

CHAPTER IV

RESULTS AND DISCUSSION

In this research, titanium nitride nanofibers were synthesized by the carbothermal reduction and nitridation of titania/polymer composite nanofibers that were obtained from sol-gel process combination with electrospinning technique. Effects of many factors involving in this synthesis were investigated and will be described in this chapter.

4.1 Preliminary Experiments

In the preliminary experiments, titania/PVP composite fibers were prepared by electrospinning of spinning solution that composed of titanium tetraisopropoxide (TTIP) as precursor, poly vinylpyrrolidone (PVP; M_w of 1,300,000) as carbon source, ethanol and acetic acid. By applying electric field strength across the syringe needle and the collector plate, ultrafine fibers were spun and deposited as a non-woven mat on the collector plate. Morphology of the titania/PVP composite fibers are shown in Figure 4.1(a) that the surface of as-spun composite fiber is smooth and the diameter ranges from 200 to 400 nm.

The as-spun fibers were pyrolyzed at 600°C for 3 h to convert PVP to free carbon, which is needed in the subsequent nitridation process. As shown by SEM micrograph in Figure 4.1(b), the pyrolyzed fibers are still in the form of fibers but the shrinkage as well as reduction in fiber diameter can be clearly observed.

The final step in the synthesis of titanium nitride is the carbothermal reduction and nitridation process. In this process, pyrolyzed fibers were nitrided at 1400°C for 3 h in nitrogen atmosphere in the tube furnace. The obtained product is consisted of 2 portions. However, majority of the product is still in the form of fibers, as shown in Figure 4.2(b).

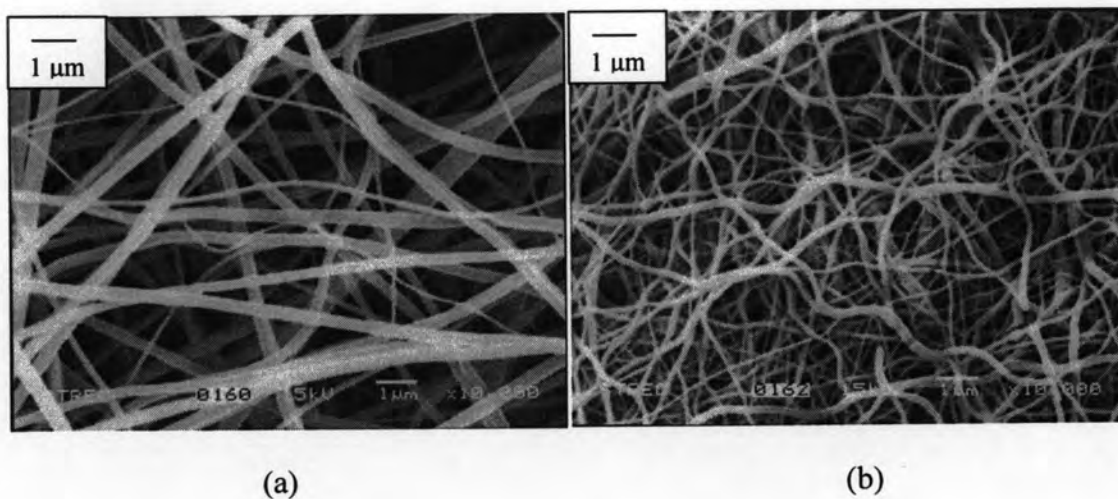


Figure 4.1 SEM images of (a) as-spun fibers and (b) pyrolyzed fibers.

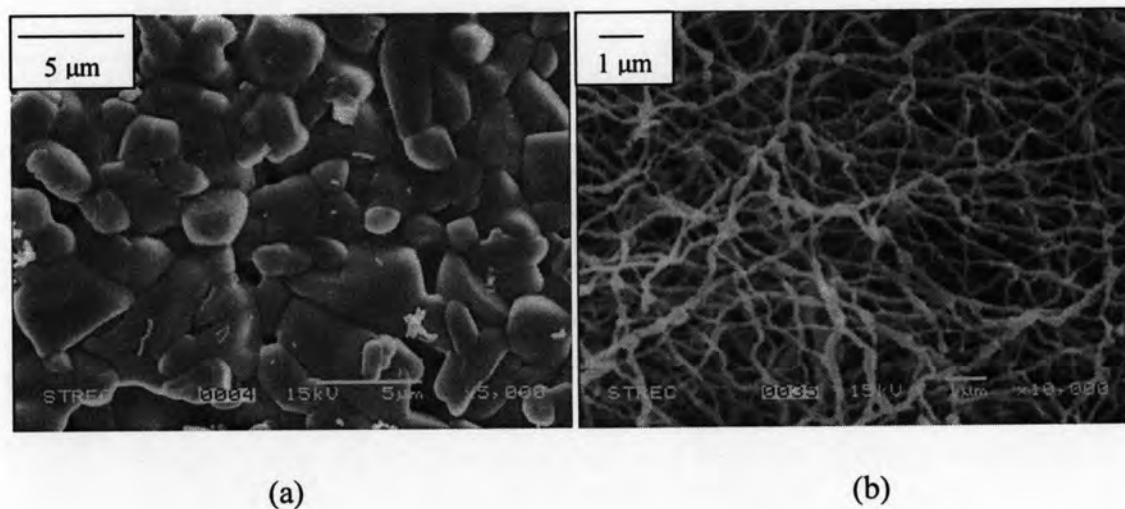


Figure 4.2 SEM images of fiber nitrated (a) upper portion and (b) lower portion.

The product obtained after the nitridation can be easily distinguished into 2 parts, i.e. thin layer of white material as the upper part of the product and yellowish-gray layer underneath. The upper part is mean that area contact to the atmosphere in the tube furnace and the lower part is mean that the area contact to the boat as shown in Figure 4.3.



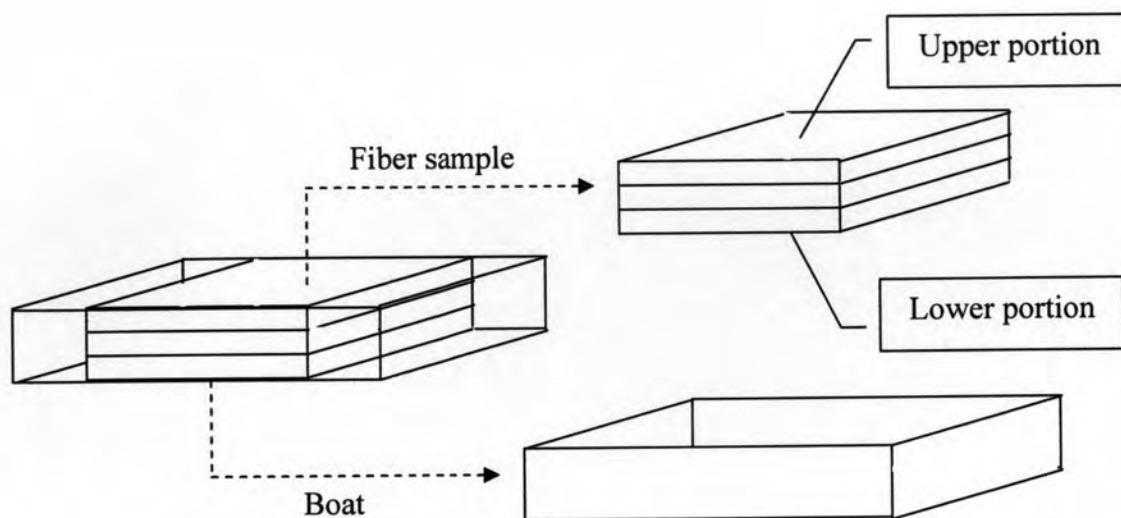


Figure 4.3 Diagram of upper and lower portion of fiber sample.

The frequency distribution for diameters of titanium nitride fibers are determined from SEM image shown in Figure 4.4, using image analysis software (Semafore). It can be seen that size of the nitrated fibers is relatively uniform, with the average diameter of 124 nm. These fibers are confirmed by XRD analysis result as shown in Figure 4.5 that they are titanium nitride. However, residual titania, in rutile phase, is observed.

