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APPENDICES

APPENDIX A

EFFECT OF CONDITIONS FOR CARBOTHERMAL
REDUCTION AND NITRIDATION PROCESS

Effects of conditions for nitridation process were studied from titania powder physically mixed with carbon black.

A1 Effect of Temperature

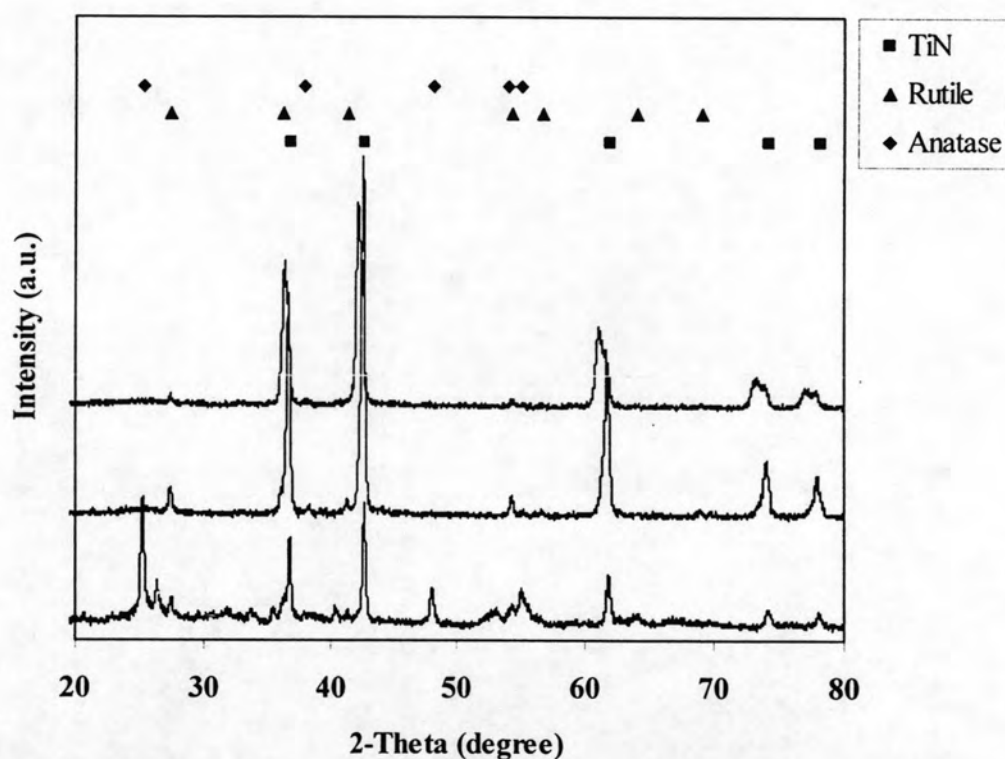


Figure A1 XRD patterns of product from the carbothermal reduction and nitridation at various temperatures: (a) 1450°C, (b) 1400°C and (c) 1300°C.

From these patterns, it is suggested that the reaction temperature should be fixed at 1400°C.

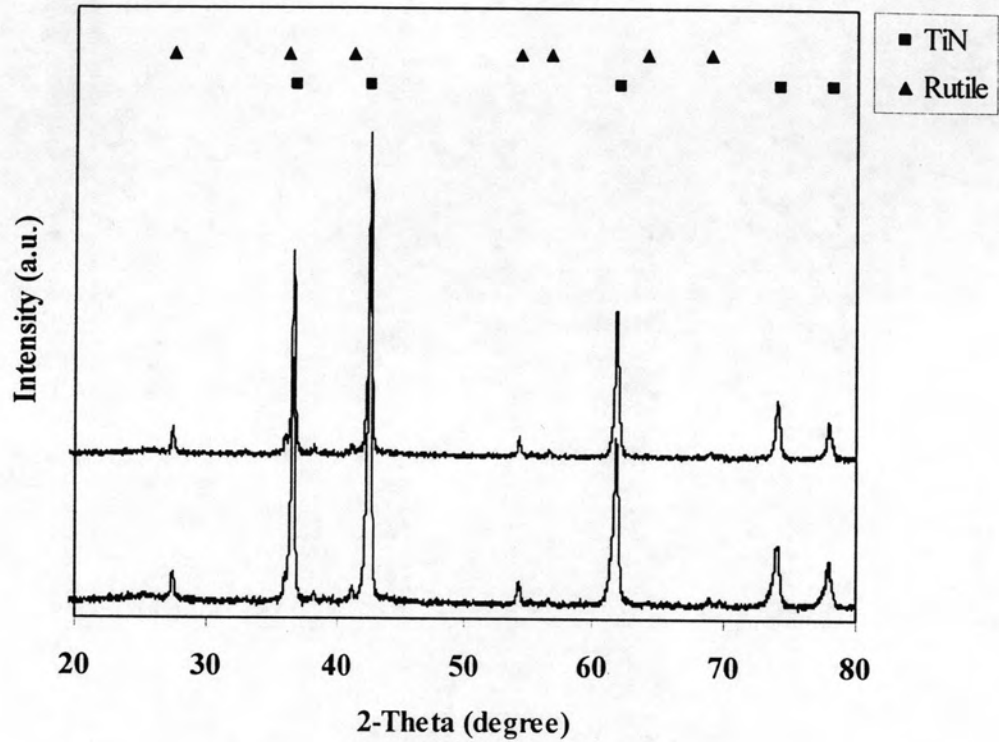
A2 Effect of Time

Figure A2 XRD patterns of product from the carbothermal reduction and nitridation at various times: (a) 6 h and (b) 3 h.

From these patterns, it is suggested that the reaction time of 3 h is sufficient to convert titania/carbon mixture to titanium nitride.

