

CHAPTER X

EFFECT OF SURFACE DEFECT (Ti^{3+}) AND BULK PROPERTIES ON TiO_2 NANOCRYSTAL ON THE ITS CRYSTAL GROWTH RATE DURING HIGH TEMPERATRE TREATMENT

Since the photocatalytic splitting of water on TiO_2 electrodes was discovered [131], TiO_2 has been extensively used in the field of photocatalytic reaction [5]. Moreover, it has been also used for the other applications such as a pigment, catalyst support, and sensor [13,132]. It has been known that the photo and chemical properties of the TiO_2 are size-dependent, especially in the nano-level. However, the significant increasing of grain size can occur when the crystalline TiO_2 was placed into the high temperature surrounding. Therefore, one of the major considerations for nano-sized crystalline TiO_2 is the improving of the thermal stability. In fact, it crucial to investigate the main parameter influencing the crystal growth rate during high temperature. Depero et al. [27] and the other researchers [28,29] reported that surface defect (Ti^{3+}) of the TiO_2 was the main factor promoting the crystal growth rate during high temperature. Chen et al. [133] also reported that the increasing of crystallite size during high temperature could be explained tentatively by surface defect as an oxygen vacancy site (Ti^{3+}) because the rate-controlling mechanism on the crystal growth of TiO_2 was the oxygen diffusion which depended on the concentration of surface defect on TiO_2 . Moreover, Hsiang et al. [29] reported that the crystal growth rate of TiO_2 during temperature evolution was controlled by the three behaviors of bulk structure including crystallinity, densification, and the concentration of hydroxyl ions in the bulk structure. Besides the surface defect (Ti^{3+}), crystallinity, densification, and the concentration of hydroxyl ions, Wang et al. [9] showed that the impurity and surface chemistry were also the main factor for controlling the crystal growth rate of TiO_2 during the increasing of temperature. Although, the main parameters controlling the crystal growth rate during high temperature were discussed by many researchers, those conclusions have not yet investigated coinciding with the impact of initial crystallite size. It has been known that the initial crystallite size was also the

important parameter controlling crystal growth rate during high temperature [134,135,136,137,138]. It was shown that the crystalline TiO_2 having the larger initial crystallite size exhibits the lower crystal growth rate than the smaller one. However, based on the lack of the useful crystal growth equation, many researchers just investigated only the effect of bulk and surface properties without the impact of initial crystallite size. Therefore, the main parameter is still under debate as well.

In this work, the effects of bulk and surface properties on the crystal growth rate during high temperature were investigated coinciding with the impact of initial crystallite size. It was performed to find out the main parameter controlling the crystal growth rate during high temperature of TiO_2 . The TiO_2 nanocrystals were prepared using the three synthesis methods including (i) 1st sol-gel method (based on precipitation process) [9], (ii) 2nd sol-gel method (based on peptization process) [139], and (iii) solvothermal method [140]. Different initial crystallite sizes of TiO_2 samples were prepared using the various conditions during preparation step. The bulk properties (such as the crystallite phase, crystallinity) and crystallite size before and after the heat treatment, at temperature ranging from 673-1173 K, were determined using XRD. The surface defect (Ti^{3+}) on the initial crystalline TiO_2 prior to the heat treatment was also monitored using ESR. The effects of the bulk properties and surface properties (as a surface defect) on the crystal growth rate during the increasing of temperature were discussed and compared among the prepared crystalline TiO_2 and the commercial one (JRC-TIO-1). In addition, some reference data were also used to confirm these discussion and comparison [9,29,141]. The nomenclatures used for the crystalline TiO_2 in this study are following:

- (i) $\text{TiO}_2(1^{\text{st}}\text{SG})$: the resulting crystalline TiO_2 from the sol-gel synthesis (based on precipitation process).
- (ii) $\text{TiO}_2(2^{\text{nd}}\text{SG})$: the resulting crystalline TiO_2 from the sol-gel synthesis (based on peptization process).
- (iii) $\text{TiO}_2(\text{SV})$: the resulting crystalline TiO_2 from the solvothermal synthesis.