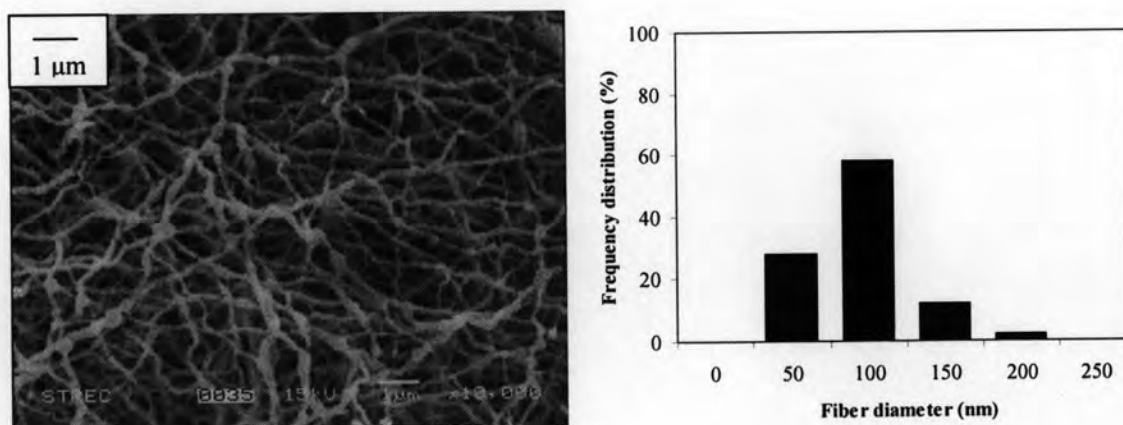


Figure 4.4 SEM image and frequency distribution of fiber diameters for the fiber nitrated at 1400°C for 3 h.

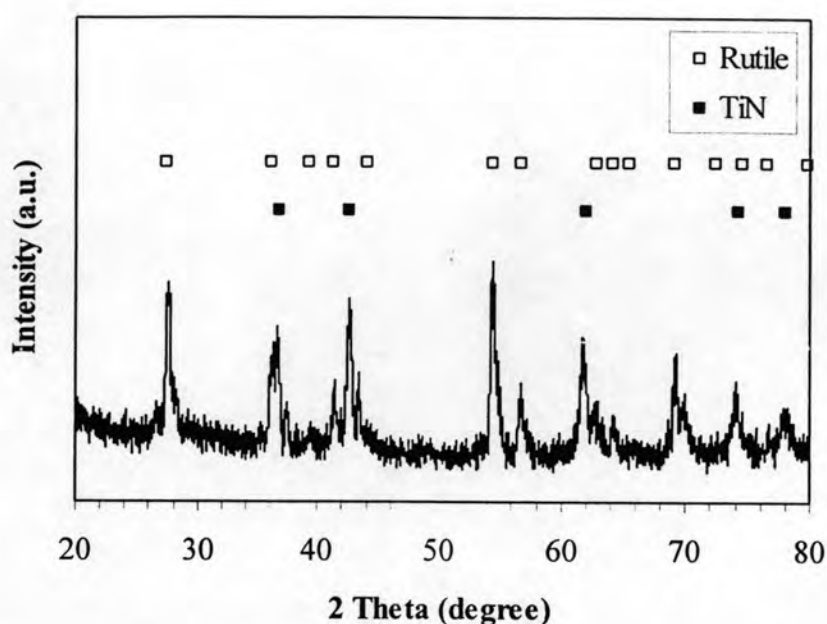


Figure 4.5 XRD pattern of fibers nitrided at 1400°C for 3 h.

4.2 Comparison of Carbon Source

In this study, effect of carbon source on composition of the final nitrided product was investigated. It should be noted that no electrospinning was conducted at the beginning of the investigation in order to avoid the coupling effect from morphology of the fiber. Three types of carbon source were used. There were carbon black, high-molecular weight poly vinylpyrrolidone (h-PVP; M_w of 1,300,000) and low-molecular weight poly vinylpyrrolidone (l-PVP; M_w of 10,000). The carbon source was mixed with titanium tetraisopropoxide (TTIP) which was used as titania precursor, acetic acid, and ethanol to make spinning solution via sol-gel process. In this mixture, Ti-to-C ratio was 1:2. In the case of carbon black, high-molecular weight PVP was added to the spinning solution in addition to carbon black, in order to assist spinability. PVP was later removed by controlled calcination and left only titania and carbon black in the mixture. The spinning solution was left for one day for hydrolysis in the atmosphere and removal of the solvent by natural evaporation. After that, the spinning solution was pyrolyzed at 600°C in argon to convert PVP to free carbon,

which was useful for the subsequent carbothermal reduction and nitridation process. However, it was confirmed by the result from TGA-DTA analysis in nitrogen atmosphere as shown in Figure 4.6 that the solvent was not completely evaporated before pyrolysis process was taking place. This TGA-DTA analysis simulates the pyrolysis process. According to the thermodiagram, large amount of solvent was left in the spinning solution, but it was eliminated when the sample was heated up to around 100°C. As the temperature was increased, volatile species were released from the sample. Mass of the sample became unchanged around 600°C, which suggested that the reaction was completed. Therefore, in the actual pyrolysis process, all samples were pyrolyzed at 600°C for 3 h to make sure that the solvent was completely evaporated and polymer was completely pyrolyzed.

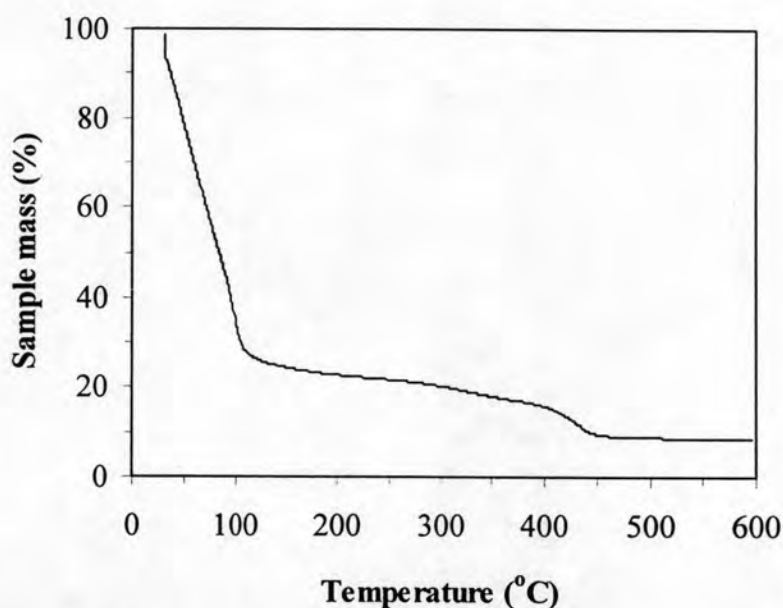


Figure 4.6 TGA-DTA thermodiagram of the spinning solution containing high-molecular weight PVP analyzed in nitrogen atmosphere.

XRD patterns of the pyrolyzed samples in Figure 4.7 show that titania in anatase phase is formed during the pyrolysis process. It should be noted that all samples are amorphous before pyrolysis. For the sample that uses carbon black as carbon source, small amount of rutile phase is found after calcinations at 400°C for 5 min in order to remove the spinability-aid species (i.e. high-molecular weight PVP),

as shown in Figure 4.7(d). After that, all samples were nitrided at 1400°C for 3 h. The result was also compared with that obtained from the nitridation of anatase titania physically mixed with carbon black by grinding. As shown in Figure 4.8, the obtained products from sol-gel process are titanium carbonitride (TiCN) while that from physical mixing is titanium nitride (TiN). However, among the mixture prepared via sol-gel process, carbon black is the carbon source which results in the product that is closer to TiN than the others. This behavior is the result from the fact that sol-gel process results in more uniformly mixed mixture and therefore carbon in sol-gel derived mixture contacts with titania more homogeneously than physical mixing. For the effect of carbon source, since carbon blacks are lump, the contact between carbon and titania in this case is less than that in PVP mixtures. Therefore, the amount of reacted carbon in the carbon black mixture and only PVP mixtures from sol-gel process are more than in physical mixing, respectively. Moreover, in sol-gel process, carbon content in the PVP mixtures is also higher than in the carbon black mixture.