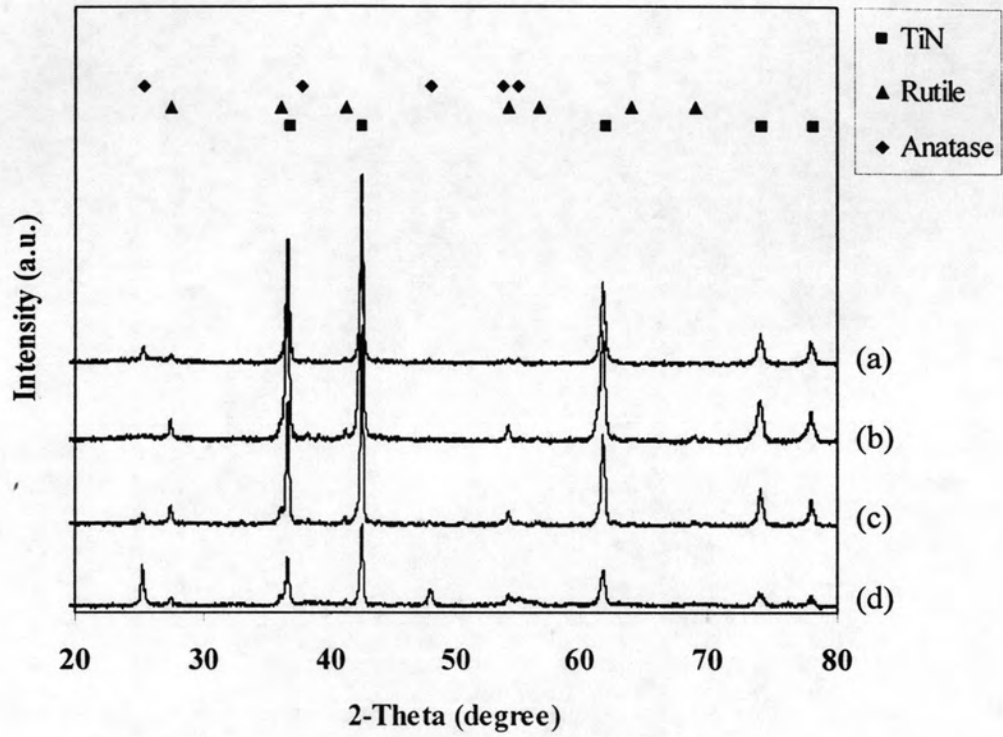
A3 Effect of Titania-to-Carbon Ratio

Figure A3 XRD patterns of product from the carbothermal reduction and nitridation at various titania-to-carbon ratios: (a) 1:4, (b) 1:3, (c) 1:2 and (d) 1:1.

For the physical mixing powder, the suitable titania-to-carbon ratio is 1:2.

APPENDIX B

TGA ANALYSIS OF PVP AND CARBON BLACK

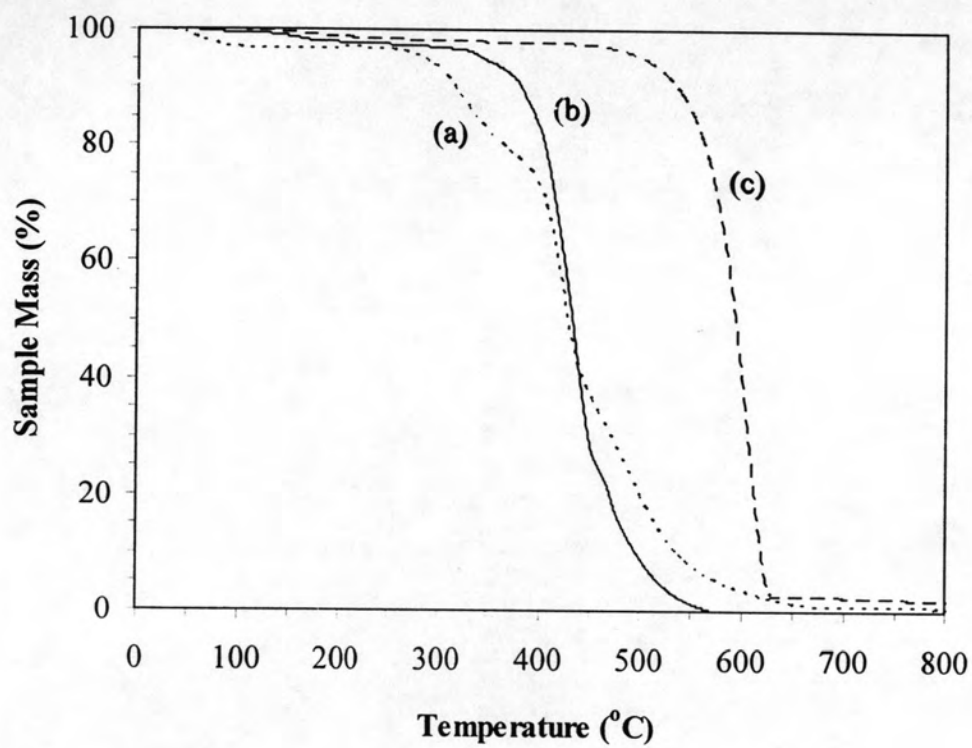


Figure B1 TGA analysis of PVP under nitrogen atmosphere using various kinds of PVP: (a) h-PVP, (b) l-PVP and (c) carbon black.