10.1 Characteristics of initial crystalline TiO₂ samples resulting from various synthesis methods

XRD patterns of various crystalline TiO₂ were shown in the Figure 10. It showed that all of resulting crystalline TiO₂ exhibited strong diffraction peaks at 26°, 37°, 48°, 55°, 56°, 62°, 69°, 71°, and 75° indicating the anatase phase [9]. Based on intensity of XRD indicating crystallinity of TiO₂, it revealed that the highest crystallinity was observed on TiO₂(SV) and then on the TiO₂(1st SG) and TiO₂(2nd SG), consequently. The high crystallinity means that the crystalline TiO₂(SV) was nearly the perfect crystal which had the less amounts of impurity and defect inside the bulk structure than the TiO₂(1st SG) and TiO₂(2nd SG) [142]. According to the work done by Inoue et al. and Kominami et al., they reported that the nano-sized metal oxides having the high crystallinity can be produced using the solvothermal method [143,144,145,146]. Moreover, Wang et al. revealed that the crystalline TiO₂ resulting from sol-gel (based on precipitation) had the impurity and defect inside the structure because of the rapid formation of hydrous TiO₂ and thermal transformation of hydrous gels that had not yet fully reacted which might be a main cause of a lower crystallinity in this work [9]. In case of TiO₂(2nd SG), it was doubtful to determine the main cause of the lowest crystallinity because, in fact, many researchers reported that the crystallinity as well as purity can be improved via the peptization or aging process [29]. However, the effect of nitric acid added might be the main cause to produce defect/impurity inside structure according to the report of Wang et al [9]. They reported that the condensation reaction during sol-gel synthesis, which is an important reaction controlling crystal structure, can be inhibited by the additives such as electrolytes, polymers, and complexing ligands. Based on Scherrer's equation, these TiO₂ had crystallite sizes in rang of 6-7 nm as seen in Figure 10.1. The TiO₂(SV) exhibited the highest crystallite size among the TiO₂(1st SG) and TiO₂(2nd SG).

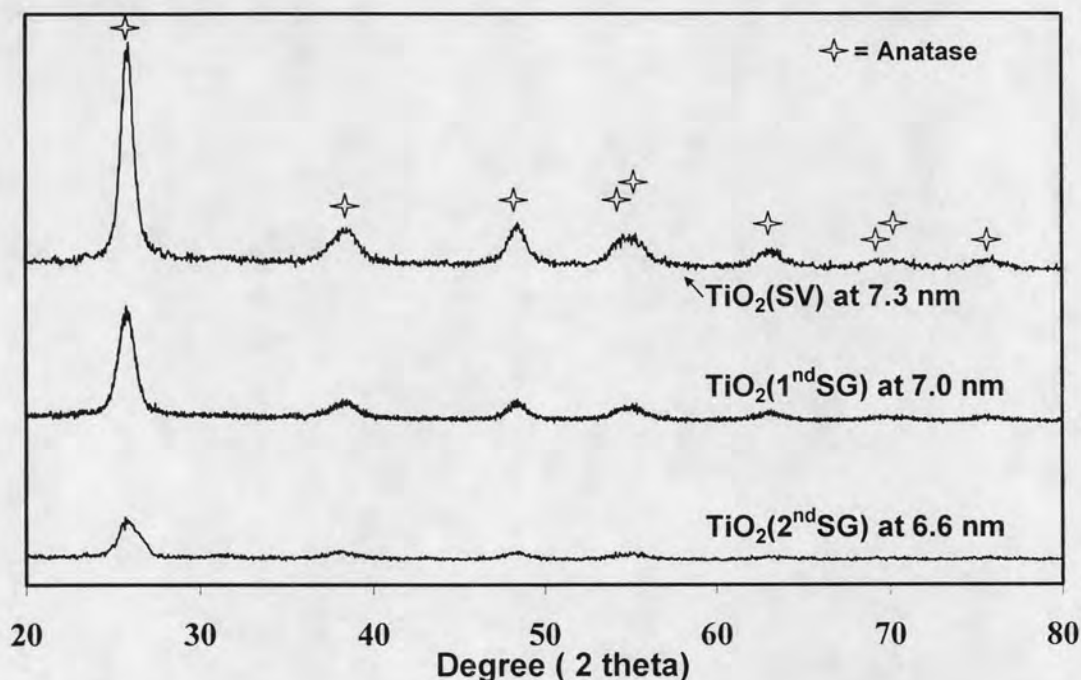


Figure 10.1: XRD patterns of initial crystalline TiO₂ resulting from various synthesis methods