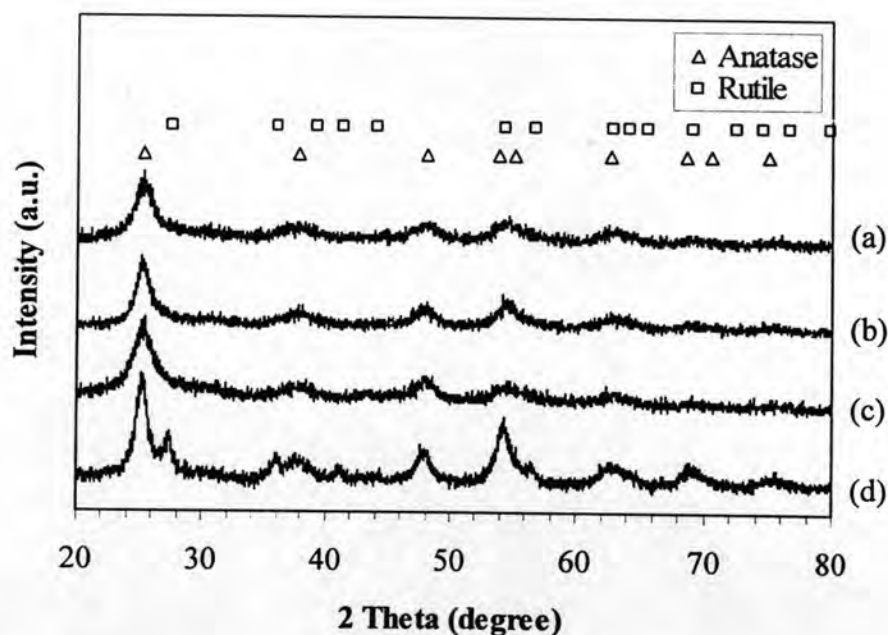


Figure 4.7 XRD patterns of the pyrolyzed spinning solution, using various types of carbon source: (a) low-molecular weight PVP, (b) high-molecular weight PVP, (c) carbon black; and (d) sample (c) after calcination.

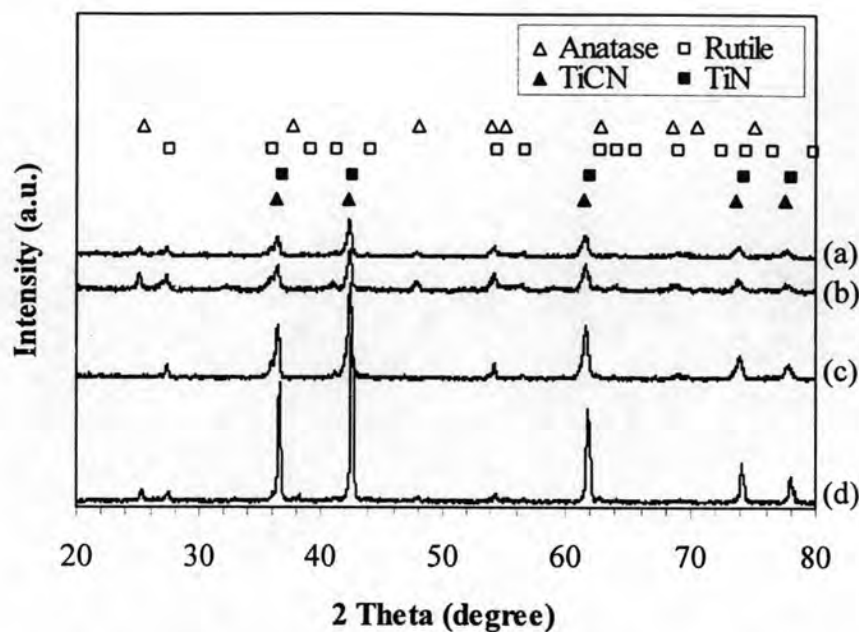


Figure 4.8 XRD patterns of the spinning solution after nitridation, using various types of carbon source: (a) low-molecular weight PVP, (b) high-molecular weight PVP, (c) carbon black and (d) nitrided sample of the mixture obtained from physical mixing.

For the electrospinning process, the spinning solution must consist of polymer of sufficient molecular weight or concentration and it must have proper viscosity. One of the factors that affects the viscosity of the solution is the molecular weight of the polymer. Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer but of a lower molecular weight (Ramakrishna et al. 2005). In this study, fibers were prepared from the spinning solution which was composed of high-molecular weight PVP mixed with low-molecular weight PVP. The high-molecular weight PVP to low-molecular weight PVP ratio was varied from 1:5, 2:4 to 3:3. These ratios were calculated on the basis of Ti-to-C ratio of 1:20 to obtain sufficient viscosity for forming fiber. By applying high electrical potential across the syringe needle and the collector plate, ultrafine fibers with smooth surface were spun and deposited as a non-woven mat on the collector plate. Morphology of titania/PVP composite fibers at each step of the process to synthesize titanium nitride fibers is shown in Figure 4.9.

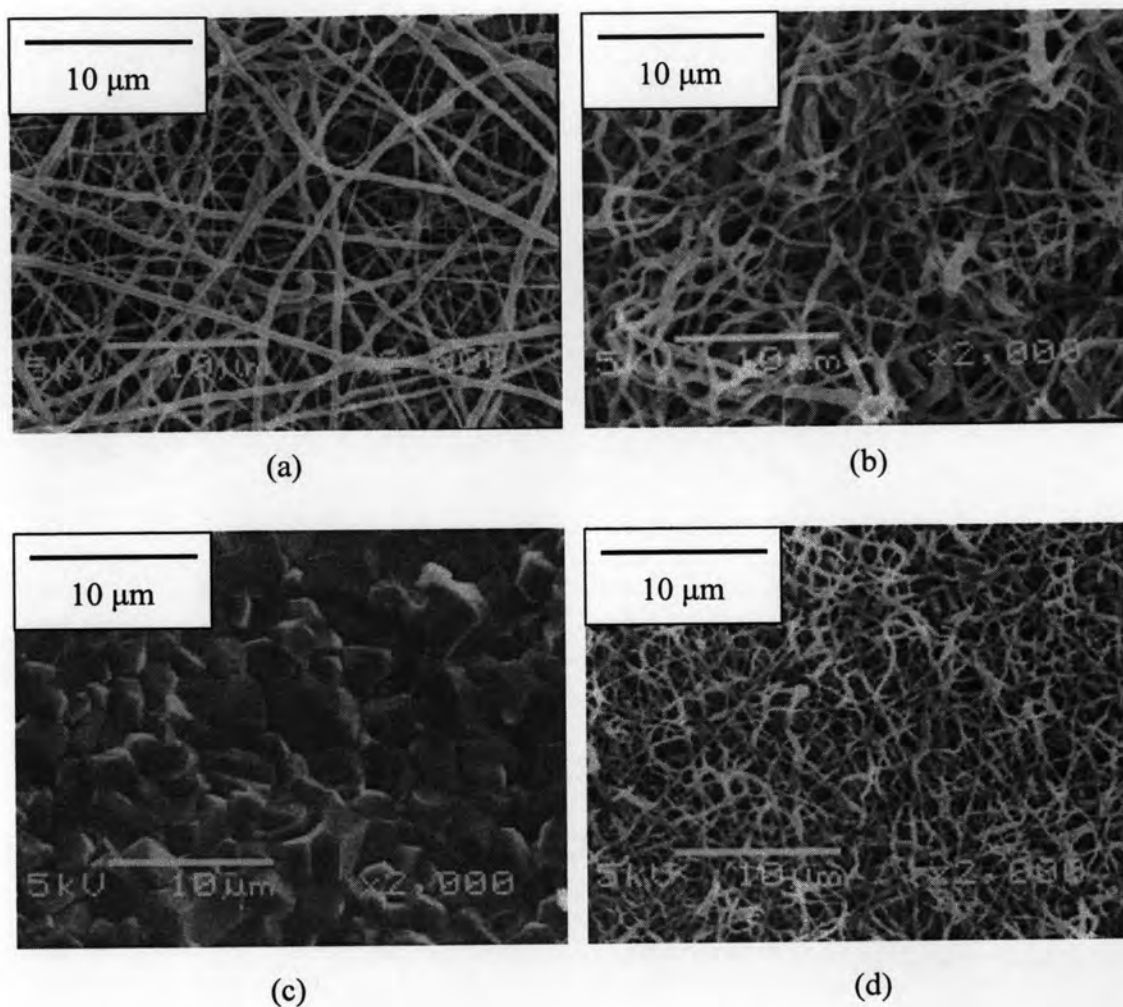


Figure 4.9 SEM micrographs of fibers with the ratio of h-PVP to l-PVP is 2:4 at each step of the synthesis procedure: (a) as-spun titania/PVP composite fibers, (b) pyrolyzed fibers, (c) upper layer of the nitrated product and (d) lower layer of the nitrated product.