APPENDIX C

CARBON CONTENT IN FIBER SAMPLES BEFORE NITRIDATION

Table C1 Carbon content in fiber samples after pyrolysis

Fiber Sample	Carbon Content (wt.%)
h-PVP : l-PVP = 1:5	44
h-PVP : l-PVP = 2:4	41
h-PVP : l-PVP = 3:3	45
13 wt.% h-PVP	36
13 wt.% h-PVP with Carbon Black	63

Table C2 Carbon content in fiber samples after calcination

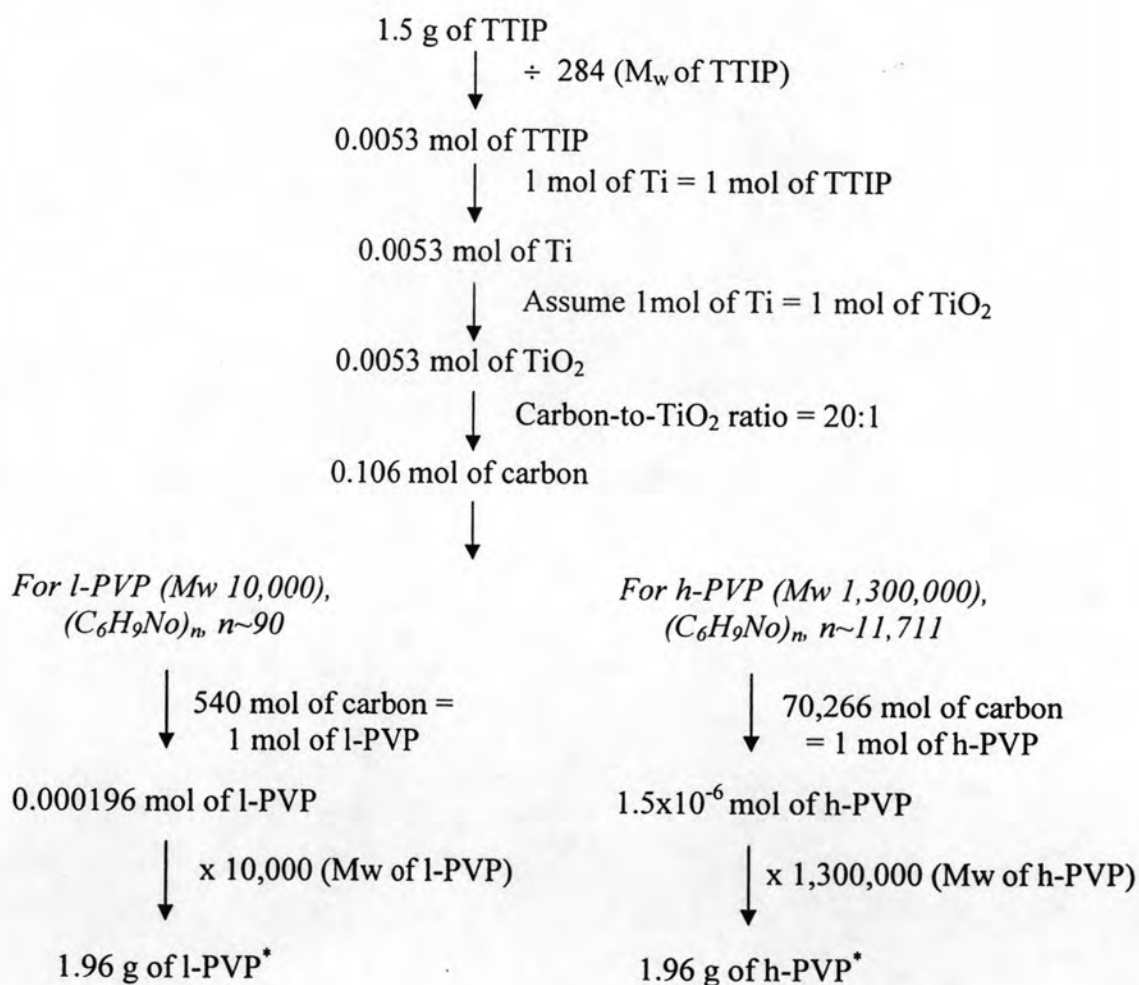
Fiber Sample (13 wt.% h-PVP with Carbon Black)	Carbon Content (wt.%)
Before calcination	63
After calcinations	
• 350°C, 5 min	32
• 350°C, 10 min	32
• 400°C, 5 min	27
• 400°C, 10 min	29

APPENDIX D

CALCULATION FOR AMOUNT OF CARBON REQUIRED FOR TITANIA/CARBON COMPOSITE

For calculation method, carbon source, i.e. l-PVP, h-PVP and carbon black were employed for preparation of titania/carbon composite.

D1 Titania/PVP Composite Using TTIP as Titania Precursor



For mixed PVP (l-PVP and h-PVP in the ratio of 5:1), there are 1.6333 g of l-PVP and 0.3267 g of h-PVP in the mixture.

D2 Titania/h-PVP (13 wt.% in Ethanol 7.5 ml) Composite Using TTIP as Titania Precursor

7.5 ml of ethanol

↓ × 0.79 (d of absolute ethanol)

5.925 g of ethanol

↓ 1 mol of Ti = 1 mol of TTIP

0.0053 mol of Ti

↓ h-PVP 13 wt.% of solution

0.8853 g of h-PVP

D3 Titania/Carbon Black Composite Using TTIP as Titania Precursor

1.5 g of APTMS

↓ ÷ 284 (M_w of TTIP)

0.0053 mol of TTIP

↓ 1 mol of Ti = 1 mol of TTIP

0.0053 mol of Ti

↓ Assume 1 mol of Ti = 1 mol of TiO_2 0.0053 mol of TiO_2 ↓ Carbon-to- TiO_2 ratio = 3:1

0.0158 mol of carbon

↓ x 12 (M_w of carbon)

0.1896 g of carbon black*

APPENDIX E

DETERMINATION OF CALIBRATION CONSTANTS FOR QUANTITATIVE POWDER X-RAY DIFFRACTION ANALYSIS OF ANATASE/RUTILE/TITANIUM NITRIDE MIXTURE

The basic relationship for quantitative X-ray diffraction analysis is

$$I_{i,\delta} = K_{i,\delta}^{\circ} \frac{W_{\delta}}{\rho_{\delta} \left(\frac{\mu}{\rho} \right)_m} \quad (\text{E1})$$

which relates the intensity of an X-rays beam diffraction from reflection I of phase δ to the mass fraction of phase δ (W_{δ}), mass absorption coefficient for the mixture $(\mu/\rho)_m$ and density of phase δ (ρ_{δ}). In the above equation $K_{i,\delta}^{\circ}$ represents a constant for a given crystal structure δ , a diffraction line i , and a set of experimental conditions.

