

## IMPROVING ANATASE TO RUTILE TRANSITION TEMPERATURE BY MILLING

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### ABSTRACT

#### IMPROVING ANATASE TO RUTILE TRANSITION TEMPERATURE BY MILLING.

An intensive investigation using X-ray diffractometry has been conducted to study the optimum mechanical and thermal conditions for the transition of anatase-to-rutile from a titanium dioxide (TiO<sub>2</sub>) powder. Milling was applied by employing a conventional ball milling instrument and a quasi-high-energy pulveriser and varying the milling period. Heat treatment was performed by calcination at 850, 900, 950, 975, 1000, 1050 and 1100°C for 1 hour, being the predicted optimum temperature to obtain fully rutile powder was 975°C. Each powder was milled and then calcined prior to the X-ray diffraction investigation. X-ray diffraction data were analysed using (1) standard identification and peak characterisation, (2) the Rietveld method to give the weight fractions, lattice constants and crystallite size and strain estimates, and (3) *Mozaix*, an own-developed software to provide strain, crystallite size and size distribution of phases. Results showed that milling speed and milling up to 24 hours does not significantly change the phases' composition, but enhances the transition temperature. Conventional milling gives better results than pulverising. Conventional milling at 100 rpm for 3 hours reduces the transition temperature from 1100°C to 1000°C. Longer milling, however, does not improve the transition temperature. The optimum process is discussed and SEM micrographs are used to support the argument.

**Key words** : Anatase to rutile transition, milling, x-ray diffraction

### ABSTRAK

**MEMPERBAIKI SUHU TRANSISIANATASE KE RUTILE DENGAN PENGGILINGAN.** Metode difraksi sinar-x telah secara intensif digunakan untuk mempelajari kondisi-kondisi mekanik dan termal optimum dalam transisi fasa *anatase* ke *rutile* dari serbuk titanium dioksida (TiO<sub>2</sub>). Pendekatan mekanik berupa penggilingan dilakukan dengan menggunakan instrumen penggiling bola konvensional dan penggiling pulveris bertenaga tinggi dan dengan variasi waktu penggilingan. Pendekatan termal dilakukan dengan kalsinasi pada suhu 850 °C, 900 °C, 950 °C, 975 °C, 1000 °C, 1050 °C and 1100 °C selama 1 jam, dengan prediksi suhu optimum untuk mendapatkan *rutile* seluruhnya adalah 975°C. Masing-masing serbuk digiling dan kemudian dikalsinasi sebelum pengukuran dengan difraktometer sinar-x. Data difraksi sinar-x dianalisis menggunakan (1) metode identifikasi fasa standar dan karakterisasi puncak, (2) metode *Rietveld* untuk mendapatkan fraksi berat, parameter-parameter kisi dan estimasi ukuran kristal dan regangan tak-seragam kristal, dan (3) *Mozaix*, sebuah perangkat lunak buatan sendiri yang dapat memberikan informasi mengenai regangan, ukuran kristal dan distribusi ukuran kristal. Hasil analisis menunjukkan bahwa kecepatan giling dan waktu giling hingga 24 jam tidak secara signifikan mengubah komposisi fasa, namun menurunkan suhu transisi. Penggilingan konvensional memberikan hasil lebih memuaskan daripada penggilingan pulveris. Penggilingan konvensional selama 3 jam menurunkan suhu transisi dari 1100°C menjadi 1000°C. Namun, penambahan waktu penggilingan, tidak memperbaiki suhu transisi. Langkah-langkah optimalisasi dibahas dan mikrografi SEM digunakan sebagai pendukung argumen dalam pembahasan.

**Kata kunci**: Transisi anatase ke rutile, penggilingan, difraksi sinar-x

### INTRODUCTION

As an important technological material with a relatively wide area of applications titania (TiO<sub>2</sub>) has attracted attention for its further exploration. For example is study on the tranformation of anatase [crystal structure is tetragonal, with lattice constants  $a = b = 3.784$  and  $c = 9.514$  Å [1]

to rutile [crystal structure is tetragonal, with lattice constants  $a = b = 4.592$  and  $c = 2.959$  Å] [2], being the latter is the most important material. Rutile is used, for example, for a component to produce electroceramic materials with high dielectricity, such as PZT [3] and BaTiO<sub>3</sub>-based materials [4]; low-thermal expansion

aluminium-titanate (AT)-based materials [5,6]; paint and printing ink [7].