According to Figure 4.9(b)-(d), it can be seen that after the pyrolysis and the nitridation process, the products are still in the form of fiber, except the upper layer of the obtained product after nitridation process. In this upper part, the product is dense sheet, which seems to be the result form particles that are joined together. This result will be discussed in more detail in the next section.

The results from TGA analysis in oxygen atmosphere of the pyrolyzed fibers synthesized with different ratios of h-PVP to l-PVP are shown in Figure 4.10. It can be seen that all samples show similar thermal behavior. So, there is no significant different from the ratio of high-molecular weight PVP to low-molecular weight PVP on the thermal properties of the fibers.

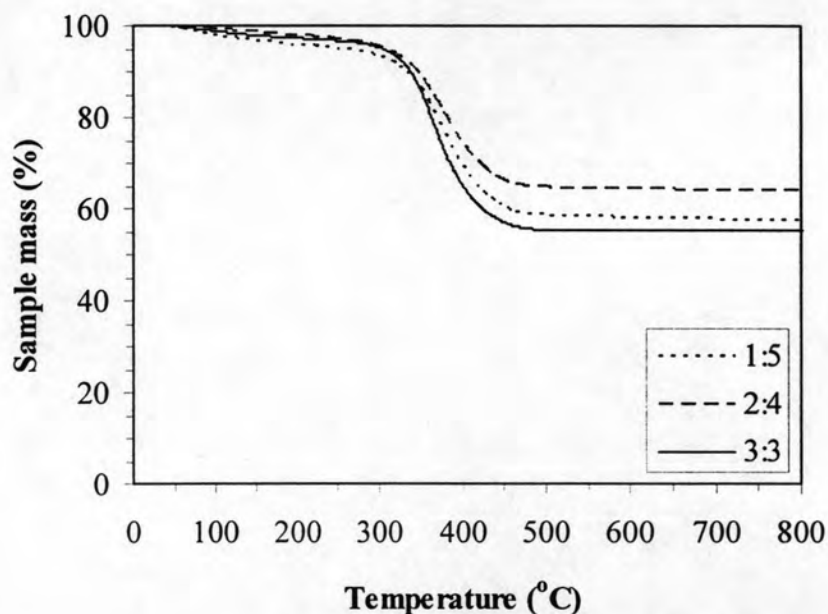


Figure 4.10 TGA-DTA thermodiagrams of pyrolyzed fibers synthesized with different PVP ratios.

All fibers were analyzed by XRD. The XRD patterns of as-spun fibers are shown in Figure 4.11. According to this graph, the as-spun fibers are amorphous in all conditions. They are transformed to crystalline titania in anatase phase during pyrolysis as shown in Figure 4.12. The XRD patterns of the pyrolyzed powders obtained directly from the spinning solution, without processing through the electrospinning step, are also shown in Figure 4.12 for comparison.

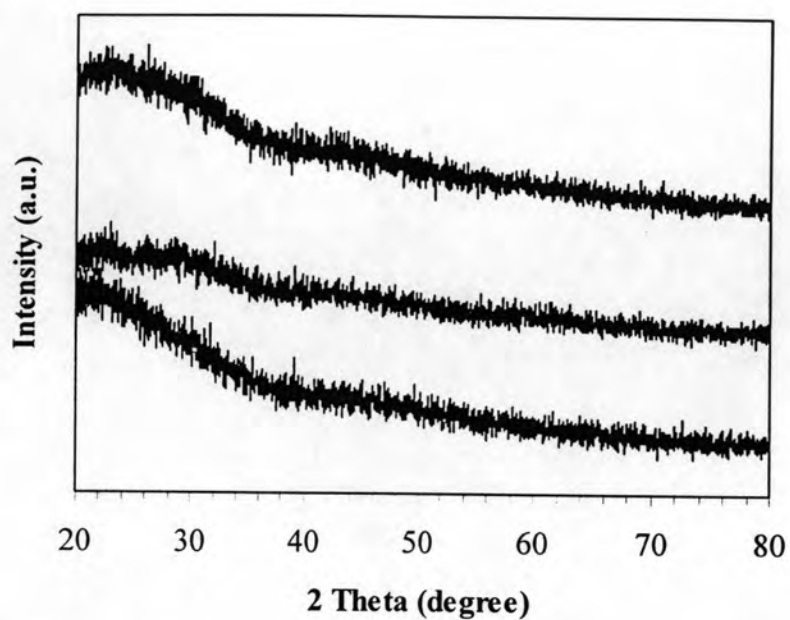


Figure 4.11 XRD patterns of as-spun fibers synthesized with different PVP ratios: (a) 1:5 (b) 2:4 (c) 3:3.

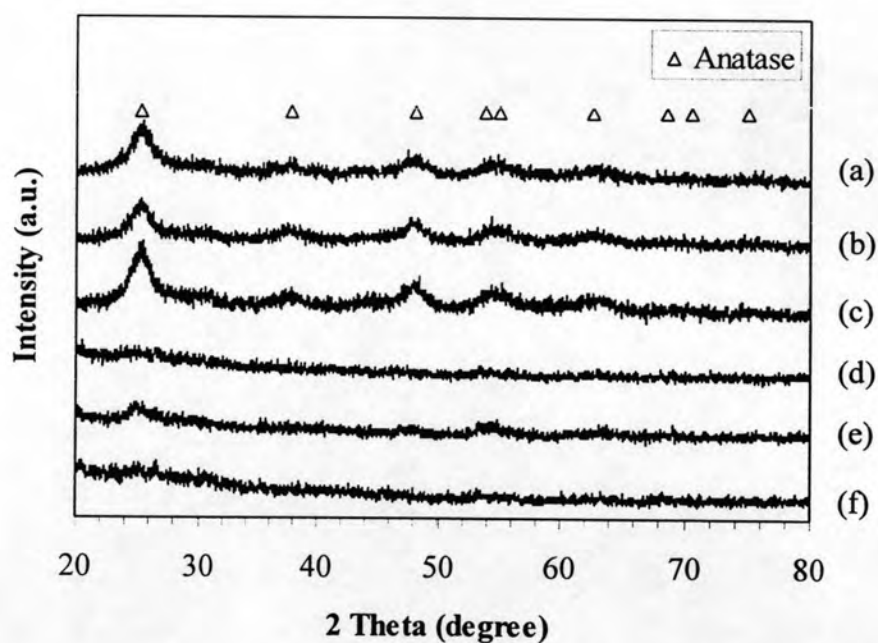
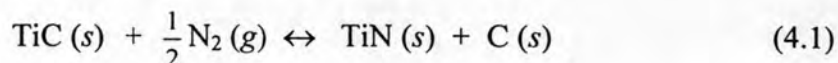


Figure 4.12 XRD patterns of the pyrolyzed powders obtained from the spinning solution with various PVP ratios: (a) 1:5, (b) 2:4, (c) 3:3; and that of the pyrolyzed fibers with PVP ratio of: (d) 1:5, (e) 2:4, (f) 3:3.

The XRD patterns of nitrated fibers and powders are shown in Figure 4.13. It is confirmed that all products are titanium carbonitride (TiCN), which is solid solution of titanium carbide (TiC) and titanium nitride (TiN). This is the result from high content of carbon source in the as-pun fibers, according to the equilibrium equation between TiC and TiN is shown as follow (Yu and Lin 1998):



When amount of carbon is increased, the reaction is shifted toward the formation of TiC. Subsequently, TiCN occurs because both TiC and TiN are presented in the sample.

From XRD patterns in Figure 4.13, trace amount of titania in rutile phase can be observed. Although titania obtained after the pyrolysis step is anatase, the anatase is transformed to rutile phase during the step of heating the system up in the nitridation process. It is confirmed by separated experiment, in which pure anatase, i.e. JRC-TIO-1, was heated under nitrogen to the same temperature of the nitrogen process. The XRD analysis results, as shown in Figure 4.14, reveal that anatase is transformed into rutile. It has been reported that titania normally undergoes anatase/rutile phase transformation at temperature in the range from 600 to 700°C (Hu et al.)