The mass ratio of phases β and γ in the same mixture may be correlated with intensity ratios of these phases according to Equation E1 as follows:

$$\frac{\sum I_{i,\delta}}{\sum I_{i,\gamma}} = K_{\delta/\gamma} \frac{W_{\delta}}{W_{\gamma}} \quad (\text{E2})$$

where

$$K_{\delta/\gamma} = \frac{\rho_{\gamma} \sum K_{i,\delta}^{\circ}}{\rho_{\delta} \sum K_{i,\gamma}^{\circ}} \quad (\text{E3})$$

represents the calibration constant for δ - / γ -phase mass ratio, which is dependent on the chosen reflections. The summation terms in the Equation E3 include several

reflections of correspondings phase, which minimizes the effects of preferred orientation in nearly randomly oriented crystals. The use of relative intensity ratios for the determination of calibration constants does not depend on a particular diffractometer used.

Since the main goal of the analysis is determination of mass fractions, Equation E2 may be rewritten in the form

$$\frac{\sum I_{i,\delta}}{\sum I_{i,\delta} + \sum I_{i,\gamma}} = K_{\delta/\gamma} \frac{W'_\delta}{1 + W'_\delta(K_{\delta/\gamma} - 1)} \quad (\text{E4})$$

where W'_δ represents the mass fraction of phase δ in the δ - γ mixture, i.e. the mass fraction on the basis free of all other phases that are present in the actual mixture:

$$W'_\delta = \frac{W_\delta}{W_\delta + W_\gamma} \quad (\text{E5})$$

Hence, in binary mixture $W'_\delta = W_\delta$. The form given by Equation E4 is commonly used in literature for graphical presentation of calibration data.

Equation E2 implies that the determination of calibration constants for mass ratios of two phases reduces to a straightforward linear regression of measured intensity ratios versus mass ratios of pure phases, or mass fraction ratios of phases in impure but specified standards.

To reliably determine calibration data, the following three standards are need:

- standard #1 – pure titanium nitride
- standard #2 – predominantly rutile
- standard #3 – pure anatase.

The mass fractions of the anatase in standard #2 are denoted as a , and is initially unknown. A number of mixtures can be prepared by mixing together arbitrary masses m_i from each of standard, where subscript i represents the standard number. The mixtures then can be analyzed by XRD to measure the intensities of the following peaks: (111), (200) and (220) peaks for titanium nitride; (110) and (211) peaks for titania in rutile phase, and (101) for titania in anatase phase.

For the chosen reflections, intensity terms in equation E2 reduce to

$$\sum I_{i,TiN} = I_{TiN}(111) + I_{TiN}(200) = I_{TiN} \quad (E6)$$

$$I_{TiN}(220) = I_{TiN}^* \quad (E7)$$

$$\sum I_{i,Rutile} = I_{Rutile}(110) + I_{Rutile}(211) = I_{Rutile} \quad (E8)$$

$$\sum I_{i,Anatase} = I_{Anatase}(101) = I_{Anatase} \quad (E9)$$

Combining Equation E2 and E6-E9 one may obtain

$$\frac{I_{TiN}}{I_{Rutile}} = K_{TiN/Rutile} \frac{W_{TiN}}{W_{Rutile}} \quad (E10)$$

$$\frac{I_{Anatase}}{I_{TiN}^*} = K_{Anatase/TiN} \frac{W_{Anatase}}{W_{TiN}} \quad (E11)$$

Once $K_{TiN/Rutile}$ and $K_{Anatase/TiN}$ are known, from measured peak intensities and Equation E10 and E11, as well as from the following additional constraint

$$W_{TiN} + W_{Rutile} + W_{Anatase} = 1 \quad (E12)$$

it is possible to determine compositions of all the components in a mixture. Hence, the main objective is to determine $K_{TiN/Rutile}$ and $K_{Anatase/TiN}$.

The mass ratios W_{TiN}/W_{Rutile} and $W_{Anatase}/W_{TiN}$ in a mixture of standard #1, #2, and #3 are given in terms of the anatase-form mass fractions a_i and the sample mass m_i of the standard # i by

$$\frac{W_{TiN}}{W_{Rutile}} = \frac{m_{TiN}}{(1-a)m_{Rutile}} \quad (E13)$$

and

$$\frac{W_{Anatase}}{W_{TiN}} = \frac{m_{Anatase} + am_{rutile}}{m_{TiN}} \quad (E14)$$

Combining Equations E10-E13, E11-E14, gives

$$\frac{m_{TiN}}{(1-a)m_{Rutile}} = \frac{1}{K_{TiN/Rutile}} \frac{I_{TiN}}{I_{Rutile}} \quad (E15)$$

$$\frac{m_{Anatase} + am_{rutile}}{m_{TiN}} = \frac{1}{K_{Anatase/TiN}} \frac{I_{Anatase}}{I_{TiN}^*} \quad (E16)$$

Equations E15 and E16 are two of a number of forms of Equations E13 and E14 that can be used as the working equations for determining the three unknowns: a , $K_{TiN/Rutile}$ and $K_{Anatase/TiN}$. From the mathematical standpoint, the equation set E15-E16 is underdetermined (two equations, three unknowns). However, if each of these equations is written into its linear form, the above set yield four parameters, two slopes and two intercepts, which are sufficient to determine the unknown parameters.