In this work, the ESR analysis was performed at 77 K and without illumination on samples for monitoring the oxygen vacancy site (Ti³⁺) on the crystalline TiO₂. The ESR spectra for all TiO₂ samples prior to the heat treatment are indicated in the Figure 10.2. Based on the results of ESR analysis as shown in Figure 10.2, it can be observed that all TiO₂ samples exhibited mainly one signal at the g value in the range of 1.996 – 1.997. According to the results as reported by Nakaoka et al., this peak can be attributed to the surface defect (Ti³⁺) on TiO₂ [16]. This corresponded with the reports of Nakamura et al. and Serwicka et al [19,63]. Apparently, they reported two signals occurred on the surface of TiO₂ during ESR analysis without illumination indicating; (i) the surface Ti³⁺ and (ii) the bulk defect. In case of bulk defect; many researchers reported that the crystalline TiO₂ has several types of bulk defect such as cationic defect and anionic defect. For the bulk Ti³⁺, based on thermodynamics, bulk TiO₂ has very less inner Ti³⁺ when compared to Ti³⁺ on surface. Therefore, ESR spectra of the initial crystalline TiO₂ prior to heat

treatment in this work did not show any signal of bulk Ti^{3+} which were corresponding to the work of Howe et al. and Lee et al [64,65]. Based on intensity of ESR spectra (which is corresponding to the amounts of Ti^{3+} present in TiO_2 surface), it showed that the $\text{TiO}_2(\text{SV})$ had the highest amount of surface defect (Ti^{3+}) when compared with those from the $\text{TiO}_2(1^{\text{st}} \text{ SG})$. In case of $\text{TiO}_2(2^{\text{nd}} \text{ SG})$, no radical was found in this work. Therefore, based on XRD and ESR analysis, it should be mentioned that the initial crystalline TiO_2 resulting from various synthesis methods had the different structure in the bulk (crystallinity as well as impurity and bulk defect) and on the surface (surface defect) which corresponded to the work done by many researchers [28,29]. They reported the differences of the bulk and surface properties of crystalline TiO_2 upon to the synthesis method and treatment condition.

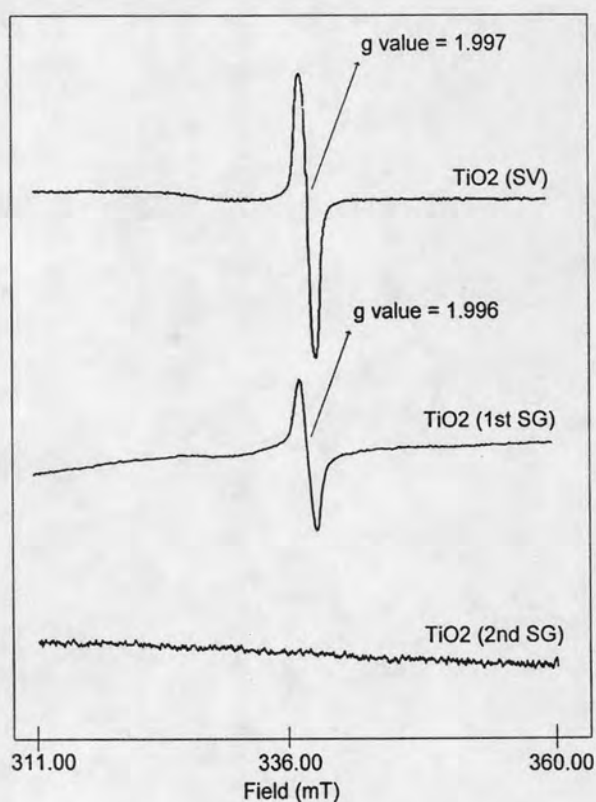


Figure 10.2: ESR spectra of initial crystalline TiO_2 obtained at 77 K in vacuum without irradiation

