Original Research Article

MICROSTRUCTURAL STUDY BY ELECTRON MICROSCOPY OF SONOCHEMICAL SYNTHESIZED TiO_2 NANOPARTICLES

V. Garibay-Febles[a], I. Hernández-Pérez[b], L. Díaz-Barriga Arceo[c], J. S. Meza-Espinoza[c], J. C. Espinoza-Tapia[b], L. González-Reyes[b] *

[a] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. 07730, México.

[b] Universidad Autónoma Metropolitana – Azcapotzalco , Departamento de Ciencias Básicas, Av. Sn. Pablo No. 180, México D. F. 02200, México.

[c] Instituto Politécnico Nacional, Departamento de Ingeniería Metalúrgica y Materiales, ESIQIE-UPALM, México, D. F. 07738, México.

*Corresponding author, E-mail: lgr@correo.azc.uam.mx, Phone: (55) 53189571, Fax: (55) 53189571

Received: June 2016. Accepted: December 2017.
Published: December 2017.

ABSTRACT

Sonochemical synthesis of nanostructured TiO_2 has been carried out successfully at room temperature. Heat-treatments have been applied to as-prepared sample and the microstructural evolution has been studied by X-ray powder diffraction and electron microscopy (SEM, TEM and HRTEM). The results showed that particle growth process and coarsening mechanism are governed by the mobility of triple junction. Also it was observed that an agglomeration of nanoparticles promotes the growth of well-oriented crystalline twin structures. Furthermore, rutile particles are attached to the anatase particles by forming a coherent interface during the phase transformation anatase-rutile, this interface is energetically preferred nucleation site for rutile phase. Finally, the complete phase transformation to rutile is related with a reduction in the total free energy of the system. Therefore, the microstructural evolution reported herein may open new perspectives for the development of TiO_2 nanoparticles as a promising material, which can be widely applied to photocatalytic system.

Keywords: Sonochemistry, microstructure, grain boundary, triple junction, electron microscopy.

ESTUDIO MICROSTRUCTURAL POR MICROSCOPÍA ELECTRÓNICA DE NANOPARTÍCULAS DE TiO_2 SINTETIZADAS POR SONOQUÍMICA

RESUMEN

La síntesis sonoquímica del TiO_2 nanoestructurado se ha llevado a cabo con éxito a temperatura ambiente. Los tratamientos térmicos se aplicaron a la muestra preparada y mostraron una evolución microestructural que se ha estudiado por difracción de polvo de rayos X y microscopía electrónica (SEM, TEM y HRTEM). Los resultados obtenidos mostraron que el proceso de crecimiento de las partículas y el mecanismo de engrosamiento se rigen por una movilidad de triple unión. También se observó que la aglomeración de las nanopartículas promueve el crecimiento de estructuras cristalinas individuales bien orientadas. Además, las partículas de rutilo se asocian a las partículas de anatasa, mediante la formación de una interface coherente durante la transformación de fase anatasa - rutilo, esta interface es energéticamente el sitio preferido de nucleación para la fase rutilo. Por último la transformación de fase completa a rutilo se relaciona con una reducción en la energía libre total del sistema. Por lo tanto, la evolución microestructural informada en este documento puede abrir nuevas perspectivas para el desarrollo de nanopartículas de TiO_2 como un material prometedor, que puede ser ampliamente aplicado a los sistemas fotocatalíticos.

Palabras claves: Sonoquímica, microestructura, límite de grano, triple unión, microscopia electrónica.