Equations E15 and E16 can be rewritten in the analogous linear forms as follow:

$$\frac{I_{TiN}}{I_{Rutile}} = \frac{K_{TiN/Rutile}}{(1-a)} \frac{m_{TiN}}{m_{Rutile}} \quad (E17)$$

$$\frac{I_{Anatase}}{I_{TiN}^*} \frac{m_{TiN}}{m_{rutile}} = K_{Anatase/TiN} \frac{m_{Anatase}}{m_{Rutile}} + K_{Anatase/TiN} a \quad (E18)$$

The Equation E17 may be represented in general regression form as:

$$Y_1 = AX_1 + B \quad (E19)$$

and equation E18 as:

$$Y_2 = CX_2 + D \quad (E20)$$

Thus

$$Y_1 = \frac{I_{TiN}}{I_{Rutile}}, Y_2 = \frac{I_{Anatase}}{I_{TiN}^*} \frac{m_{TiN}}{m_{rutile}} \quad (E21)$$

$$X_1 = \frac{m_{TiN}}{m_{Rutile}}, X_2 = \frac{m_{Anatase}}{m_{Rutile}} \quad (E22)$$

$$A = \frac{K_{TiN/Rutile}}{(1-a)}, B = 0 \quad (E23)$$

$$C = K_{Anatase/TiN}, D = K_{Anatase/TiN} a \quad (E24)$$

A number of samples were prepared by mixing these standard powders, in different mass ratios, for 10 min by grinding. XRD analysis of the sample was performed by using a SIEMENS D5000 diffractometers with CuK_α radiation. Each sample was scanned in the range of $2\theta = 20\text{-}80^\circ$ with a step size of $2\theta = 0.02^\circ$. Peak areas, background noise, and separation of overlapped peaks were determined by fitting the diffraction patterns using the Pseudo-Voight function (McCusker et al. 1999) in the Xfit-Koalariet software package from the Collaborative Computational Project number 14 (CCP14).

Table E2 summarizes the experimental results. These samples were used for linear regression based on Equation E17 and E18.

From measured peak intensities, I_{TiN}^* , I_{Rutile} and I_{Anatase} , and masses of standard #1, #2 and #3 in mixtures, (m_{TiN} , m_{Rutile} and m_{Anatase}) the value of Y_2 and X_2 were first calculated and plotted as presented in Figure E1a. The $K_{\text{Anatase/TiN}}$ given by the slope of the fitted line was then used with the intercept of this fitted line to calculate value of a (Equation E24). The second, the value of Y_1 and X_1 were calculated and plotted as presented in Figure E1b. The $K_{\text{TiN/Rutile}}$ given by the slope of the fitted line and the value of a from the former calculation.

Equations E23-E24 relate the fitted parameters from Figure E1 with two calibration constants and the compositions of anatase in standard #2 as follow:

$$K_{\text{TiN/Rutile}} = 0.7127, K_{\text{Anatase/TiN}} = 3.1405, a = 0.1242$$

Table E1 The summary of the results obtained by using standard #1, #2 and #3.

No	m_1	m_2	m_3	$I_{TiN}(111)$	$I_{TiN}(200)$	$I_{TiN}(220)$	$I_{rutile}(110)$	$I_{rutile}(101)$	$I_{rutile}(211)$	$I_{Anatase}(101)$
1	0.0314	0.0461	0.9518	571.6843	769.4037	443.7392	42.2576	17.7763	29.3513	57.1259
2	0	0.0491	0.9557	584.6017	826.6183	468.8553	45.7106	16.4313	25.5125	8.3098
3	0.0317	0.0570	0.9513	573.6313	794.3326	466.1295	52.5054	20.8890	33.6780	58.6809
4	0.0146	0.0619	0.9584	613.2730	828.4709	480.9186	53.0235	24.1091	30.5874	36.3180
5	0.0201	0.0381	0.9541	564.2993	852.1716	464.2444	37.5020	15.9379	19.0699	46.6475
6	0.0283	0.0463	1.1923	581.1007	854.5282	468.1834	31.7500	13.3745	20.2400	36.7725
7	0.0186	0.0491	1.1577	607.4316	838.0441	461.0691	35.2451	19.0542	22.3187	34.7961
8	0.0246	0.0470	0.8833	575.8802	843.0472	461.7168	39.2970	19.1884	31.1574	40.6969
9	0.0136	0.0452	0.8816	587.8008	845.6187	446.3647	40.7683	19.1858	22.9514	27.8701