10.2 Investigation of the main parameter influencing the crystal growth rate during high temperature

In particular, to investigate the main factor controlling the crystal growth rate during high temperature, the standard equation should be used to compare the data obtained among the research groups. However, in the past, it did not have too much the convenient equation used for the data interpretation. Thus, most researchers simply used only the common plot between crystallite sizes versus the temperature. This was difficult to identify the relation between temperature and the crystal growth as well as crystal growth rate. This is because normally most data did not have the linear relationship and then resulted in an incorrect discussion for determining the main parameter controlling the crystal growth rate. In this work, based on the proposed linear correlation in log-log scale of Prasertdam et al. [134,135], this correlation (relating between crystal growth and initial crystallite size as seen in the equation 10.1) was applied to investigate the main parameter influencing to the crystal growth rate during high temperature.

$$\frac{d}{d_0} = A \left(\frac{T}{(d_0)^{1/2}} \right)^n \quad (10.1)$$

Where CG (crystal growth) = $\frac{d}{d_0}$, d_0 and d refer to crystallite size of TiO_2 before (initial crystallite size) and after heat treatment, respectively, T = heat treatment temperature (K), n = slope of graph, and A = arbitrary constant.

Based on this correlation, it can be interpreted that crystal growth (CG) was affected by both initial crystallite size (d_0) and heat treatment temperature (T). Therefore, in order to use this correlation, the reaction temperature during solvothermal synthesis was varied to the higher temperature at 573 K for preparing another initial crystallite size at 14 nm as seen in Table 10.1. The water:alkoxide during sol-gel synthesis (based on precipitation process) was also varied to the lower ratio at 50 for preparing another initial crystallite size at 9 nm. All initial crystalline TiO_2 samples were placed to the box furnace and heated it up to the desired temperature in the range of 673-1173 K at the rate of 10

K/min. Then it was kept at that temperature for 1 h. The changes of crystallite size after heat treatment was summarized in the Table 10.1. Based on equation 10.1, the plot in log-log scale between crystal growth (d/d_0) versus the ratio of heat treatment temperature (T) and the square root of the initial crystallite size (d_0) of all crystalline TiO_2 (from the data in Table 10.2) was shown in the Figure 10.3. It was shown that the crystal growth data of all TiO_2 fitted well with the equation 10.1 and located around the same linear line (the same slope) indicating that all crystalline TiO_2 had nearly the same crystal growth rate. Hence, when all crystalline TiO_2 was placed into the same high temperature (T), based on the same crystal growth rate, it can be predicted that all of them will have the same crystal growth (d/d_0). Then, the crystallite size (d) after heat treatment of each initial crystalline TiO_2 will increase to the different value upon each initial crystallite size (d_0).

Table 10.1: Crystallite size of the crystalline TiO₂ before and after heat treatment calculated by the Scherrer's equation

Method	Reaction temp ^a , K Water:alkoxide ^b	Initial crystallite size, <i>d</i> ₀ (nm)	Crystallite size after heat treatment, <i>d</i> (nm)				
			673 K	773 K	873 K	973 K	1073 K
Solvothermal ¹⁷	523	7.3	-	21.9	34.9	51.3	-
	573	14.2	-	15.1	22.6	32.5	-
1 st Sol-Gel ^{c,10}	163	7.0	-	17.1	30.0	45.0	-
	50	8.8	-	17.0	30.0	36.0	-
2 nd Sol-Gel ^{d,16}	e	6.3	7.7	10.4	24.1	-	-
JRC-TIO-1 ^f	-	109.8	-	148.4	148.4	148.5	148.9

^a The reaction temperature during the solvothermal synthesis.