INTRODUCTION

A particular interesting type of nanocrystalline (NC) materials is characterized by a strong tendency for grain boundary (GB) segregation [1]. The generation of such small structures is essential to the advance of many areas of science, biological and others fields of engineering science and technology, and a number of physical and chemical technology have been developed [2,3]. Particles with more than one crystal structure, or polymorphs, represent a good candidate for study the microstructural and grain boundary evolution during heat treatment. Therefore, two polymorphs can be affected in a different manner by temperature and, as a result, significantly changes will be produced in the microstructure, crystalline phase, densification, porosity modifications, and the nanoparticles dimensions of nanostructured materials [4]. Analyzing the microstructural modifications in polymorphs materials, is the great effect of temperature on interfacial energy, diffusion, grain growth coefficients, and equilibrium solubility at the microstructural level influences crystal or grain properties during the phase transformation is evident (from metaestable-to-stable thermodynamically).

Therefore, thermodynamics, energetic, physical, chemical and mechanical effects are generated through temperature effects. In fact, the effect of temperature during the nucleation, growth, and coarsening (Oswald ripening) constitute the three basic processes during the microstructural evolution, and phase transformation [5].

Although, it is well known that the grain boundaries play an important role on the microstructural properties, the reduction in grain size to nanocristalline range leads to an increase in the volume fraction of atoms at grain boundary, triple junction and quadruple junction. Therefore, the increase in the interfacial area has been associated with many interesting properties such as photocatalysis [6].

However, in the analysis and understanding of microstructural evolution, grain growth and densification, during thermal effects, it has been conventionally assumed that interfacial energies, including surface and grain boundary energies are isotropic [6, 7]. In reality, however, the interfacial energies are often anisotropic, and thus the surface and grain boundary are faceted at heat treatment temperature. For faceted grain boundaries, the conventional understanding of heat-treated behavior should not be valid since the mobility of the faceted boundary is different to that of a rough boundary [8], and a faceted boundary would not be a perfect atom source with no energy barrier for densification. In contrast to the fairly good understanding of the correlation between grain growth behavior and grain boundary type and triple junction either rough or faceted, the effect of grain boundary structure on densification and phase transformation has rarely been studied. Therefore, TiO_2 nanoparticles were studied in this research, which were synthesized by means of sonochemical process due to its novel, simple and clean production method (considered as environmental friendly). Then, the nanoparticles that were produced by the above mentioned method route exhibit more than one crystal structure (polymorphism). The synthesis had two specific objectives: i) To identify the effect of grain boundary structure on grain growth and densification behavior during heat treatment in a wide temperature range, and ii) To Identify the critical criteria for grain growth being limited by triple junctions, because there are very limited information available on triple junctions mobilities. The analysis was examined rigorously by electron microscopy study (SEM, TEM and HRTEM). The results are present and discussed herein.

MATERIALS AND METHODS

Sonochemical synthesis of TiO_2 nanoparticles

All chemicals were of the highest purity available and were used as received without further purification. Titanium tetraisopropoxide $[(CH_3)_2CHO]_4Ti$ (TTIP,

>97%) was used as titanium source. For specific details about TiO_2 nanoparticles produced sonochemically its have been reported in previous studies [9-11]. TiO_2 nanoparticles synthesized by sonochemical method will be named along this paper such as-prepared sample.

Heat-treated treatment

The as-prepared sample was thermally treated in a temperature range from 400, 500, 600, 700, and 800 ºC for 2 hours at each temperature. The thermal treatment was carried out in a conventional electrical resistance furnace under ambient atmosphere at a rate of 10 ºC min^{-1}. After heat treatment, six samples (including, as-prepared sample) were obtained and they were identified for its temperature range along this paper (x ºC; where x denotes heat treatment temperature in Celsius degrees).

CHARACTERIZATION METHODS

Structure and characteristic by XRD

The crystal structure and phase identification of the samples were done by powder X-ray diffraction (XRD) patterns using a Bruker D8 Focus diffractometer, θ-2θ scans were recorded with Cu Kα radiation (35 kV, 25 mA). XRD patterns were obtained for all samples, including as prepared sample and heat-treated samples. Full scans were obtained in the range of 20° to 60° 2θ, which includes most major anatase and rutile diffractions peaks. The scan speeds and point intervals were kept at 1° min^{-1} and 0.02°, respectively. Diffraction patterns of both anatase and rutile powders were compared with reference to database cards ICDD PDF 21-1272 (anatase) and ICDD PDF 21-1276 (rutile) [12]. Particle size was estimated according to Scherrer´s equation [13]. The phase content of anatase and/or rutile present in the composition after heat-treated were calculated from the integrated intensities of anatase (101) reflection of anatase and (110) reflection of rutile respectively, according to the Spurr and Myers equation [14].