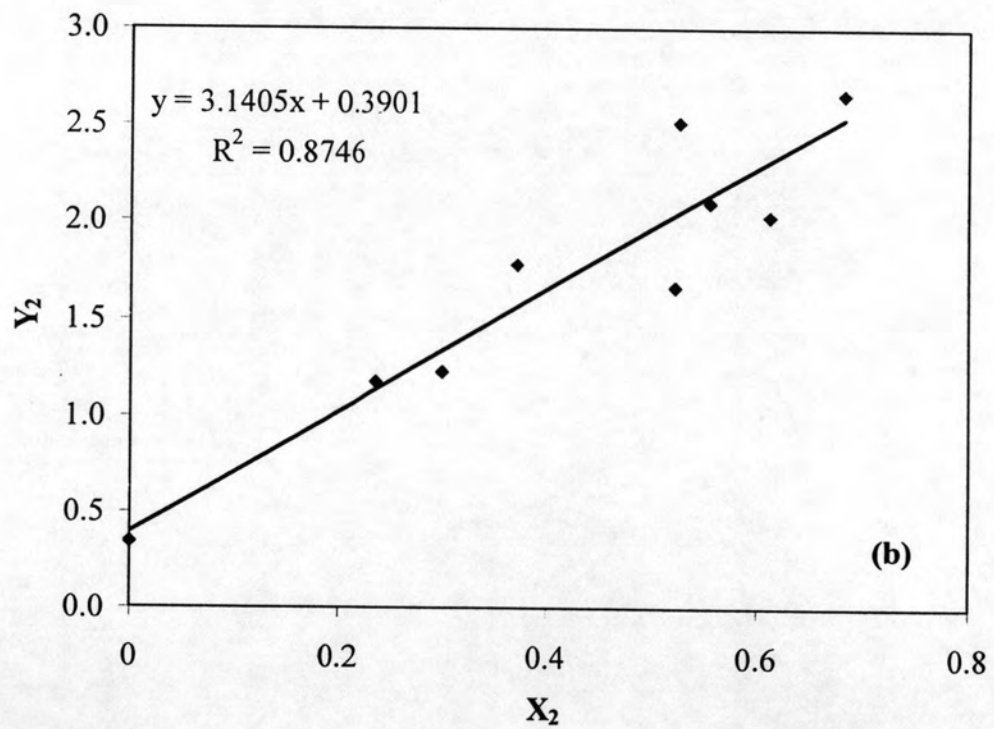
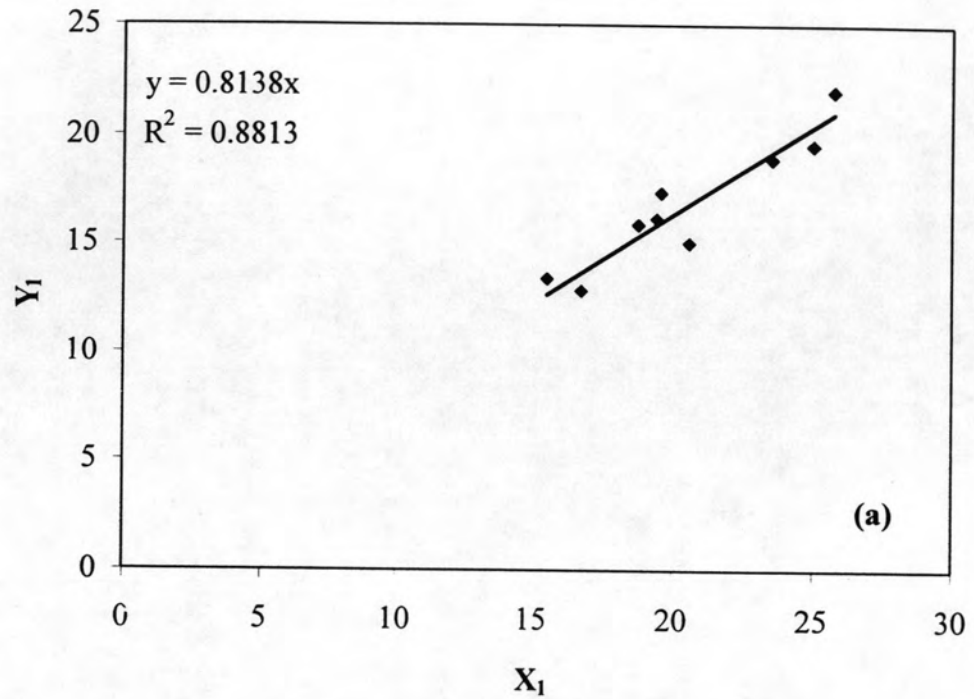


Figure E1 Determination of parameters defined by Equations (a) E21 and E23, and (b) E22 and E24.

APPENDIX F

EXAMPLE FOR THE DETERMINATION OF
THE REACTION CONVERSION

An example of X-ray diffraction pattern of synthesized titanium nitride product and the calculation are given as following.

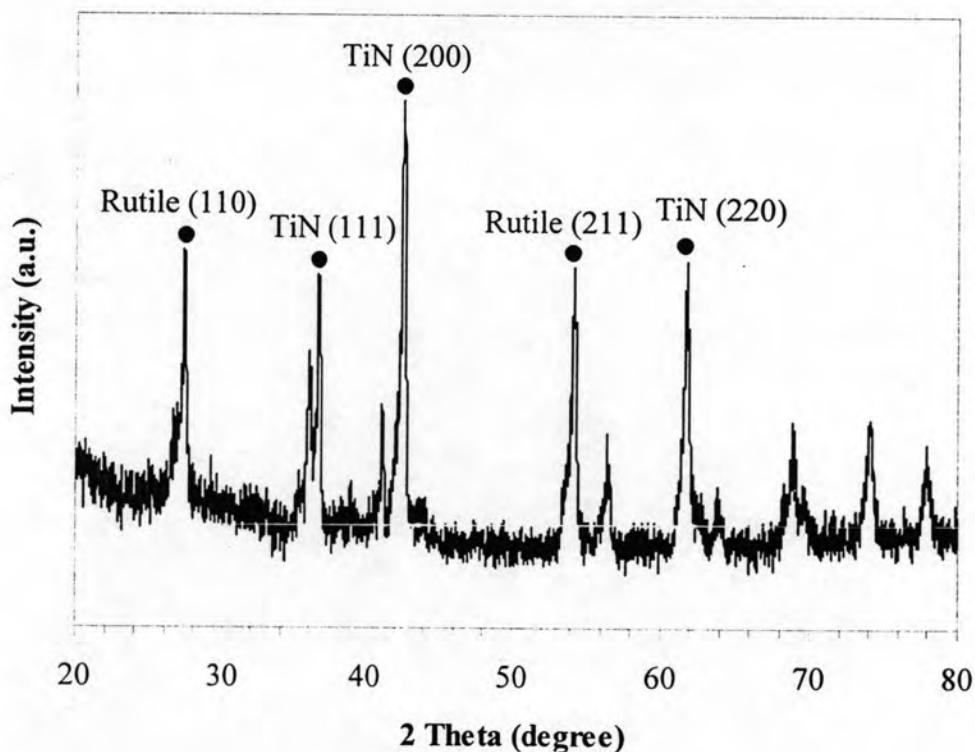


Figure F1 A sample of XRD pattern of product obtained from the nitridation of titania/carbon composite nanofibers.