^b The water:alkoxide molar ratio of the 1st sol-gel synthesis.

^c The sol-gel synthesis (based on the precipitation process).

^d The sol-gel synthesis (based on the peptization process).

^e The water:alkoxide molar ratio followed the reference number 16.

^f The crystalline TiO₂ in anatase phase from the Catalysis Society of Japan.

Table 10.2: Crystal growth (d/d_0) and the $T/(d_0)^{1/2}$ data of the crystalline TiO₂

Method	Reaction temp, K Water:alkoxide	Heat treatment temp, K	Crystal Growth (d/d_0)	$T/(d_0)^{1/2}$ (K/nm ^{1/2})
Solvothermal	523	773	3.0	286.1
		873	4.8	323.1
		973	7.0	360.1
	573	773	1.1	205.1
		873	1.6	231.7
		973	2.3	258.2
1 st Sol-Gel	163	773	2.4	291.5
		873	4.3	329.3
		973	6.4	367.0
	50	773	1.9	261.0
		873	3.4	294.8
		973	5.1	328.6
2 nd Sol-Gel	-	673	1.2	268.8
		773	1.7	308.7
		873	3.8	348.6
JRC-TIO-1	-	773	1.35	73.7
		873	1.35	83.3
		973	1.35	92.8
		1073	1.35	111.9

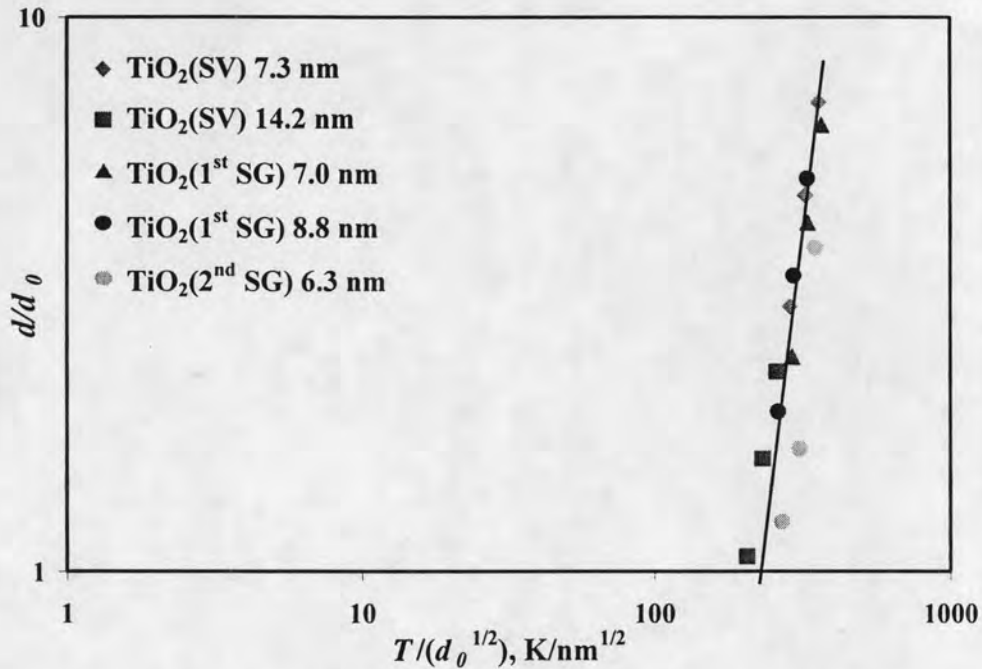


Figure 10.3: Relationship between crystal growth (d/d_0) and $T/(d_0)^{1/2}$ of crystalline TiO_2 resulting from various synthesis method