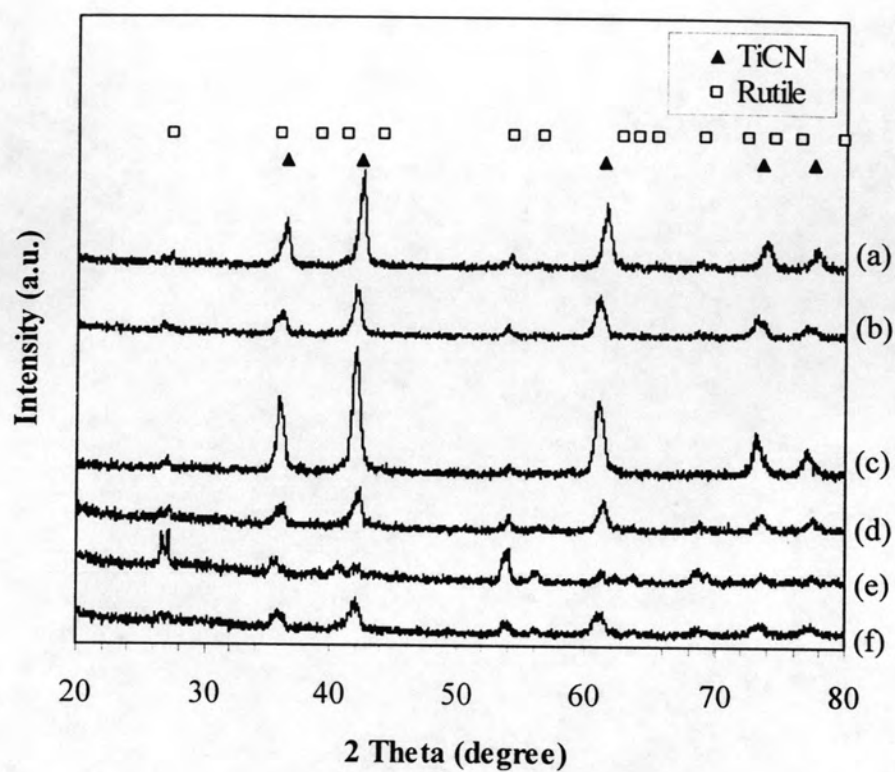


Figure 4.13 XRD patterns of the nitrided powders obtained from the spinning solution with various PVP ratios: (a) 1:5, (b) 2:4, (c) 3:3; and that of the nitrided fibers with PVP ratio of: (d) 1:5, (e) 2:4, (f) 3:3.

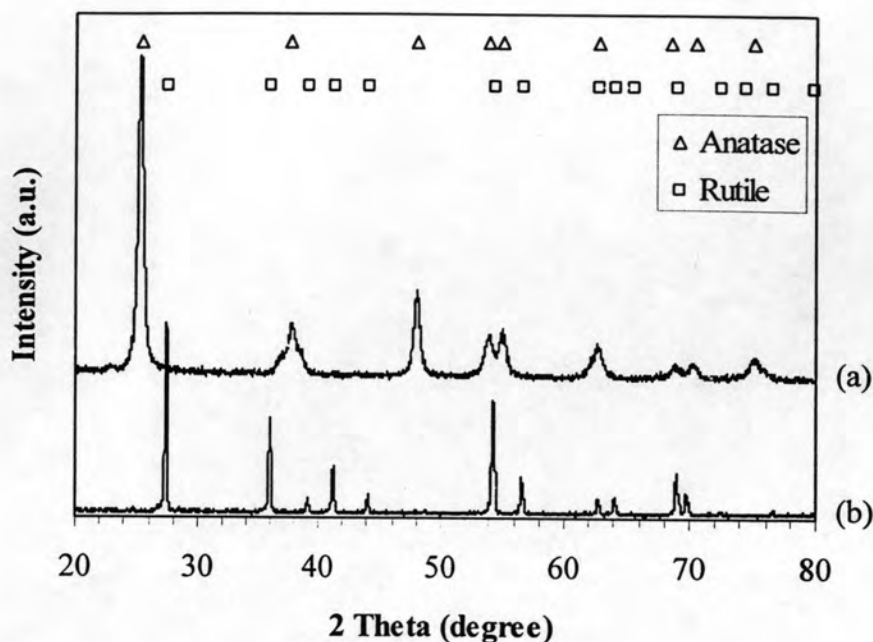


Figure 4.14 XRD pattern of titania anatase phase (a) before nitridation and (b) after nitridation (1400°C for 3 h).

4.3 Synthesis of Titanium Nitride Fibers from Titania/PVP Composite Fibers.

In this section, titania/PVP composite fibers were prepared by sol-gel process followed by electrospinning. The composite was then converted to titanium nitride via the carbothermal reduction and nitridation process. As mentioned earlier for the preparation of spinning solution, TTIP was mixed with 13wt. % PVP (M_w of 1,300,000), acetic acid, and ethanol. By applying electric field strength of 15 kV across the syringe needle and the collector plate, which was set at 7 cm apart, ultrafine fibers with smooth surface were spun and deposited as a non-woven mat on the collector plate. Electrospinning micrographs of the titania/PVP composite fibers are shown in Figure 4.15.

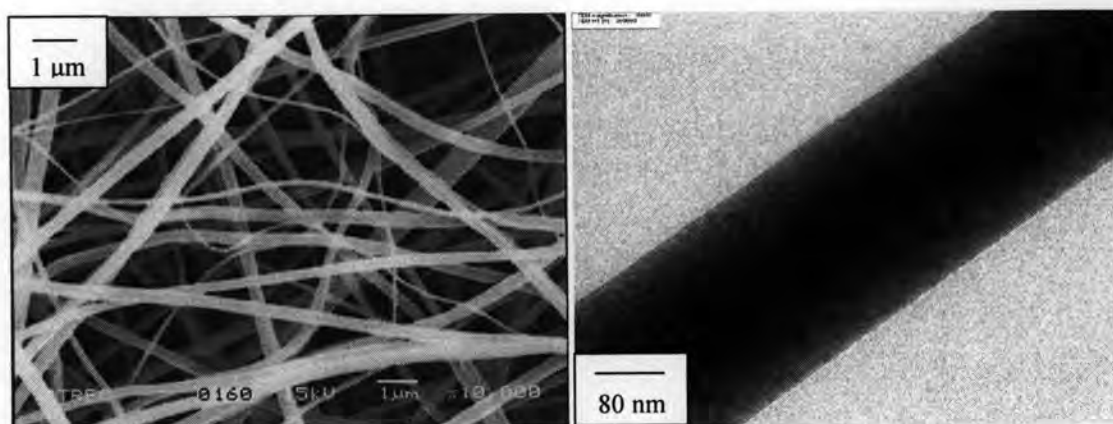


Figure 4.15 SEM and TEM micrographs of the as-spun titania/PVP composite fibers with 13 wt. % PVP content.

Figure 4.15 shows SEM and TEM images of the as-spun titania/PVP composite fibers. From this Figure, it can be seen that the obtained fibers generally have diameter in nanometer scale, but the length of fiber is very long. The diameter of the as-spun composite fibers ranges from 200 to 400 nm. The surface of the as-spun fiber is smooth due to the amorphous nature of the titania/PVP composite. Moreover, ethanol used as solvent in this work has low surface tension, which encourages the formation of smooth fibers (Fong et al. 1999). The solvent evaporates in-flight, when the solution is injected from the tip of the needle toward the collector. These fibers have slightly broad size distribution because of high PVA content in the spinning solution. It has been indicated that the increased PVP concentration leads to an increase in the average fiber diameter as well as a broader size distribution (Ramakrishna et al. 2005). The increase in the average fiber diameter with increasing PVP concentration is a result of the increase in viscosity of the spinning solution (Mittupatham et al. 2004). However, the increase in the viscosity of the spinning solution could lead to non-uniform ejection of the jet, which is responsible for broad size distribution of fibers (Frenot and Chronakis 2003; Huang et al. 2003). When the viscosity is too high, the solution may dry at the tip of the needle before electrospinning can be initiated. If the electric field strength is lower than 15 kV, the fiber diameters are increased, but if the electric field strength is too low, no stable

liquid jet is formed. On the other hand, if the electric field strength is too high, the needle is clogged up.