As described in chapter III, the intensities of (110) and (211) peaks of titania in rutile phase and those of (111), (200) and (220) peaks of titanium nitride were determined by using the Pseudo-Voigt function in the Xfit-Koalariet software package from the Collaborative Computational Project number 14 (CCP14). The results of the integrated intensity are presented in Table F1.

Table F1 Integrated intensities of main peaks

Peak	Integrated intensity of peak
Rutile (110)	35.8157
TiN (111)	25.9434
TiN (200)	53.9311
Rutile (211)	22.7389
TiN (220)	27.4788

Mass fraction of each phase as well as the conversion from titania to titanium nitride were calculated in similar number as the calculation method for silicon nitride proposed by Jovanovic and Kimura [1994] as follow:

$$\frac{I_{TiN}(111) + I_{TiN}(200) + I_{TiN}(220)}{I_{Rutile}(110) + I_{Rutile}(211)} = K_{TiN/Rutile} \frac{W_{TiN}}{W_{Rutile}} \quad (F.1)$$

and

$$W_{TiN} + W_{Rutile} = 1 \quad (F.2)$$

where $I_{\delta}(hkl)$ signifies the integrated intensity of the hkl reflection of phase δ , and W_{δ} is the mass fraction of corresponding phase δ in a mixture. The linear regression calibration constant, $K_{TiN/Rutile}$ is evaluated to be 0.7127, according to the results shown in the Appendix E.

Substitute the values in Table F1 to equation (F.1) and (F.2):

$$\frac{25.9434 + 53.9311 + 27.4788}{35.8157 + 22.7389} = 0.7127 \frac{W_{TiN}}{W_{Rutile}} \quad (F.3)$$

and

$$2.5725W_{Rutile} + W_{Rutile} = 1 \quad (F.4)$$

Thus,

$$W_{Rutile} = 0.2799, W_{TiN} = 0.7201$$

the overall conversion of titania, X , was calculated as:

$$X = \frac{1 - W_{Rutile}}{1 + \left(\frac{M_{TiN}}{M_{Rutile}} - 1 \right) W_{Rutile}} \quad (\text{F.5})$$

where M_{TiN} and M_{Rutile} are the molar masses of titanium nitride and titania, and $(M_{TiN}/M_{Rutile}) - 1 = -0.2252$ is a converting factor.

Substitute W_{Rutile} to equation F.5:

$$X = \frac{1 - 0.2799}{1 + (-1.2252)0.279} = 0.7685 \quad (\text{F.6})$$

APPENDIX G

LIST OF PUBLICATION

1. Tawiporn Wongkhearw, Pitt Supaphol and Varong Pavarajarn, "Carbothermal Reduction and Nitridation of Sol-Gel Derived Titania/Carbon Composites", Regional Symposium on Chemical Engineering 2006, Nanyang, Singapore, December 3-5, 2006.

Carbothermal Reduction and Nitridation of Sol-Gel Derived Titania/Carbon Composites

Tawiporn Wongkhearw^a, Pitt Supaphol^{b,*} and Varong Pavarajarn^{a,*}

^a Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b Technological Center for Electrospun Fiber and the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330 Thailand

* Corresponding authors (Tel. +66-02-218-6890, Fax: +66-02-218-6877)

Email: pitt.s@chula.ac.th (P. Supaphol), fchvpv@eng.chula.ac.th (V. Pavarajarn)

ABSTRACT

Titanium nitride (TiN), a non-oxide ceramic with high thermal, mechanical and chemical stabilities, was synthesized via the carbothermal reduction and nitridation of titania/carbon composites. Titanium tetraisopropoxide (TTIP) was used as a precursor for sol-gel derived titania using poly(vinyl pyrrolidone) (PVP) as the carbon source. Pyrolysis of the obtained gel mixtures at a temperature in the range of 400-600°C resulted in homogeneously mixed titania/carbon composites, which could react with nitrogen at a temperature higher than 1300°C to form titanium nitride. The products were characterized by various analytical techniques such as X-Ray diffraction (XRD), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM) and infrared spectroscopy (IR). The main advantage for the use of sol-gel derived composites was the shape of the products which could be conveniently controlled. Effects of parameters, such as reaction temperature, reaction time, Ti-to-C ratio in the composites, and flow rate of nitrogen, were investigated. The process was also compared with the carbothermal nitridation of physically mixed titania/carbon black powder.

INTRODUCTION

Titanium nitride (TiN) is a non-oxide ceramic material that is inert, biocompatible and extremely hard (i.e., ~85 Rockwell C Hardness or ~2,500 Vickers Hardness). Typically, TiN is formed in rock-salt structure with roughly 1:1 stoichiometric ratio, but TiN can also exist over a wide composition range due to vacancies in nitrogen sublattice [1]. Due to the high thermal, mechanical and chemical stabilities of titanium nitride, it has often been used as coating on titanium alloy, steel, carbides and aluminum components to improve surface properties of the substrate for aerospace and military applications. Furthermore, since TiN is non-toxic, it meets the US Food and Drug Administration (FDA) guidelines to be used in medical devices and implants.