Based on the XRD data of crystalline TiO_2 resulting from the various synthesis methods, it seemed that the crystallinity, impurity, and bulk defect of the TiO_2 were not the main factors controlling the crystal growth rate during high temperature contradicting with the suggestion of the other researchers [29,9]. In case of ESR results, there are many researchers which also suggested that the surface defect (Ti^{3+}) on the crystalline TiO_2 was the main factor controlling crystal growth rate during high temperature [27,28,29,133]. However, the impact of initial crystallite size (d_0) of TiO_2 never has been discussed in these work. Therefore, this is the first report which used the initial crystallite size (d_0) participating in the discussion step and it can be concluded that the main factor controlling the crystal growth rate during high temperature should be the initial crystallite size (d_0) according to the relation in equation 10.1. This does not mean that these bulk and surface properties have no effect on the crystal growth rate of TiO_2 during high temperature. However, when compared relatively to the effect of an initial crystallite size (d_0), it was revealed that the initial crystallite size have mainly impact on the crystal growth rate of TiO_2 .

Based on the equation 10.1, these bulk and surface properties could be represented in term of the parameter A (arbitrary constant). The Herring model, which have the initial crystallite size as a main parameter in this model, can be used to confirm the conclusion in this work [136]. It can be interpreted that the small crystallite size has higher crystal growth rate than the larger one. In this work, based on the correlation in equation 10.1 and the data in the Table 10.1, it can also be shown that the crystalline TiO_2 with a larger initial crystallite size has the lower crystal growth rate than the smaller ones, which is in accordance with the report from Yan and Rhodes [137]. In fact, the initial crystallite size has the relation with a surface energy which comes from the strain in crystal, especially in the nano-level [138]. It has been known that the smaller crystallite size has the higher surface energy than the larger one leading to the formation of the unstable grain accelerating the crystal growth. Therefore, it indicates that the crystal growth rate of TiO_2 during high temperature is mainly controlled by the initial crystallite size as well as the surface energy which is corresponded with the report of Doremus [138].

In addition, some of the reference data were also used to confirm this conclusion as summarized in the Table 10.3. Hsiang et al [29], investigated the effect of aging time during TiO_2 synthesis on the crystal growth rate during high temperature. It was shown that the hydroxyl ions existing in the anatase lattice and oxygen vacancy concentration (Ti^{3+}) decreased with increasing the aging time. Moreover, it was found that the crystallinity and densification of TiO_2 increased with increasing aging time. In order to confirm the exact parameter controlling the crystal growth rate during high temperature, the three data (indicating the crystal growth during increasing temperature) of crystalline TiO_2 in the work of Hsiang et al [29], were used for discussion in this work. As seen in Figure 10.4, the linear relation of the data of the TiO_2 (resulting from the various aging time including 12, 24, and 48 h) were plotted in the log-log scale following the correlation in the equation 10.1. It was shown that all data of crystalline TiO_2 resulting from various aging time corresponded with this correlation and also located around the same linear line of the data in this work. Therefore, in this work, based on the first report discussing the impact of the bulk and surface properties coinciding with the impact of initial crystallite size (d_0), it is suggested that the hydroxyl ions in structure, oxygen vacancy site (Ti^{3+}), crystallinity and densification of crystalline TiO_2 are not the main factors controlling

the crystal growth rate during high temperature. Instead the initial crystallite size is. It was shown that when the initial crystallite size participating in the discussion step was used. The opposite conclusion on the impact of bulk and surface properties can be observed. Therefore, it should be mentioned that the interpretation coinciding with the impact of initial crystallite size was necessary for the study to determine the main parameter influencing the crystal growth rate.