Particle size evolution and phase transformation

Scanning electron microscopy (SEM) was conducted on a Phillips XL-30 operated a 20 kV to determine the morphological changes of anatase structure during the phase transformation anatase-to-rutile of the samples heat-treated. Grain boundaries and structural changes were observed under a transmission electron microscopy (TEM) JEOL-2000FXII operated at 100 kV. The crystallinity of the TiO_2 nanoparticles, grain boundaries, and triple junction was revealed from the high resolution transmission microscopy (HRTEM) and was performance on a Tecnai G2 F30 microscope operated at 300 kV with a point-to-point resolution of 0.20 nm and Cs= 1.2 nm.

Specific surface area (BET)

Specific surface area (S_{BET}) was determined using a Micrometrics ASAP 2000 nitrogen adsorption apparatus by Brunauer-Emmett-Teller (BET method). All the samples measured were degassed at 100 ºC for 24 h before the actual measurements.

RESULTS AND DISCUSSION

Powder X-ray diffraction analysis

A phase transition of anatase into rutile is detected by XRD for the as-prepared and heat treated samples until 800 °C. X-ray pattern of the as-prepared shows that all the reflection can be readily indexed to a pure body-centered tetragonal anatase phase [(space group I41/amd (141)] and no characteristic reflections peaks of rutile or brookite phases were detected within the x-ray detection limit. This fact, confirms which the anatase phase, with nanometric size can be successfully synthesized by this sonochemical method. The average crystalline size of the as-prepared sample was determined to be 4 nm (see Table 1), by means of Scherrer´s equation. This means, that the sonochemical synthesis of nanocrystalline TiO_2 having the anatase structure, reported herein, can be obtained at low temperatures. At complete series of heat

treatment was carried out; the intervals of temperature were from 400 to 800 °C for 2 h, where the anatase structure transforms to stable rutile phase.

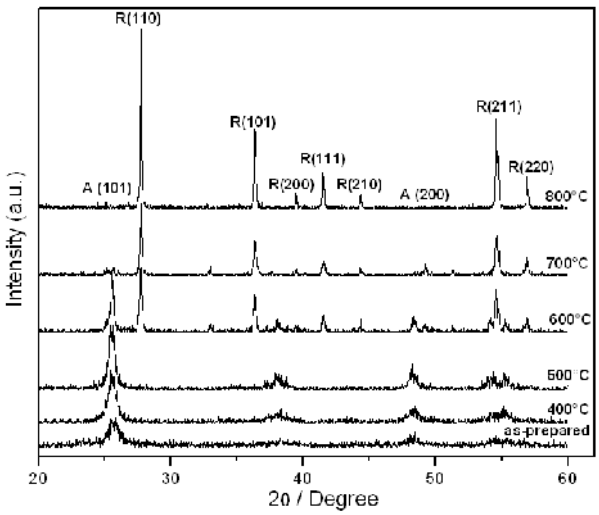

Fig. 1. XRD patterns of TiO_2 powders of as-prepared and heat-treated samples.