It is well known that anatase can transform into rutile by heating [8]. Recently, it was found that rutile can also be obtained by a mechanical process, ie by milling [9]. Reports showed that heating at 915 °C or vibrating cup milling for more than 300 hours can completely transform anatase into rutile. However, there is no report on the effect of heating or milling on the particle or grain size distribution of the materials. Moreover, there was no further study reported on the improvement of the processes to obtain optimum conditions of the transition.

Grain size distribution is an important parameter of materials which may strongly influence the characters of products made from the materials. For example, broader grain size distribution resulted in a lower breakdown voltage and nonlinear coefficient in electroceramic materials [10]. Recent research showed that size distribution information can be extracted from x-ray diffraction peak broadening using an appropriate physically-based model [11-13]. This model also accomodates crystallite size and strain parameters from peak broadening.

This paper reports the optimum milling and calcination conditions to which anatase and rutile can be composited through phase tranformation of titania. The optimum conditions were studied using x-ray diffractometry after conventional or pulverised milling followed by calcination at several designated temperatures. The outcome of the research is a recommendation of milling and calcined conditions to obtain particular anatase-rutile mixture.

## EXPERIMENTAL METHOD

The raw material was anatase TiO<sub>2</sub> powder (Merck, Germany). The first batch of the powder was milled using a conventional mill with alumina balls (0.5 cm in diameter), acetone as the milling media and 1:50 of powder:balls weight ratio. Milling speed was 100 rpm and milling time were 1, 3, 6, 12, and 24 hours. Another batch of the powder was milled using a pulverised instrument with zirconia balls (0.5 cm in diameter), acetone as the milling media and 1:50 of powder:balls weight ratio. Milling speeds were 100, 250 and 350 rpm, while milling time was fixed at 1 hour. Calcination trials were performed at 850, 900, 950, 975, 1000, 1050 and 1100°C for 1 hour referring to differential thermal analysis results.

X-ray diffraction (XRD) data were collected for the raw powder, milled powders and milled and calcined powders. Configuration of the XRD data measurement was as follows-Cu tube operating at 40 kV and 30 mA (K<sub>α</sub> wavelengths: 1.54060, 1.54439 Å); fixed slit optics with incident beam divergence = 1°, receiving slit = 0.15°, post-diffraction graphite analyser; and NaI detector with pulse

discrimination. In collecting data sets, the 2θ step size was 0.02°; the counting time per step was 1s; and the 2θ range = 10° - 120° for whole-pattern data. Some data were collected at 20° - 30°. 2θ-range for quick inspection as well as for peak-ratio quantitative analysis using the following approximation [14]:

$$W_r = \frac{1}{1 + 0.8 \frac{I_a}{I_r}} \dots\dots\dots (1)$$

where *W* is approximate weight fraction and *I* represent integrated intensity. Subscripts *r* and *a* denote rutile and anatase, respectively.

Rietveld analysis by means of Rietica [17] was used to determine the lattice parameter and the phase content of each phase in the treated powders. The crystallite size and non-uniform strain of each phase were also estimated from the Rietveld refinement output following procedure given by Pratapa et al. (2002). Program Mozaix [13] was used to calculate crystallite strain, size and size distribution of the phases.

The microstructure of the materials was examined using a scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

Figure 1 shows the XRD short-range patterns of the milled anatase powders. The figure qualitatively indicates that there is no significant effect of both conventional milling and pulverising on the integrated intensity development of rutile. Further investigation showed that the approximate rutile content increases only in the order of 0.5% which is presumably, however, within the weight fraction tolerance.