As mention earlier, the solvent evaporated in-flight, when the solution was injected from the tip of the needle to the collector. However, the evaporation was not complete. Therefore, the as-spun fibers were left for 1 day in the ambient atmosphere for the solvent to evaporate, as well as allowing hydrolysis and condensation of the precursor to take place. Nevertheless, after aging for 1 day, the solvent was still left in the sample because the as-spun fibers were piled up on the collector during the electrospinning process. The remaining solvent was finally removed in the pyrolysis process. In this work, the as-spun fibers were pyrolyzed at 600°C to break long hydrocarbon chains into free carbon, which is required for the subsequent carbothermal reduction and nitridation process. The time for pyrolysis process was varied between 3 and 6 h. However, there was no difference in the thermal behavior of the fibers pyrolyzed for 3 and 6 h, as shown in Figure 4.16.

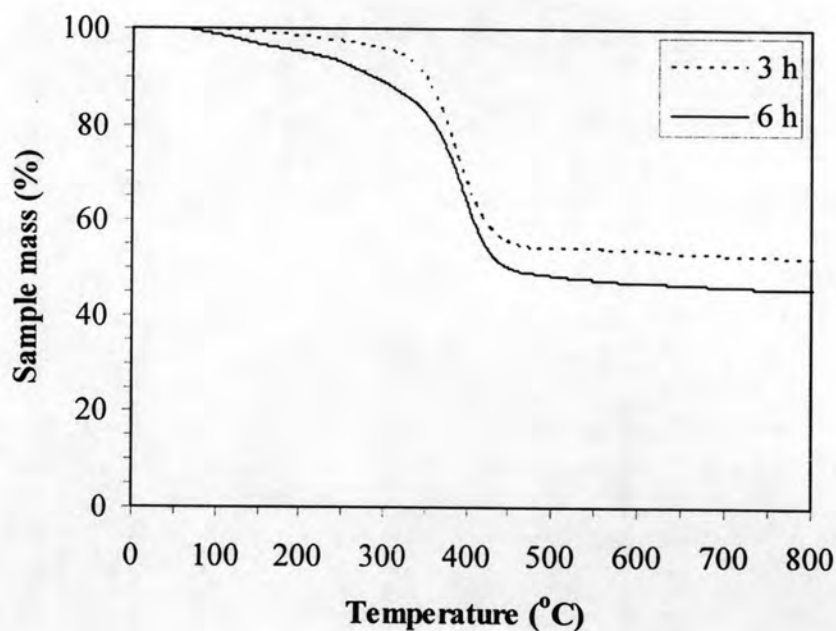


Figure 4.16 TGA-DTA thermodiagrams for the pyrolyzed titania/PVP composite fibers at 600°C for 3 and 6 h.

Pyrolyzed fibers were analyzed by TGA-DTA in oxygen atmosphere to find amount of free carbon in these samples. According to the thermodiagrams in Figure 4.16, the free carbon is oxidized at temperature about 350°C. The carbon content in the fibers pyrolyzed for 3 and 6 h is about 50 and 45 wt.%, respectively. It should be note that parts of carbon are also removed during the pyrolysis, as mention earlier. So the amount of the remaining carbon in the pyrolyzed sample is less than that is present in spinning solution. It should be noted that, the samples were put in the tray in the form of thick layer. Nevertheless, it is concluded that there is no big different in amount of free carbon in the fibers pyrolyzed for 3 and 6 h. The pyrolysis is complete with in 3 h.

SEM images of the fibers pyrolyzed for 3 and 6 h (Figure 4.17) show that the morphology of both pyrolyzed products is still in the form of fibers. The titania fibers obtained after pyrolysis exhibit significant shrinkage as well as a reduction in fiber diameter due to the evaporation of solvent and the decomposition of PVP (as well as the partial removal of organic content, which was already proved by TGA analysis). The fibers pyrolyzed for 6 h are more densely packed than that obtained from 3-h pyrolysis. So, the period of 3 h was chosen as the pyrolysis time for further studied because of the proper overall morphology of the obtained fibers.

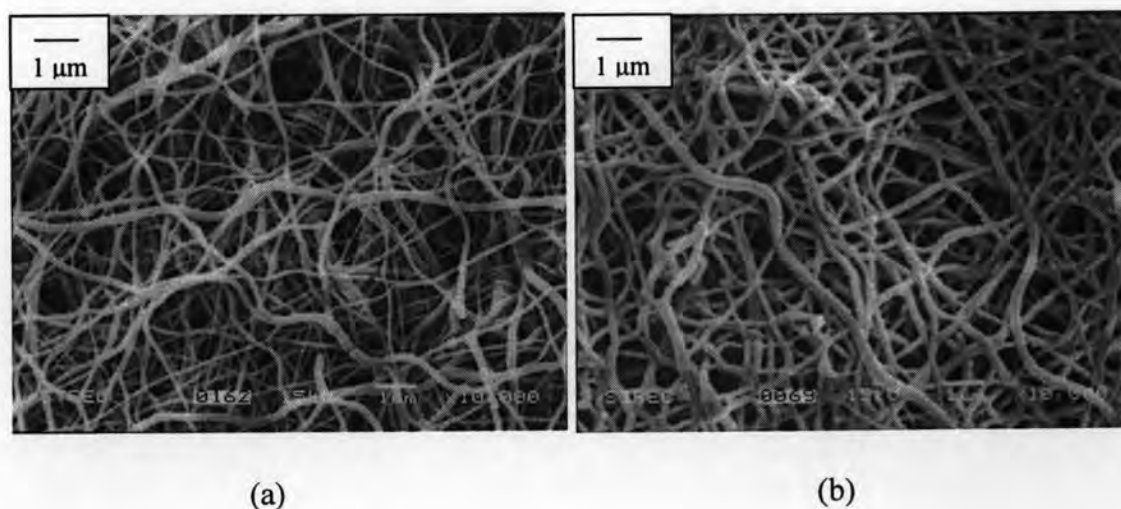


Figure 4.17 SEM micrographs of fibers pyrolyzed at 600°C for (a) 3 h and (b) 6 h.

Crystallization, however, takes place during the pyrolysis process, as evidenced by the XRD analysis results in Figure 4.18. The XRD pattern of the pyrolyzed fibers shows crystalline peaks corresponding to anatase phase, while that of as-spun fibers is amorphous. The presence of crystal entities can also be observed from TEM micrograph in Figure 4.19, especially at high magnification (Figure 4.19(b)), in which lattice fringes are clearly shown. The sharp circular pattern in the selected area electron diffraction pattern (SAED) taken from the fiber in overall (Figure 4.19(b)) indicates that the fiber is polycrystalline with high crystallinity. It is also suggested that the fiber is, in fact, consisted of many particle, which are all single crystals. This result supports the finding from SEM analyses and agrees with report in literature (Choi et al., 1999). These particles are embedded in the amorphous matrix of carbon.

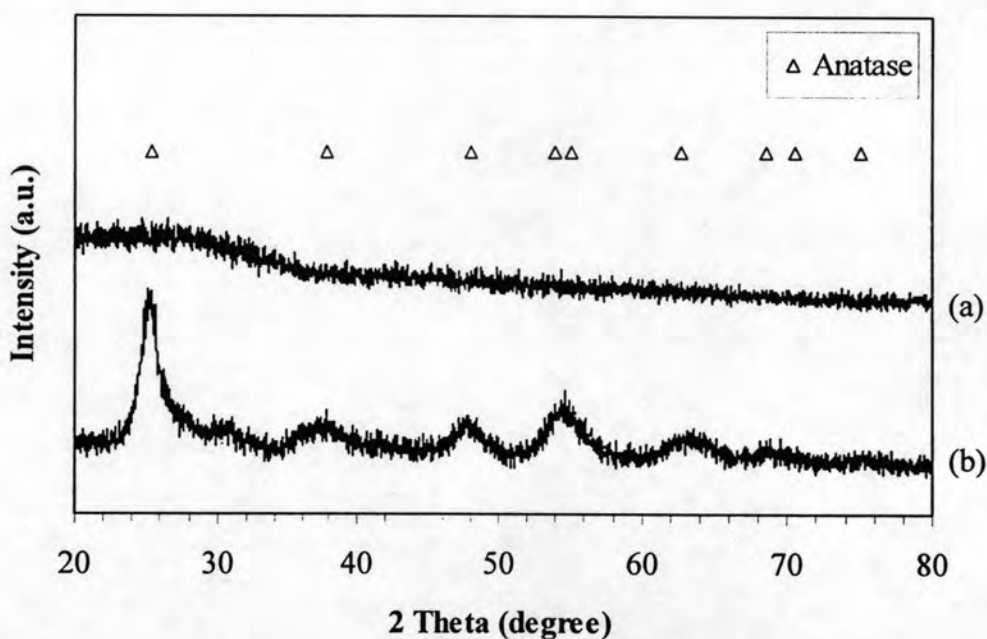


Figure 4.18 XRD patterns of (a) as-spun fibers and (b) pyrolyzed fibers.

