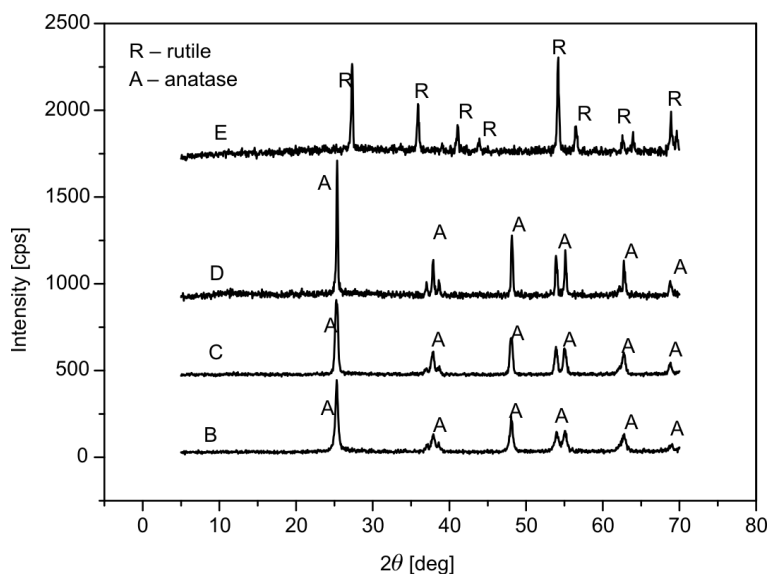


Fig. 5. XRD patterns. Hydrothermal synthesis in microwaves. Homogeneous precipitation in the presence of urea. Calcinations at 650 °C (B), 800 °C (C), 900 °C (D) and 960 °C (E)

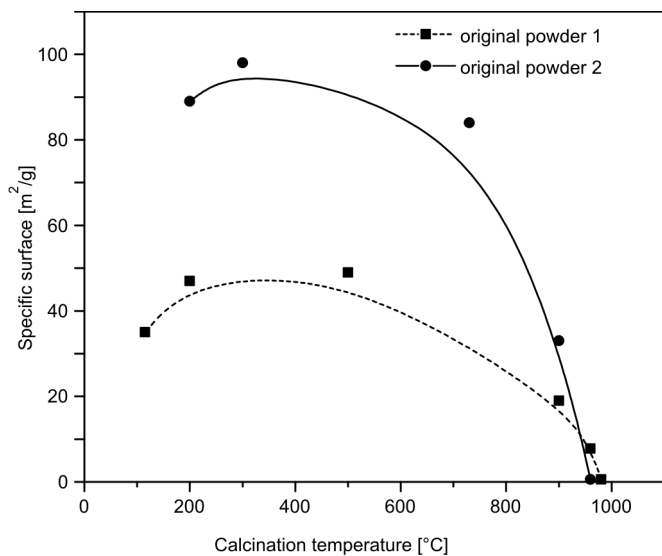


Fig. 6. Dependence of BET surface area on calcination temperature in hydrated TiO_2 without sonication

3.1. Sonication experiments

The influence of the calcination temperature on the rutile content for different periods of sonication, concentration, and types of solvents employed is shown in Fig. 7.

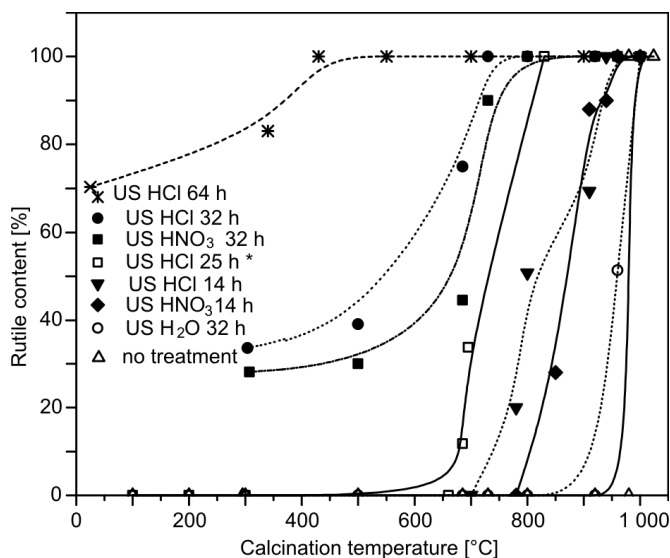


Fig. 7. Dependences of rutile content on calcination temperature; 0, 14, 32, and 64 h of sonication (US); solvents: HNO_3 , HCl and water

The results clearly show the important effects of sonication on the kinetics of the anatase–rutile transformation. While materials that had not been sonicated were completely converted to rutile after calcination at around 1000 °C, materials that had been sonicated for 14 h have their transformation rate altered and complete conversion attained at calcinations near 900 °C and those sonicated for 32 h reached complete conversion at 730 °C. Materials sonicated for 64 h reached extensive conversion close to room temperature, which was complete after calcinations at 430 °C.