By contrast, milling has affected the thermodynamical properties of the powder. As can be seen from Figure 2, the DTA endothermic peak shifts to lower temperature as milling time increases. The peak for the as-received powder is about 949°C, while those for the 1 hour and 24 hours milled powders are 939°C and 913°C, respectively. This behaviour also predicts that the anatase@rutile transition temperature would decrease with milling time. The transition would be favored by milling as can be seen further from the DTA curve slope between 300°C and 900°C. The as-received powder exhibits slow decrease curve between 300°C and 600°C and then relatively rapid drop of the curve between 600°C and 900°C, while the milled powders exhibit more sloping curve between 300°C and 900°C. It appears that milling has increased the energy capacity of anatase powder to favor its transition into rutile. This result is consistent with that acquired by Kostic et al. [9]. Moreover, it was argued that transition of TiO<sub>2</sub> are attributed to the increased temperature and pressure of the colliding parts of the powder and the balls and also to the extra energy acquired from grain refinement and formation of defects and lattice distortion [14]. In current investigation, however, no

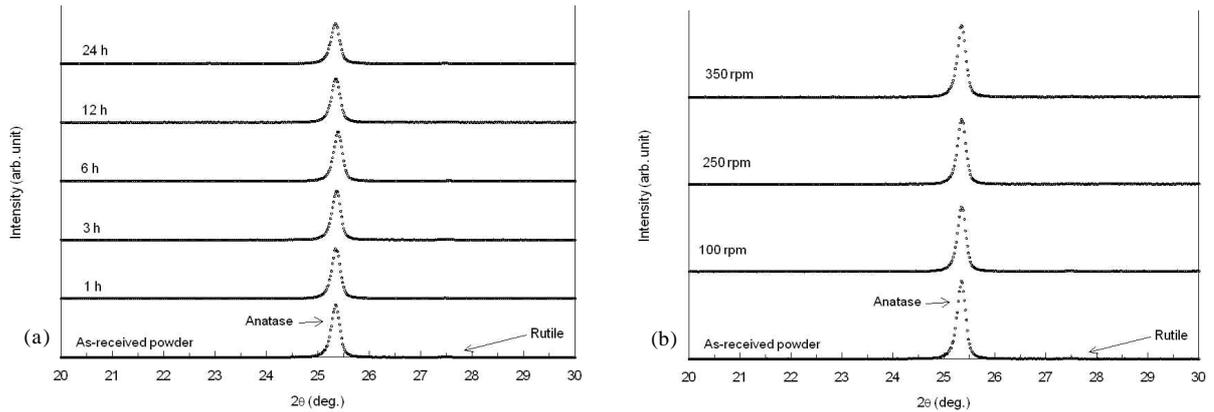


Figure 1. XRD patterns for milled anatase powder with variation of milling time (left) and speed (right).

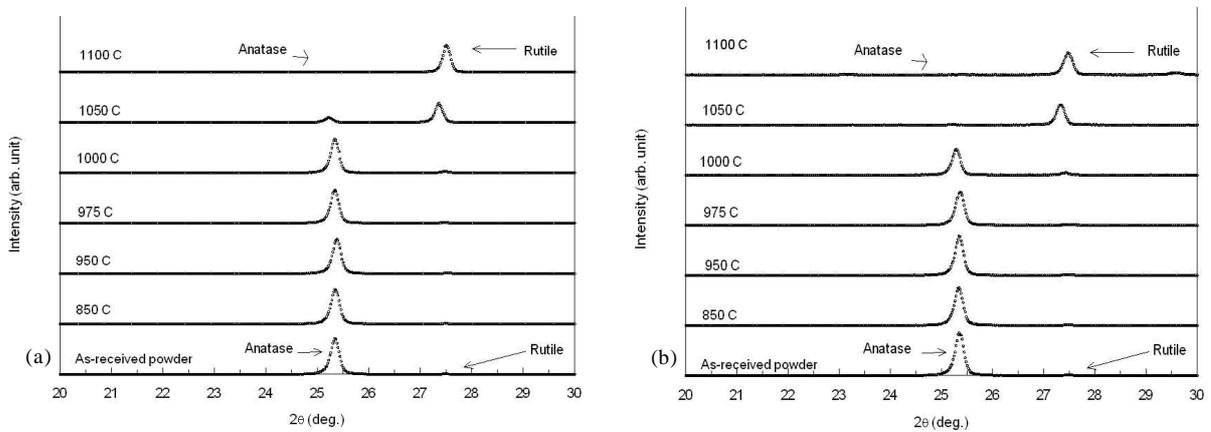


Figure 2. XRD patterns for unmilled (left) and conventionally milled for 1 hour (right) anatase powder after calcination at various temperatures.