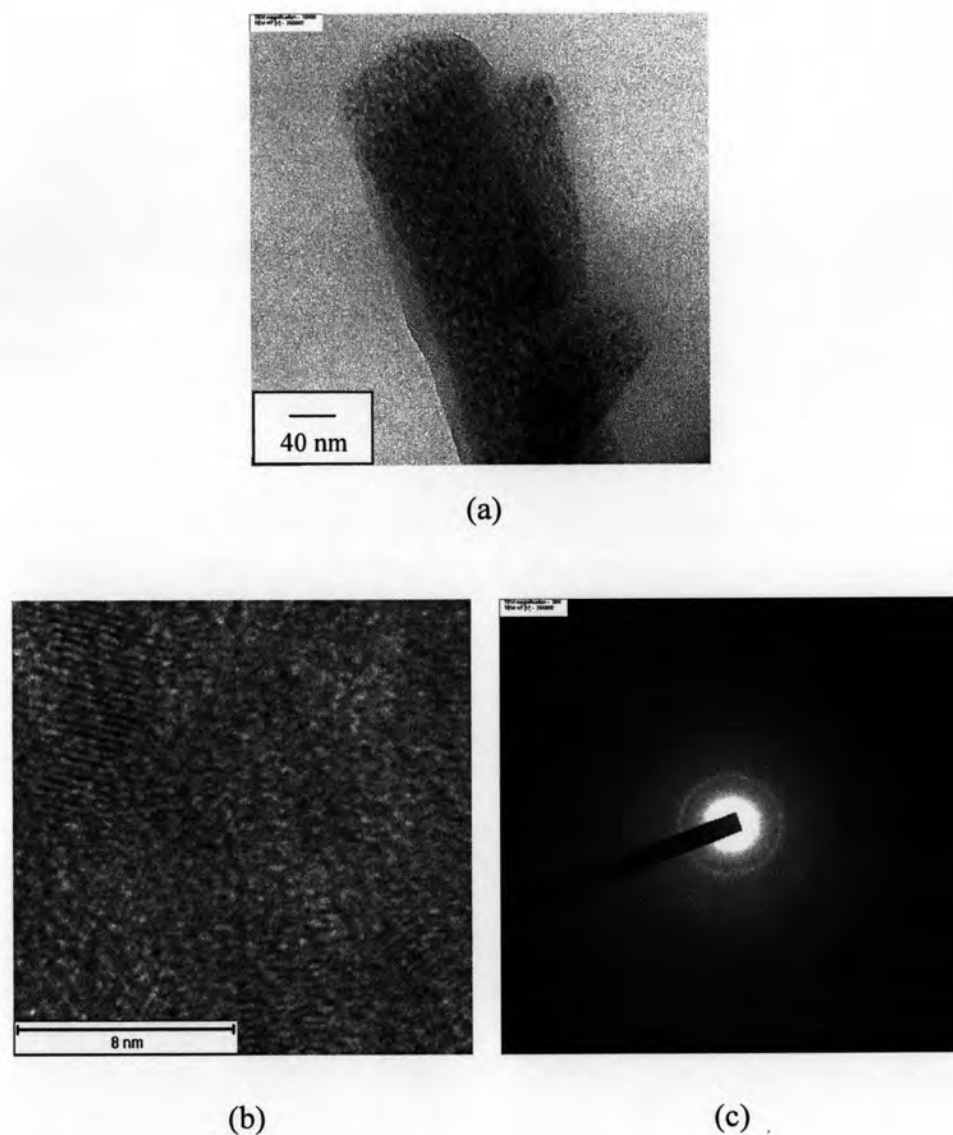


Figure 4.19 TEM micrographs of the pyrolyzed titania/PVP composite fibers: (a)-(b) TEM images and (c) SAED pattern.

After pyrolyzed, the fibers were nitrated at 1400°C for 3 h. From the visual observation of final product, it can be obviously distinguished into two parts. For the first part, which is the layer of fibers that were directly exposed to the reaction atmosphere, the product is white and contains no carbon. It is confirmed by TGA analysis as shown in Figure 4.20, since there is no mass loss observed for the analyzed samples. For the rest of the product, TGA analysis shows an increase in

sample mass at temperature about 400°C, which is oxidation temperature, of titanium nitride.

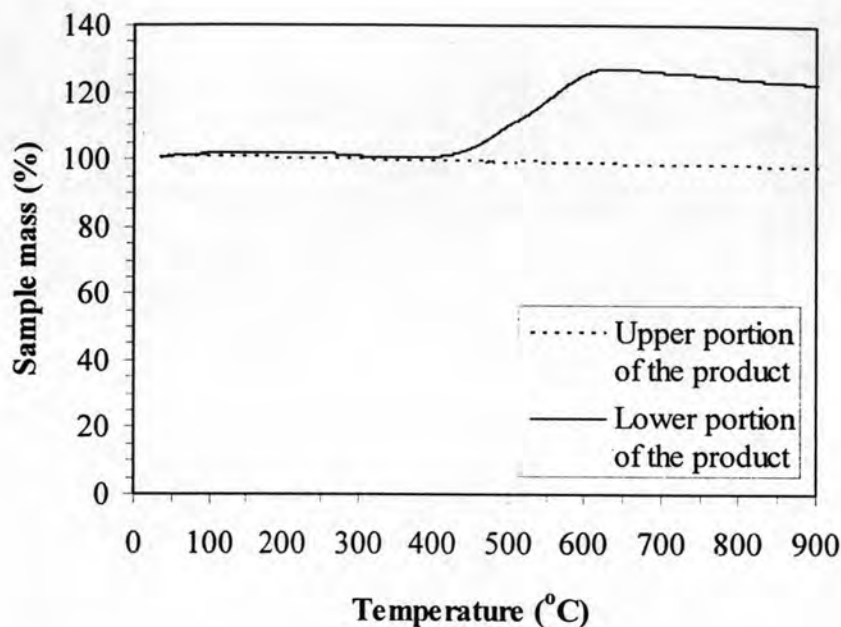


Figure 4.20 TGA-DTA thermodiagrams for the fibers nitrided at 1400°C for 3 h.

For the investigation of the reaction process, the reaction time was varied from 0, 30 and 180 min. The reactin for 0 min refer to the process of heating the system up to 1400°C and immediately cooling down without supplying nitrogen into the system. For such process, the upper portion of the product has morphology that appears to be beaded particles joining into fibers, as shown by SEM images in Figure 4.21(a). It is suggested that these big particles occur from the sintering of the small particles during the heating up process. On the other hand, the lower part of the product is still in the same form as the pyrolyzed fibers (Figure 4.21(a)). After 30 min of reaction, the upper layer of the product is no longer in the form of fibers, but it is a layer of heavily agglomerated particles (Figure 4.21(b)). It should be noted that the size of particles seems to be larger than particles observed from 0 min of reaction. The lower product in this case is still in the form of fiber but fiber shrinkage is observed (i.e. the fiber is no longer straight). For longer reaction time, particles in the upper layer of the product are more sintered to form very large particles as shown in Figure 4.21(c), but the

lower portion of the still remains in fiber from although significant shrinkage is observed. Although the change in morphology of the fibers was clearly observed along the course of reaction, the attempt to describe reaction mechanism was not successful. Further investigation is needed.