Titanium nitride powder can be synthesized by various approaches, such as direct reaction between titanium and nitrogen, physical vapor deposition (PVD), chemical vapor deposition (CVD) and thermal decomposition in liquid phase [2]. In this work, TiN was synthesized via the carbothermal reduction and nitridation of titania/carbon composites. The composites were fabricated either by sol-gel process or by physical mixing of titania and carbon in powder form, in order to investigate the effects of the precursors and homogeneity of the composites on properties of titanium nitride.

MATERIALS AND METHODS

For the preparation of titania/carbon composites via sol-gel process, 1.5 g of titanium (IV) isopropoxide (TTIP) was mixed with 3 ml of acetic acid and 3 ml of ethanol. The solution was then added into 7.5 ml of polyvinylpyrrolidone (PVP) solution in ethanol. PVP was employed as the carbon source for subsequent carbothermal reduction and nitridation process. The concentration of the PVP solution was varied to achieve the Ti-to-C ratio from 1:1 to 1:4. The resulting mixture was constantly stirred for 1 h, aged for a predetermined period of time and then subjected to pyrolysis at a temperature in the range of 400-600°C in argon for 3 h, to get titania/carbon composites.

The composites were converted to titanium nitride by reacting with nitrogen at a temperature in the range of 1300-1450°C via the carbothermal reduction and nitridation process for 3 h. The products were characterized by various techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and infrared spectroscopy (IR). The obtained products were compared with the products obtained from the physical mixture of titania (anatase phase) and carbon black powder which was used as the starting materials.

RESULTS AND DISCUSSION

For the nitridation of the physically mixed titania/carbon black powder, it was found that the majority of the starting materials was converted into titanium nitride if the reaction temperature was higher than 1300°C. The conversion increased when the temperature increased to 1400°C. Nevertheless, further increase in the temperature to 1450°C did not result in a significant improvement in the conversion. Furthermore, it was found that the progress of the reaction started to level off after about 3 h (viz. the conversion achieved from a 6-h reaction was roughly the same as that from a 3-h reaction).

The effect of Ti-to-C ratio in the starting materials, in the range of 1:1 to 1:4, was investigated. It was found that an excess amount of carbon was required for the reaction to progress towards completion. The nitridation of the starting mixtures with a low carbon content, e.g., 1:1 or 1:2, resulted in a significant amount of unreacted titania, while almost all titania was consumed when a high carbon content was used. This behavior was a result of the nature of the solid state reaction, in which physical contact between titania and carbon powder was crucial for the reaction. An excess amount of carbon ensured such contact. However, if the amount of carbon was too high, too much residual carbon would remain in the products. It should be noted that titania in the obtained products was completely transformed to rutile phase because the reaction temperature was much higher than the anatase-to-rutile phase transition temperature.

Comparing with TiN synthesized from the titania/carbon powder mixture, TiN crystals prepared from sol-gel derived composites were smaller and more uniform because of the better homogeneity of the titania/carbon mixtures in the composites. According to the TGA analysis of the pyrolyzed gel, i.e., titania/carbon composites before the nitridation, the mass of the pyrolyzed gel decreased sharply at a temperature around 350°C, while that from carbon black powder appeared at about 600°C. This suggested that carbon in the pyrolyzed gel was more reactive than the carbon black powder. This was also confirmed by XRD in that the nitrated gel composites showed a lower amount of unreacted titania than that from the physically mixed powder.

Further investigation on the effects of gel preparation parameters showed that molecular weight of PVP and gel aging time were also important factors affecting the formation of titanium nitride in the final products. The titania/carbon composite prepared from a mixture of low molecular weight PVP (MW of 10,000 Da) and high molecular weight PVP (MW of 1,300,000 Da) in the ratio of 5:1 by mass resulted in a better conversion toward titanium nitride than using only the high molecular weight PVP. It should be noted that the high molecular weight PVP was needed to increase the viscosity of the mixture for subsequent processing of the obtained gel. For the effect of gel aging time, it was found that the longer the aging time, the better the composites for nitridation. It was suggested that a long gelation time could lead to the formation of anatase titania with completed crystalline structure, which would readily react with carbon and nitrogen to form titanium nitride.

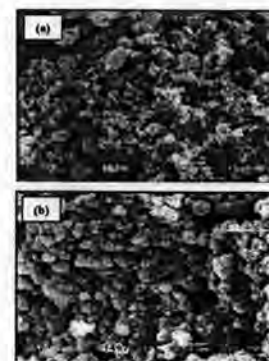


Fig. 1. SEM images of TiN (a) physically mixed (b) sol gel process

CONCLUSION

Titanium nitride was successfully synthesized via the carbothermal reduction and nitridation of titania/carbon composites produced from sol-gel and subsequent pyrolysis processes. The products were superior to titanium nitride synthesized from the physical mixture of titania and carbon black powder, in term of uniformity, smaller grain size and better conversion. For the nitridation to proceed progressively, the reaction temperature needed to be higher than 1300°C. Moreover, the amount of carbon in the starting materials had to be present in an excess amount to ensure sufficient contact with titania, which was required for the reaction to take place. The use of sol-gel derived titania/carbon composites not only increased the homogeneity of the titania/carbon mixtures, but also exhibited better reactivity during the nitridation. A low molecular weight of PVP as the carbon precursor and a long gelation time could enhance the effectiveness of the subsequent carbothermal reduction and nitridation process.

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VITA

Miss Tawiporn Wongkhearw was born on 16th October, 1982, in Chiangrai, Thailand. She received her Bachelor degree of Engineering with a major in Chemical Engineering from King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand in May 2005. She continued her Master study in the major in Chemical Engineering at Chulalongkorn University, Bangkok, Thailand in June 2005.