A details analysis about Fig. 1, confirms the structural evolution which was accompanied by grain growth, coalescence, and coarsening, parameters which correspond to polymorphic phase transformation mechanism [15]. Furthermore, it provided that between 400 and 500 ºC the predominant phase was anatase with an average particle size around 13 and 24 nm, respectively. Inside the detection limit of XRD, the anatase phase appears destabilized near to 600 °C and its average particle size decreased around 18 nm, implication a denucleation process is present which leads to a diminution in the number of anatase particles. Thus the critical size value corresponding to the beginning of phase transition into rutile, which was about 24 nm. At the same time at 600 and 700 °C the presence of rutile peaks (110) with an average particle size of 30 and 45 nm, respectively is revealed. Indicating that at 600 y 700 °C there is a mixture of anatase and rutile phases, with a denucleation process of anatase phase. At 800 ºC phase transformation anatase-to-rutile is complete and the rutile reflections intensity increases significantly [space group P421/mnm (136)] while the anatase reflection was not detected. Using the relative intensities of the (101) peak of anatase and (110) peak of rutile, a composition approximate of both phases can be estimated according to the Spurr and Myers equation. These values are reported in Table 1.

Table 1. Microstructural evolution, crystalline size and specific surface areas for as-prepared and heat-treated samples

Temperature	Crystalline size (nm)		Anatase phase	BET, Surface area
(°C)	Anatase	Rutile	(%)	($m^2 g^{-1}$)
As-prepared	4	-	100	310
400	13	-	100	220
500	24	-	100	148
600	18	30	38	78
700	14	45	7	40
800	-	61	-	12

Electron Microscopy Characterization

For a better comparison and analysis between electron microscopy images (SEM, TEM and HRTEM) they are organized and identified at the top of each technique and according to heat-treated temperature.

Scanning Electron Microscopy (SEM)

The synthesis of nanostructured TiO_2 and subsequent heat treatment has been follow by SEM. Essentially, all the stages during the heat treatment: nucleation, grain growth, and coarsening are shown in the line corresponding to SEM images, Fig. 2 (a-f). As the system coarsens, it has been conventionally assumed as a diffusional process in which a system lowers its total energy by reducing the total interfacial energy, including surface and grain boundary energies. This phenomenon is evident from by observing the fine particles of the as-prepared sample in the anatase phase Fig. 2 (a) and their subsequent growth in Fig. 2 (b-c). In Fig. 2 (d), coarsening of these fine particles occurs in the surface of a larger size particle. According to XRD results fine

particles correspond to anatase phase during their growth process they form larger particles with rutile phase. At 700 °C the rutile phase dominates the system with 93 % presence. This is evidenced in the SEM images by the large particles with smoother surfaces, on which small particles of anatase are still present.

Finally to 800 °C, only rutile phase is present (see Fig. 1 and Table 1). Rutile crystal shape is tetragonal; in Fig. 2 (f) a particle with a well-defined shape is observed. If the surface plane is carefully observed, it is easy to observe that is shape is similar to one of the planes formed in the {110} typical twinning of rutile. When this kind of particles is close to each other, they use to form twin elbows [16, 17]. Therefore, it is possible that during the formation and growth of rutile phase lodged twin formation mechanism that are typical even in phase transformation [18].

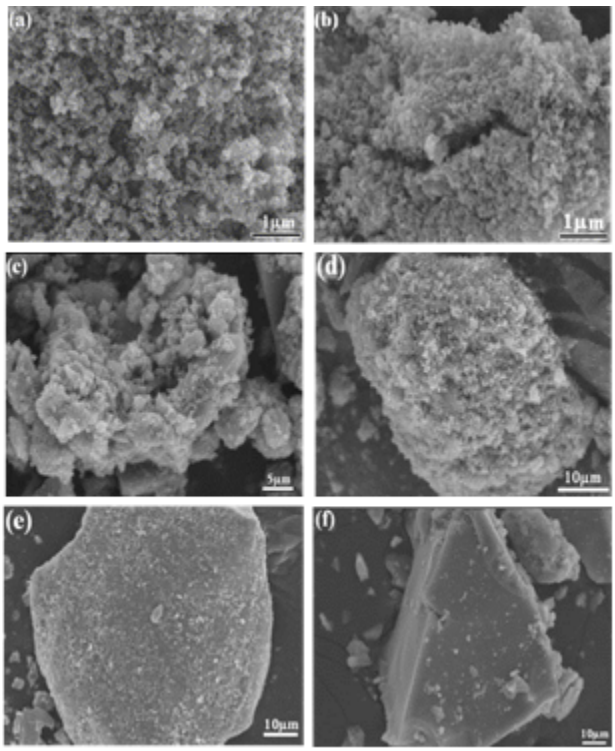

Fig. 2. SEM images of morphological evolution. (a) as-prepared, (b) 400, (c) 500, (d) 600, (e) 700 and (f) 800 °C samples respectively.