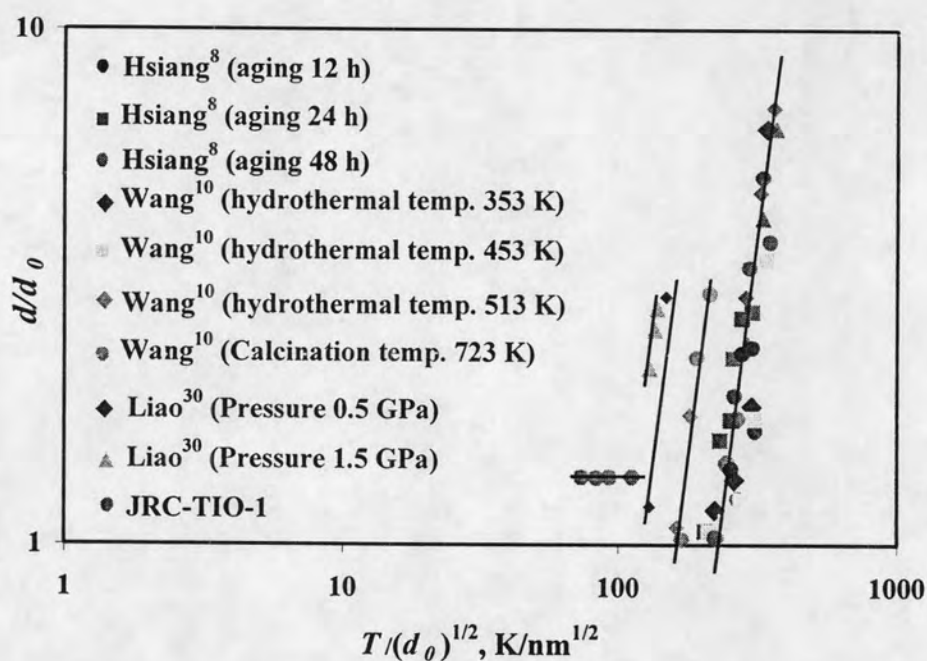


Figure 10.4: Relationship between crystal growth (d/d_0) and $T/(d_0)^{1/2}$ of crystalline TiO_2 from the other work (color point) including work of (i) Hsiang et al., (ii) Wang et al., (iii) Liao et al., and (iv) JRC-TIO-1. These data located on the linear line of the data in this work (gray point)

Table 10.3: Crystal growth (d/d_0) and the $T/(d_0)^{1/2}$ data of the crystalline TiO₂ from references data

Sample	Initial crystallite Size (d_0), nm	Heat treatment temp, K	Crystal Growth (d/d_0)	$T/(d_0)^{1/2}$ (K/nm ^{1/2})
Hsiang et al. (Aging 12 h)	17.85	1073	1.4	253.9
		1173	2.3	277.6
		1273	2.4	301.3
Hsiang et al. (Aging 24 h)	17.81	1073	1.7	254.2
		1173	2.7	277.9
		1273	2.8	301.6
Hsiang et al. (Aging 48 h)	22.85	1073	1.0	224.4
		1173	1.7	245.4
		1273	2.0	266.3
Wang et al. (Hydrothermal temp. 353 K)	6.6	573	1.2	223.0
		673	1.3	261.9
		773	1.8	300.8
		873	6.4	339.8
Wang et al. (Hydrothermal temp. 453 K)	10.0	673	1.0	212.8
		773	1.1	244.4
		873	1.2	276.0
		973	1.7	307.7
		1073	3.5	339.3
Wang et al. (Hydrothermal temp. 513 K)	28.8	873	1.1	162.6
		973	1.8	181.3
Wang et al. (Calcination temp. 723 K)	20.8	773	1.0	169.5
		873	2.3	191.4
		973	3.0	213.3
Liao et al. (Pressure 0.5 Gpa)	27.0	673	1.2	129.5
		773	3.0	148.7
Liao et al. (Pressure 1.5 Gpa)	27.0	603	2.2	129.5
		703	2.6	135.3