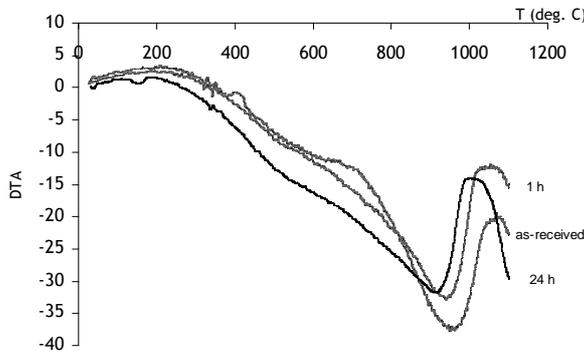


Figure 3. DTA curves for anatase powders after milling by conventional mill for 1 and 24 hours. Data for the as-received powder is also given for comparison.

longer milling was performed in this research as it is aimed to optimise the milling and calcination conditions while maximum milling time chosen was 24 hours.

Examination of XRD data from the as-received and conventionally milled powders resulted in phase content and characters as shown in Table 1. Results reported here are only for these specimens as they are more interesting and promising in terms of optimisation of the transition. As can be seen from the table, anatase@rutile transition is completed after calcination at 1050°C for 1 hour, except for the as-received powder.

As noted by Farrel [15], such transition is affected by a large number of aspects with results in temperature which may be wide-ranging. For instance, unspecified anatase powder transform into rutile at 915 °C [8], while such transition in nanocrystals occurs at 700°C [16] or influenced by the dopant type and concentration as well as type of precursors [15]. It is believed that the higher transition temperature in this research was resulted from the use of fine powders rather than nano-size or ultra-fine powders.

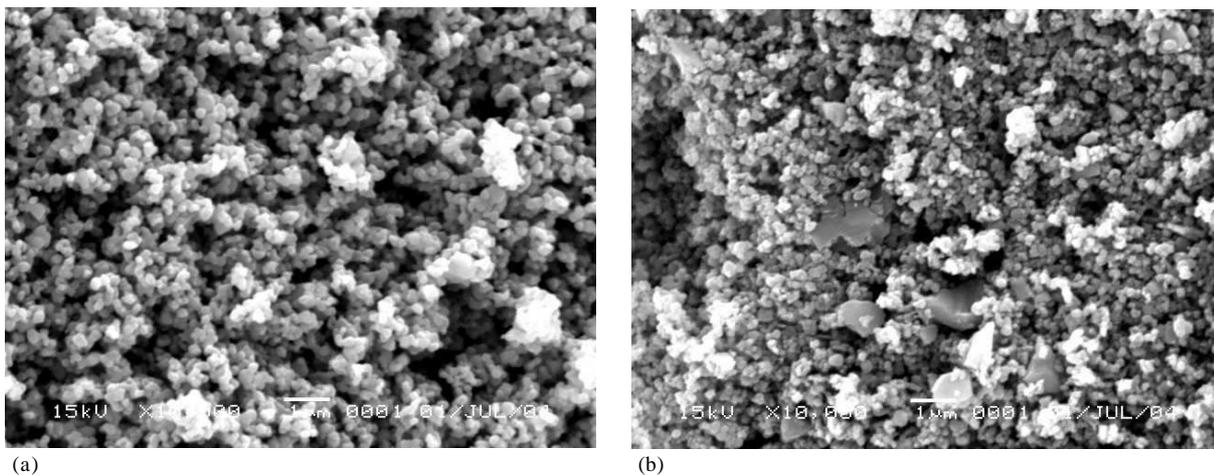
Table 1 shows that heat treatment obviously favours the transition as expected. While the milled powders transform into rutile at temperature higher than 1000°C, it is found that milling time does not necessarily linearly promote the transition. For example, at 1000°C, full transition can be found only after milling for 3 hours. Even, further milling does not give full transition after calcination. It is therefore economically unreliable to mill anatase powder for long period to obtain pure rutile.