In Fig. 2 (a), the as-prepared sample is shown as a nanostructured material with a primary particle size of 4 nm (Table 1). In Fig. 2 (b) it the can be observed that large amount of nanoparticles resist particle growth thanks to its large surface area. This fact is very important because it allow us to explain what happens in the sample heat treated at the temperature of 400 °C for 2 h , the nanostructure is maintained because atoms do not have enough energy to migrate and transform phase. In contrast, in Fig. 2 (c) at 500 °C, the anatase phase particle size is increased and particle coarsening took place. In Fig. 2 (d), the phase transformation has started, according To the analysis, indicating that at 600 °C the nucleation rate has increased and a more compact or dense structure in observed. Additionally, it is important to note that symmetry changes are present, and thermodynamic equilibrium was achieve in the system under new external conditions due to the temperature range. Finally, in Fig. 2 (e, f) grain growth behavior started to show at the faceted boundaries. This phenomenon was explained by Muyung-Koo Kann et al. [21]; the energy of a rough interface is isotropic while that of a singular interface is anisotropic. As a result, the equilibrium shape of a grain with a rough interface is spherical while that with a singular interface is angular.

Transmission Electron Microscopy (TEM)

In Fig. 3 bright field TEM images of the microstructural evolution of TiO_2 are shown. Fig. 3 (a) to (f) are conventional micrographs of as prepare sample and heat treated samples with no atomic resolution. This kind of microscopy allows analyzing migration of grain boundary (GB) and the formation of triple junctions (TJ) during heat treatments, as well to study their connection to anatase to rutile transformation.

Fig. 3 (a) corresponds to the as-prepared sample; in good agreement with XRD results average particle is 4 nm. It is easy to observe a porous morphology in this sample

due to a very large specific surface area (Table 1). Not well-defined boundaries between nanoparticles are observed. However, the treatment led to grain growth from an initial grain size of 4 to 13 nm (averages) (Fig. 2 (b)). A TEM inspection of the 400 °C sample showed only a few grain boundaries, as indicated by the inset circles. This phenomenon is clearly associated with grain size and the desire to maintain the thermodynamically prescribed angles at the lines where boundaries encounter one another. In Fig. 3 (c), at 500 °C, an average grain size of about 24 nm is observed. This image also shows a larger amount of grain boundaries, the formation of elbows and triple junctions. However, it is clear that particle growth and coarsening are governed by the mobility of the triple junction at 600 and 700 °C, Fig. 3 (d) and 3 (f) respectively, a mixture of the anatase and rutile phases is present, both phases could be identified because they have they have different densities and this fact is observed by the differences in their image contrast. Rutile grains are surrounded by anatase meaning that rutile´s nucleus attracts further atoms of anatase which take up positions on its faces in accordance with its three dimensional periodicity [19].

Furthermore, at 700 °C, large rutile grains are observed as well as anatase small grains surrounded them; it is possible to perceive transformation of anatase to rutile due to the presence of several triple junctions and evident densification at 800 °C, as shower in Fig. 3 (f). This behavior is usually observed in macroscopic crystal, tetragonal geometries twin elbow, and is now being observed for nanostructures. This is highly relevant for the joints in grain boundaries [20].