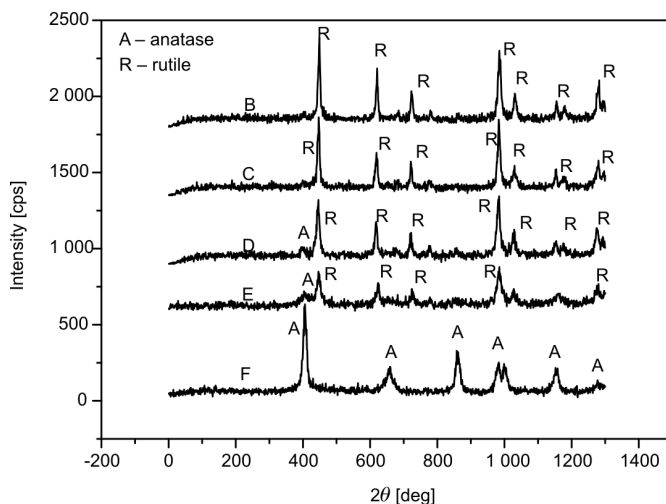


Fig. 8. XRD patterns. Sonicated titania, 64 h, 0.5 M HCl, calcinations at 510 °C (B), 430 °C (C), 340 °C (D), no calcinations (E); anatase not sonicated calcined at 500 °C (F)

XRD patterns of sonicated titania in 0.5 M HCl for 64 h and calcined at three different temperatures up to 510 °C are shown in Fig. 8. XRD diffractographs of not sonicated titania calcined at 530 °C (anatase) was also included for comparison. The findings are surprising and revealing. Analyses of these diagrams suggest nearly complete crystallization to rutile at room temperature making calcinations almost unnecessary.

3.2. Scanning electron microscopy

Scanning electronic micrographs of TiO₂ powder obtained as previously described and calcined at 980 °C for 3 h are shown in Fig. 9. The micrographs show some prismatic crystals, grown simultaneously to phase transition.

Figure 10 shows the electronic micrograph of amorphous hydrated TiO₂ sonicated for 32 h in 1M HCl solution and calcined at 730 °C. Its crystalline structure is a hundred percent single-crystalline rutile. Nevertheless, its texture remains porous, as indicated by BET surface area value – 28 m²/g. Highly porous structures with high concentration of defects favour diffusion in a solid state, which is the most important mode by which transformations evolve during calcinations.

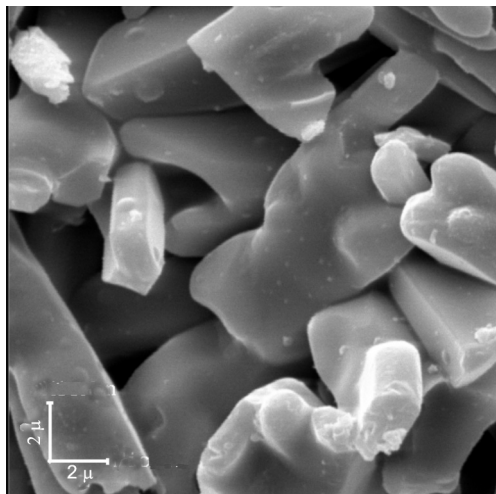


Fig. 9. Powder micrograph. Calcinations at 980 °C; rutile crystalline structure (3000×)

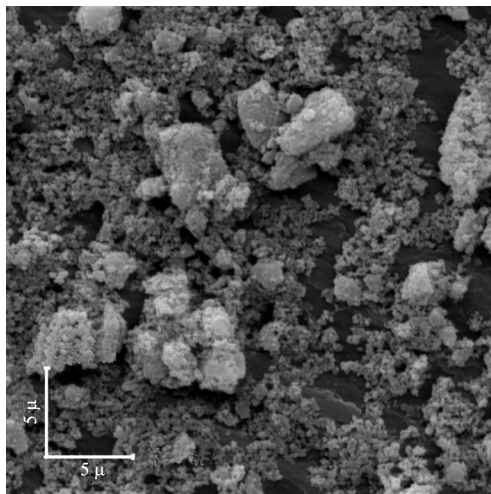


Fig. 10. SEM. Sonicated powder (rutile) for 32 h, 0.5 M HCl, calcination at 730 °C (3000×)

Primary particle sizes derived from the sonication treatment ranged between 13 and 18 nm, which are higher than those obtained by the sol–gel routes yielding particle sizes suitable for fast transformations at 600 °C [15]. The high density of surface defects generated by sonication plays a key role for increasing the kinetics of the transformation and for decreasing the transition temperature what agrees with the results of experiments reported by Gribb and Banfield [16].

4. Conclusions

In this work, a new technique was developed to increase the kinetics of the anatase–rutile transformation by incorporating sonication treatment before calcination. As a result, transformation to rutile phase occurs at great extent at room temperature, and complete transformation is achieved at a relatively reduced temperature of 430 °C. According to the results of this work, kinetics and diffusion processes related to the anatase–rutile transformation are enhanced, by increase in concentration of surface defects of the material, due to chemical-mechanical action of micro jets and shock waves generated by the pre-treatment proposed.

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