The microstructural characters of the powders presented in Table 2 were extracted from the diffraction data using Mozaix [13]. The software models non-uniform strain (linearly proportional to  $FW_{strain}$ ), crystallite average size (inversely proportional to  $FW_{size}$ ) and size distribution (b). In general, milling and calcination do not significantly affect the strain and average size. Most

**Table 1.** Phase fraction and microstructural characters of anatase and rutile after conventional milling and calcination. Milling time was fixed at 1 hour. Phase fraction (W%) was approximated using Equation (1). Microstructural characters were extracted using Mozaix (Pratapa 2003). Figures in parantheses are the standard deviation for the associated values to the left. Note: reproductivity of the results has been checked by repeating the measurement and analysis.

Milling	Calc. Temp. (°C)	Anatase					Rutile				
		Int.	W(%)	FW <sub>Size</sub>	FW <sub>Strain</sub>	β	Int.	W(%)	FW <sub>Size</sub>	FW <sub>Strain</sub>	β
As-received	RT	3581	99.0	0.098(2)	0.090(10)	0.97(6)	29	1.0	0.070(10)	0.075(6)	1.73(1)
	975	3349	97.9	0.062(3)	0.090(10)	0.50(2)	58	2.1	0.070(10)	0.090(10)	1.43(7)
	1000	3401	94.7	0.067(3)	0.080(40)	0.32(1)	153	5.3	0.130(10)	0.050(10)	0.81(2)
	1050	491	17.2	0.046(7)	0.095(8)	0.17(1)	1894	82.8	0.063(3)	0.080(20)	0.47(2)
100 rpm - 1 hour	RT	3407	98.8	0.098(3)	0.090(30)	1.02(6)	34	1.2	0.060(20)	0.080(10)	0.49(1)
	975	2650	97.7	0.065(3)	0.090(10)	0.54(2)	49	2.3	0.060(20)	0.100(10)	1.20(8)
	1000	2085	89.9	0.074(4)	0.090(50)	0.37(5)	188	10.1	0.040(10)	0.080(20)	0.25(3)
	1050	-	-	-	-	-	1659	100.0	0.065(6)	0.090(10)	0.58(2)
100 rpm - 3 hour	RT	3373	98.5	0.098(1)	0.093(2)	0.77(1)	42	1.5	-	-	-
	975	556	22.2	0.104(4)	0.079(6)	1.04(1)	1560	77.8	0.068(1)	0.085(3)	1.39(1)
	1000	-	-	-	-	-	1665	100.0	0.099(2)	0.082(4)	1.62(1)
	1050	-	-	-	-	-	2886	100.0	0.084(1)	0.075(3)	1.37(1)
100 rpm - 6 hour	RT	3318	98.7	0.098(1)	0.095(2)	0.79(1)	35	1.3	0.043(3)	0.110(10)	1.30(4)
	975	2044	67.6	0.095(2)	0.086(4)	1.03(1)	785	32.4	0.099(3)	0.079(6)	1.53(2)
	1000	49	2.7	0.100(30)	0.100(30)	0.68(3)	1418	97.3	0.100(20)	0.089(4)	1.47(1)
	1050	-	-	-	-	-	1951	100.0	0.054(2)	0.102(5)	1.13(1)
100 rpm - 12 hour	RT	3309	98.8	0.105(2)	0.093(2)	0.84(1)	32	1.2	0.078(2)	0.070(6)	1.27(3)
	975	2724	93.0	0.099(2)	0.089(3)	1.13(1)	163	7.0	0.099(9)	0.084(2)	1.83(1)
	1000	1590	63.0	0.093(2)	0.100(6)	1.15(2)	747	37.0	0.098(4)	0.096(8)	1.45(2)
	1050	25	1.1	0.027(3)	0.130(10)	1.01(8)	1762	98.9	0.090(2)	0.100(5)	1.17(1)
100 rpm - 24 hour	RT	3296	99.1	0.091(2)	0.096(2)	0.71(2)	23	0.9	0.053(4)	0.120(20)	1.94(1)
	975	1778	63.5	0.098(2)	0.090(4)	1.18(2)	819	36.5	0.099(3)	0.080(6)	1.50(2)
	1000	217	7.3	0.099(7)	0.079(1)	0.97(6)	2206	92.7	0.097(2)	0.079(3)	1.46(1)
	1050	-	-	-	-	-	2640	100.0	0.096(1)	0.070(2)	1.30(9)