Wang et al. [9] investigated the effect of processing parameter of hydrothermal and calcination process, using the sol-gel synthesis on the crystal growth rate during high temperature of crystalline TiO₂. They reported that the crystalline TiO₂ resulting from hydrothermal process at 513 and 453 K had the lower amount of impurity than the hydrothermal process at 353 K and the calcinations process at 723 K. Moreover, it was also reported that the crystallinity increased with increasing of hydrothermal temperature. In this work, the crystal growth data of crystalline TiO₂ in the work obtained by Wang et al. [9] were also used as a reference to confirm the main parameter controlling crystal growth rate during the high temperature. As shown in Figure 10.4, the data of crystalline TiO₂, resulting from hydrothermal process (at temperature of 353, 453, and 513 K) and calcinations process at 723 K, were also plotted in the log-log scale using the correlation in the equation 10.1. It showed that all data corresponded with the equation 10.1 and located around the same linear line of the TiO₂ in this work. In contrast, the TiO₂ obtained from the hydrothermal process at 513 K and calcination process at 723 K exhibited a shift of linear line to a lower $T/(d_0)^{1/2}$. This was probably due to the impact of non-uniform grain shape of these TiO₂ samples. However, considering the slope of these linear lines (representing the crystal growth rate), it revealed that no effect of non-uniform grain shape on the crystal growth rate can be observed. Wang et al. [9] reported that the crystalline TiO₂ obtained from the hydrothermal process had less impurity than that from the calcination process. However, based on the same slope of all linear line as seen in the Figure 10.4, it revealed that the impurity, crystallinity, and shape of crystal grain of crystalline TiO₂ were not the main parameters controlling the crystal growth rate during high temperature, but the initial crystallite size of crystalline TiO₂ is (as respected to equation 10.1). This case can be also used to confirm that the impact of the initial crystallite size is counted as the main parameter involving the crystal growth rate. However, considering on the plot of crystal growth data of TiO₂ obtained from the hydrothermal at 353 and 453 K, there was the curve having an exponential line on the initial part of data. This revealed that the impurity and crystallinity as well as bulk defect also have a little effect on the crystal growth rate during high temperature (could be represented in the term A in equation 10.1).

Besides the properties of the crystalline TiO_2 , the reference work concerning the process parameter during heat treatment was also used for confirmation as referred to the work done by Liao et al. [141]. They investigated the effect of process pressure during heat treatment at high temperature on the crystal growth. The crystal growth of TiO_2 data at 0.5 and 1.5 Gpa were plotted in the log-log scale following the equation 1 as seen in the Figure 10.4. It showed that the data of the both of crystalline TiO_2 exhibited the linear line according the equation 10.1. However, both data did not locate in the same linear line as seen in the former data, but it shifted to a lower ratio of $T/(d_0)^{1/2}$ when the process pressure increased. Considering on the same slope of linear line, however, it shows that the rate of crystal growth was also independent regarding the effect of process pressure.

The commercial crystalline TiO_2 from the Catalysis Society of Japan (JRC-TIO-1) was also used for the confirmation. The initial crystallite size of JRC-TIO-1 is 109.8 nm which is over the range of nano-level. In Figure 10.4, the crystal growth data of this commercial crystalline TiO_2 was also plotted in the log-log scale following the equation 10.1. It was shown that the linear line of this data located at the different position and different crystal growth rate. Therefore, it should be noted that the main parameter controlling the crystal growth (as an initial crystallite size) should be applied for only in the range of nano-level.

It should be mentioned that the independence between the rate of crystal growth and surface defect (Ti^{3+}) was the valuable knowledge for many applications of the TiO_2 nanocrystal such as photocatalyst and support. In case of photocatalyst, it has been known that surface defect (Ti^{3+}) plays a significant role for enhancing the photoactivity via the photoelectron trapping [3]. In addition, the surface defect of TiO_2 also plays the important role as a strong metal-support interaction (SMSI) to enhance a metal dispersion on TiO_2 support [101]. Moreover, it has been known that the crystallite size of TiO_2 was also the main parameter controlling the photo and SMSI properties. Based on the reports of many researchers as mentioned before, they suggested that when the crystalline TiO_2 was used under the high temperature condition, it must trade off between the surface defect and crystal growth. It is because when the large amounts of surface defect (Ti^{3+}) were created to improve the photo and SMSI properties, they must lose the thermal stability via a rapid crystal

growth rate by the promoting of surface defect as mentioned by many researchers [27,28,29,133]. However, based on the independent relation between the surface defect and crystal growth rate as shown in this work, this ideal should be rethought. And, the amounts of surface defect (Ti^{3+}) can be created as much as possible because it revealed that the rate of crystal growth was independent on the amounts of surface defect (Ti^{3+}) on TiO_2 nanocrystal.