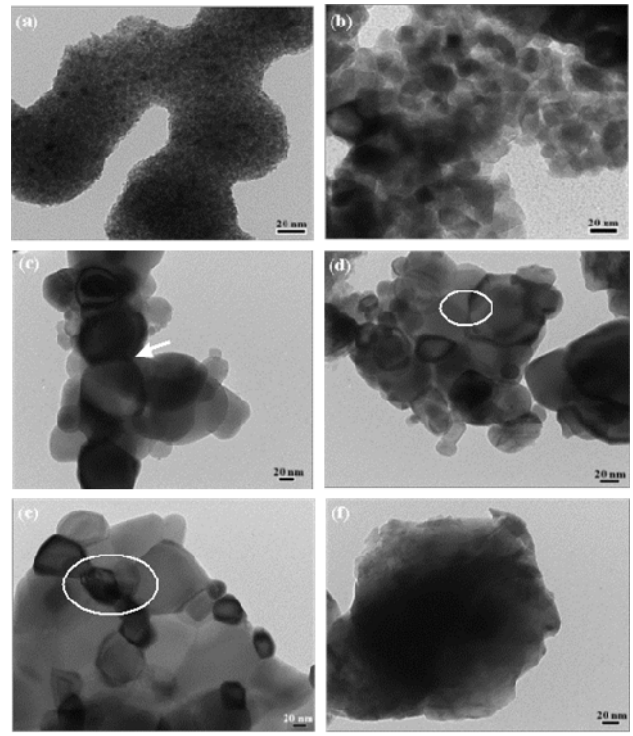

Fig. 3. Low magnification TEM images of microstructural evolution (a) as-prepared, (b) 400, (c) 500, (d) 600, (e) 700 and (f) 800 °C samples, respectively.

High Resolution Transmission Electron Microscopy (HRTEM)

The crystallinity of the as-prepared sample of TiO_2 is revealed by HRTEM bright field images showed in Fig. 4 (a-f). In Fig. 4 (a) in the corresponding micrograph of as prepared sample. In this micrograph interplanar lattice spacing is measured, d_{101} = 0.35 nm reveals the presence of a tetragonal TiO_2-anatase phase good agreement with XRD results. The high crystallinity of the as-prepared sample, observed in their atomic arrays, has been achieved using sonochemical synthesis at room temperature and a short time span compared to conventional methods of synthesis.

The HRTEM image of the TiO_2 heat treated sample at 400 °C shows an agglomeration of nanoparticles which form islands and well-oriented crystalline structures. These oriented agglomerations of anatase particles

promote the growth of twin structures as indicated by circle in Fig. 4 (b) (a schematic representation is shown in the insert). Fig. 4 (c) shows an HRTEM image of TiO_2 at 500 °C. The particle size is 24 nm and still corresponds to the anatase phase. Arrows show an interfacial region appearing as a result of such anatase particle agglomeration, which can serve as nucleation sites for the rutile phase Fig. 4 (d) shows, with lattice resolution, the interface between a rutile crystal and a anatase crystal. On the upper half of the image the rutile crystal (d = 0.31 nm) is attached to the anatase crystal (d = 0.35 nm) by forming a coherent anatase-rutile interface. The average crystalline sizes were about 18 and 30 nm for anatase and rutile respectively. Furthermore, the coherent anatase-rutile interface could provide an energetically and kinetically preferred nucleation site for rutile phase (compared with the HRTEM images before the phase transformation). The structural evolution during the heat treatment at 700 °C, Fig. 2 (e) shows a boundary which corresponds only to the rutile phase. The anatase crystal size is 14 nm while the predominant phase is rutile, 93 %, presents an average particle size of 45 nm (see Table 1). When these particles of dissimilar size come into contact, they fuse into a single rutile phase particle due to continuous process of grain boundary and surface motion. Furthermore to support this hypothesis, the growth of anatase particles beyond the critical size, for anatase-rutile, is energetically unfavorable since anatase has a higher total energy compared to rutile. Finally, at 800 °C (Fig. 4 (f)), it is evident that the interface elimination process and the structural defects density had been reduced due to thermal effects. The BET surface area also decreased dramatically; from 310 $m^2 g^{-1}$ for the as-prepared sample to 12 $m^2 g^{-1}$ at 800 °C. This was due to densification which related to a reduction in pore volume and the total free energy of the system decrease.