Note: Int. = integrated intensity. FW = full-width at half-maximum, where  $D$  is crystallite size; and  $\beta$ , where  $\beta$  is non-uniform strain.  $\beta$  is the size distribution parameter; the higher  $\beta$  value, the narrower the crystallite distribution (Pratapa 2003).



**Figure 4.** SEM images of the as-received powder before (left) and after (right) calcination at 1000 C for 1 hour.

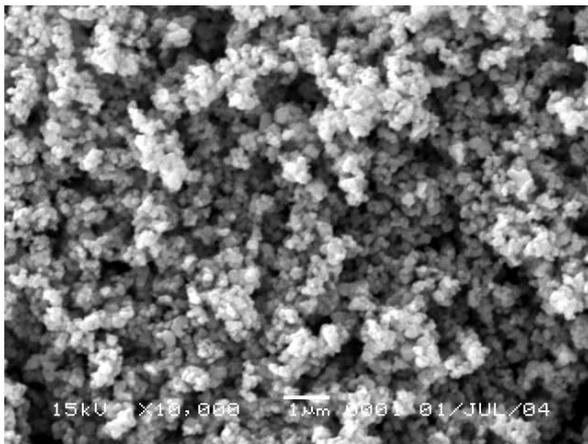
of the values are within the standard deviation tolerance. Interesting behaviour is found for the size distribution, both for anatase and rutile, which is generally narrower

(higher  $\beta$  value) for lower calcination temperature. In other words, the distribution of anatase is broader when transition occurs. Simultaneously, the formed rutile has

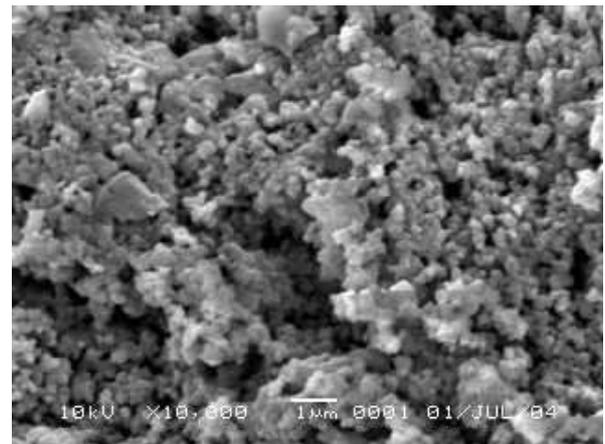
*Improving Anatase To Rutile Transition Temperature By Milling (Suminar Pratapa)*

**Table 2.** Results of Mozaix profile fitting of the diffraction patterns of the conventionally milled powders with milling time variation.