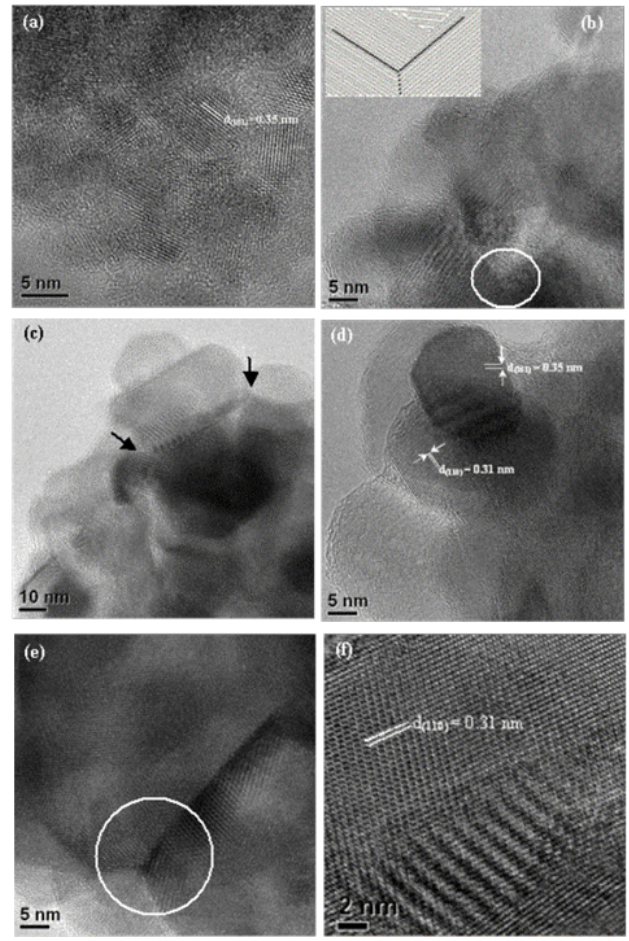

Fig. 4. High Resolution Transmission Electron Microscopy images of microstructural evolution (a) as-prepared, (b) 400, (c) 500, (d) 600, (e) 700 and (f) 800 °C samples, respectively.

CONCLUSIONS

Single-crystalline nanoparticles of TiO_2 have been synthesized using a simple sonochemical method carried out at room temperature. High-resolution electron microscopy images demonstrate that the oriented agglomeration of anatase particles promotes the growth of twin structures if a heat treatment is applied. This behavior is usually observed in macroscopy crystals, tetragonal twin elbow geometries, and is now being observed for nanostructures and is highly relevant for the relationship that may exist between the physical and chemical behavior and the number of joints in grain boundaries. Furthermore, using lattice resolution

imaging, the rutile crystal is seen to be attached to the anatase crystal by forming a coherent anatase-rutile interface, during the anatase-rutile phase transformation. At 700 °C, triple junction and quadruple points are present and the growth of the nucleus is characterized by a parallel displacement of its faces. At 800 °C, densification is evident, where the total free energy of the system decreases and only the rutile phase is present. The synthesis method and electron microscopy characterization described here provides a reliable and easy approach for suitable applications such as photocatalysis.

REFERENCES

[1] Feng Liu, Reiner Kirchheim, (2004) "Grain boundary saturation and grain growth" *Scripta Materia* 51:521-525.

[2] V.A. Snyder, J. Alkemper, P.W. Voorhees, (2001) "Transient Ostwald Ripening and the Disagreement between Steady-State Coarsening Theory and Experiment" *Acta Mater* 49:699-709.