Sample	Calc. Temp. (°C)	Anatase [0 1 1]						Rutile [1 1 0]					
		Int	FWHM	Mixing	Size	Strain	$\beta$	Int	FWHM	Mixing	Size	Strain	$\beta$
As-received	25	3581	0.0997(9)	0.56(4)	0.098(2)	0.09(3)	0.97(6)	29	0.082(6)	0.79(1)	0.07(2)	0.075(6)	1.730(3)
	975	3350	0.0950(8)	0.54(4)	0.062(3)	0.09(2)	0.50(2)	58	0.094(5)	0.35(7)	0.07(2)	0.09(1)	1.43(7)
	1000	3401	0.0925(8)	0.48(4)	0.067(3)	0.08(4)	0.320(5)	153	0.076(5)	0.97(2)	0.13(1)	0.05(1)	0.81(2)
	1050	491	0.092(2)	0.56(1)	0.046(7)	0.095(8)	0.17(4)	1894	0.090(1)	0.47(5)	0.063(3)	0.08(2)	0.47(2)
100rpm 1 hour	25	3407	0.0997(8)	0.48(5)	0.098(3)	0.09(3)	1.02(6)	34	0.081(6)	0.63(7)	0.06(2)	0.08(1)	0.49(1)
	975	2650	0.0991(9)	0.40(5)	0.065(3)	0.09(1)	0.54(2)	49	0.100(5)	0.20(6)	0.06(2)	0.10(1)	1.20(8)
	1000	2085	0.096(1)	0.44(5)	0.074(4)	0.09(5)	0.37(5)	188	0.087(3)	0.41(2)	0.04(1)	0.08(2)	0.25(3)
	1050	-	-	-	-	-	-	1659	0.097(1)	0.34(6)	0.065(6)	0.09(1)	0.58(2)
100rpm 3 hour	25	3336	0.1008(8)	0.47(1)	0.098(2)	0.093(2)	0.77(1)	-	-	-	-	-	-
	975	556	0.089(2)	0.537(4)	0.108(4)	0.079(6)	1.044(3)	1560	0.0856(7)	0.30(1)	0.068(1)	0.085(3)	1.39(1)
	1000	-	-	-	-	-	-	1665	0.0911(9)	0.275(1)	0.099(2)	0.082(4)	1.62(1)
	1050	-	-	-	-	-	-	2886	0.0863(8)	0.279(1)	0.084(1)	0.075(3)	1.37(1)
100rpm 6 hour	25	3318	0.1029(8)	0.45(1)	0.098(1)	0.095(2)	0.79(1)	35	0.114(9)	0.31(3)	0.043(3)	0.11(1)	1.30(4)
	975	2044	0.0931(9)	0.426(2)	0.095(2)	0.086(4)	1.03(1)	785	0.089(1)	0.29(2)	0.099(3)	0.079(6)	1.53(2)
	1000	49	0.034(2)	0.152(5)	0.10(3)	0.10(3)	0.68(3)	1418	0.0969(8)	0.25(1)	0.100(2)	0.089(4)	1.47(1)
	1050	-	-	-	-	-	-	1951	0.0966(7)	0.212(2)	0.054(2)	0.102(5)	1.13(1)
100rpm 12 hour	25	3309	0.1009(8)	0.514(1)	0.105(2)	0.093(2)	0.84(1)	32	0.075(1)	0.37(3)	0.078(2)	0.070(6)	1.27(3)
	975	2724	0.0957(8)	0.42(1)	0.099(2)	0.089(3)	1.13(1)	163	0.090(3)	0.269(7)	0.0997(9)	0.084(2)	1.83(1)
	1000	2037	0.105(1)	0.53(6)	0.100(4)	0.10(6)	1.056(9)	245	0.104(2)	0.32(7)	0.0173(1)	0.11(4)	0.49(3)
	1050	25	0.12(1)	0.0097(4)	0.027(3)	0.13(1)	1.01(8)	1762	0.1100(9)	0.26(1)	0.090(2)	0.10(5)	1.17(1)
100rpm 24 hour	25	3296	0.1005(8)	0.50(1)	0.091(2)	0.096(2)	0.71(2)	23	0.119(1)	0.32(4)	0.053(4)	0.12(2)	1.94(1)
	975	1778	0.098(1)	0.37(2)	0.098(2)	0.09(4)	1.18(2)	819	0.094(1)	0.27(2)	0.099(3)	0.08(6)	1.50(2)
	1000	218	0.090(3)	0.43(8)	0.09997)	0.079(1)	0.97(6)	2206	0.0894(7)	0.29(1)	0.097(2)	0.079(3)	1.46(1)
	1050	-	-	-	-	-	-	2640	0.0858(7)	0.34(1)	0.096(1)	0.07(2)	1.301(9)

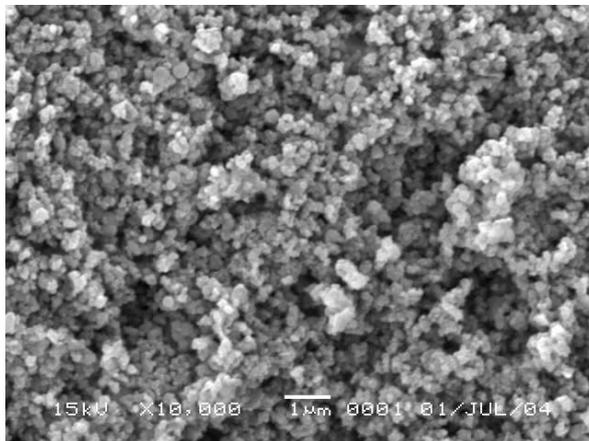


(a)

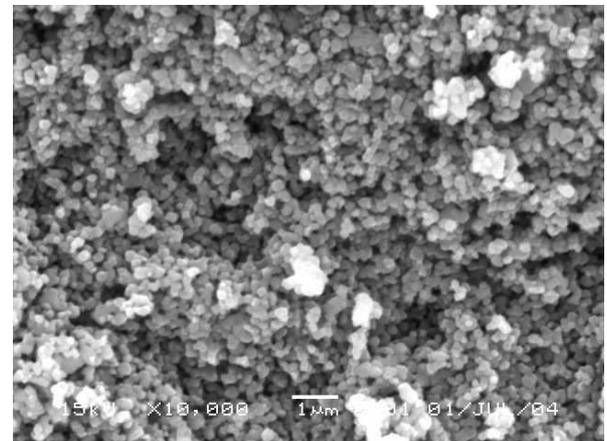


(b)

**Figure 5.** SEM images of the conventionally milled powder before (left) and after (right) calcination at 1000 C for 1 hour.



(a)



(b)

**Figure 6.** SEM images of the pulverised powder before (left) and after (right) calcination at 1000 C for 1 hour.

also broader distribution. Further calcination seems to favour even-size development as shown by specimens with 100% rutile.

The SEM images of the as-received, conventionally milled and pulverised powders before and after calcination at 1000°C for 1 hour are presented in Figures 4 – 6, respectively. Relatively homogeneous grain size are obvious for the as-received both before and after calcination. However, the conventionally-milled powder indicates some plate-like grains. The pulverised powder exhibits only a slight inhomogeneity. It appears that this inhomogeneity correlates with the anatase@rutile phase transition, that is inhomogeneous, milled powder transform more easily.

### Optimising the Process

There were thermodynamical effects introduced by milling or pulverising anatase powder. Conventional ball milling provides better results than pulveriser. It is evident however that milling alone cannot be used to fully transformed anatase into rutile when milling speed is 100 rpm and maximum milling time is 24 hours. Moreover, the maximum time does not necessarily mean the optimum time. Table 1 shows that full transition occurs when anatase powder was milled for 3 hours and then calcined at 1000 °C, however the rutile content for the 1 hour-milled powder and calcined at the same temperature is only 10.1%, while that for the associated 6 hour-milled specimen is 97.3%. The optimum process to produce full transition therefore is presumably milling at 100 rpm for 2–3 hours and followed by calcination at 1000 °C. The calcination temperature for full transformation of the as-received powder is 1100°C. As a result, the optimum condition reduces calcination temperature by 100 °C which is equivalent to an energy saving as much as  $1.1 \times 10^6$  J.

### CONCLUSIONS

It can be concluded from this study that (1) milling favours anatase@rutile transition, (2) the optimum condition for the transition of the specific powder is conventional milling for 3 hours at 100 rpm followed by calcination at 1000°C for 1 hour. This condition reduces the transition temperature up to 100°C at calcination time of 1 hour which means an energy saving of approximately  $1.1 \times 10^6$  J, (3) milling speed does not significantly affect the transition, and (4) milling change the crystallite size and grain size distribution being some of the grains presumably act as thermodynamical energy capacitor for the transition.

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