[3] Paulo R. Bueno, Jose A. Varela, Elson Longo, (2008) "SnO_2, ZnO and related polycrystalline compound semiconductors : An overview and review on the voltage-dependence resistence (non-ohmic) feature" *JECS* 28:505-529.

[4] Leonardo González-Reyes, Isaias Hernández-Pérez, F.C. Robles Hernández (2011) "Effect of coarsering of sonochemical synthesized anatase on BET surface characteristics" *Chemical Engineering Science* 66:721-728.

[5] Giridhar Madras, Benjamin J. MacCoy, (2005) "Nucleation, growth, and coarsening for two and three dimensional phase transitions" *J. Crystal Growth* 279:466-476.

[6] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, (2001) "Photocatalytic degradation for environmental applications-a review" *J. Chem. Technol. Biotechnol*. 77:102-116.

[7] Douglas Gouvea, Ricardo H. R. Castro, (2003) "Sintering the role of interface energies" *App. Surf. Sci.* 217:194-201.

[8] Giridhar Madras, Benjamin J. MacCoy, (2002) "Transition from nucleation and growth to Oswald ripening" *Chemical Engineering Science* 57:3809-3818.

[9] Dongmei Zeng, Wanqi Jie, Tao Wang, Hai Zhou (2009) "Tranmission electron microscopy observations of twin boundaries and sub-boundary networks in bulk CdZnTe crystals" *J. Crystal Growth* 311: 4414-4417

[10] González-Reyes, L., et al., (2008) "Sonochemical synthesis of nanostructured anatase and study of the kinetics among phase transformation and coarsening as a function of heat treatment conditions" *J. Eur. Ceram Soc.* 28:1585–1594.

[11] González-Reyes, et. al., (2010) "Temperature effects during Ostwald ripening on structural and bandgap properties of TiO_2 nanoparticles prepared by sonochemical synthesis" *Mater. Sci. Eng. B* 175 (1):9–13.

[12] *JCPDS PDF-2* release 2001, ICDD Newtown Square, PA, USA.

[13] Cullity, B.D., Stock, S.R., "Elements of X-ray diffraction". *Prentice Hall*, NJ USA, (2001). pp. 385–433.

[14] Spurr, R.A., Myers, H., (1957) "Quantitative analysis of anatase-rutile mixture with and X-ray diffractometer". *Anal. Chem. Res.* 29:760-762.

[15] F. Wakai, M. Yoshida, Y. Shinoda, T. Akutsa., (2005) "Coaesening and grain growth in sintering of two particles of different sizes" *Acta Metall.* 53:1361-1371.

[16] Klein C. and Hullburt C., (1999) "Manual of Mineralogy 21 st ed." *John Wiley and Sons USA* (Ch 2. pp. 105).

[17] Giacovazzo C., (1992) "Fundamentals of Crystallography IUCr Text" *Oxford University Press* (Ch 2. pp. 234).

[18] Mehmet Sarikaya M., Aksay I. A. and Kikuchi R., "Mechanism of twin formation during the tetragonal to orthorhombic transformation in YbA2Cu307-X" *Mat. Res. Soc. Symp. Proc.* Vol. 169, pp. 805-809. Materials Research Society.

[19] Hu Gui Yang, et. al., (2008) "Anatase TiO_2 single crystals with a large percentage of reactive facets" *Nature* 453: 638-641.

[20] Hu W., Lu S., Zhang Y., Xiang J., Wen F., Xu B., He J., Yu D., Tian Y., and Liu Z., (2012) "Annealing-Induced {011}-Specific Cyclic Twins in Tetragonal Zirconia Nanoparticles" *J. Phys. Chem. C* 116:21052-21058.

[21] Muyung-Koo Kann, Doh-Yeon Kim, Nong M. Hwang., (2002) "Oswald ripening kinetic of angular grains dispersed in a liquid phase by two-dimensional nucleation and abnormal grain growth" *J. Eur. Ceram Soc.* 22:603-612.