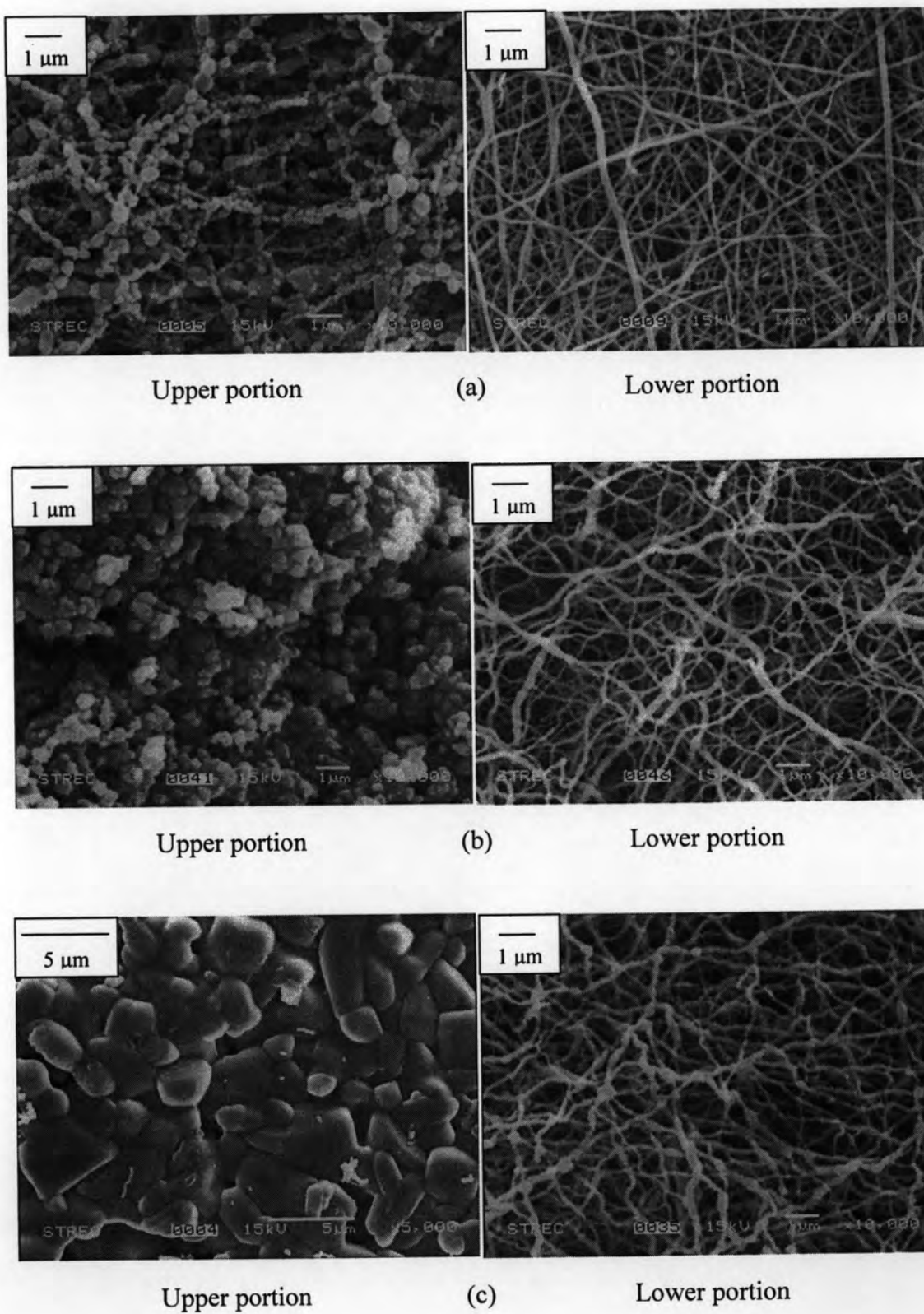


Figure 4.21 SEM micrographs of the final products at various reaction times: (a) 0 min, (b) 30 min and (c) 180 min.

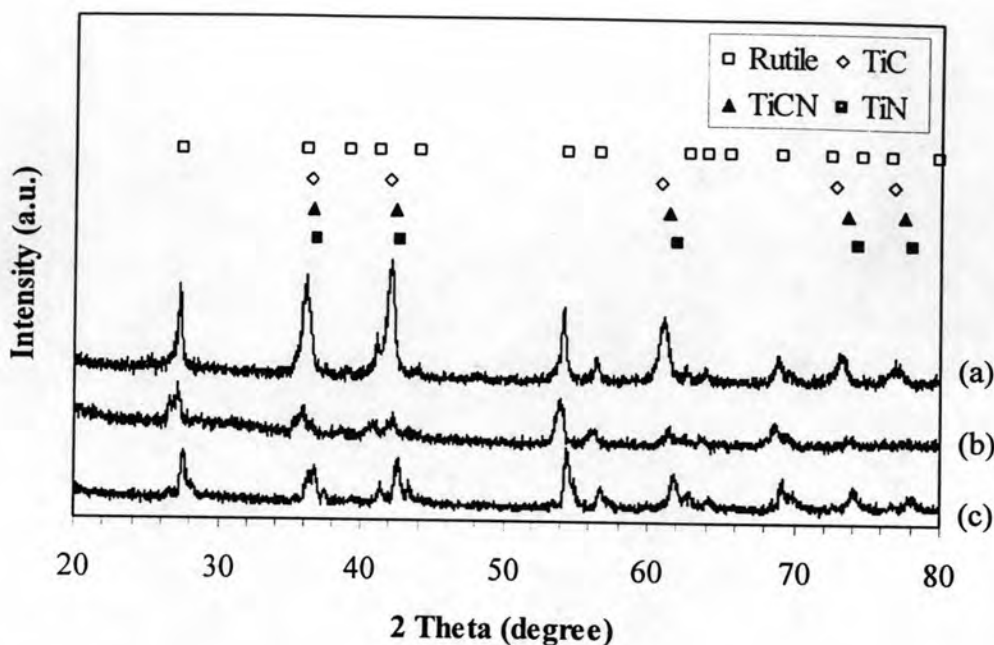


Figure 4.22 XRD patterns of products nitrated for various times: (a) 0 min, (b) 30 min and (c) 180 min.

XRD patterns of the nitrated products in Figure 4.22 show that there are titania in rutile phase residing in all products, even the product from 0-min reaction. This result suggests that anatase transforms to rutile phase during heating up to the reaction temperature. It also suggests that the nitridation is not completed, even after 3 h of the reaction. Regarding phase of the product obtained, the XRD pattern of the product from 0-min reaction shows peaks that are corresponding to titanium carbide (Figure 4.22(a)). At 30 min, there is titanium nitride formed in solid solution with titanium carbide, i.e. titanium carbonitride. When the reaction time is prolonged to 180 min, titanium nitride is obtained as the product (Figure 4.22(c)). From this XRD pattern, the conversion of the reaction to form titanium nitride is found to be 0.61, after 180 min.

In this case, although titanium nitride can be synthesized from titania/carbon composite fiber, the nitrated product of the same composite in powder form is titanium carbonitride. This is expected to be the result from limited amount of nitrogen diffused through the bed of powder to react with titania/carbon composite underneath. For the spun sample the fibers were collected as a non-woven mat on the collector plate. Therefore, the diffusion of nitrogen gas through fiber sample is easier than the powder sample. More nitrogen results in more titanium nitride.

Therefore, the reaction steps for the synthesis of titanium nitride via the carbothermal reduction and nitridation of titania can be assumed as following. First, titania in anatase phase is transformed to rutile phase. Next, TiC is formed from the solid-state reaction between titania and carbon when the temperature reaches 1260°C (Xiang et al. 2000). These reactions occur during heating up process in this work, in which only argon is supplied to the reactor. Then, when the temperature reaches 1400°C and nitrogen is fed to the system, titanium nitride is formed. In this step, nitrogen replaces carbon in TiC structure, since both TiN and TiC have the same rock-salt crystalline structure, with a roughly 1:1 stoichiometry (Walker et al. 1998). The experimental results suggest that the reaction starts from the top layer of the sample and moves toward the bottom of sample. Nevertheless, it is highly probable that titanium nitride is also formed via the direct reaction among titania, carbon and nitrogen, according to Eq. (2.4).

From this study, it is proved that titanium nitrides can be synthesized by the carbothermal reduction and nitridation of titania/PVP composite fibers. Nevertheless, as observed earlier in the study of the effect of carbon source, carbon black also gives good result for titanium nitride synthesis. Therefore, in the next study, carbon black is used as carbon source. The result of changing carbon source would be shown in the next topic.

4.4 Synthesis of Titanium Nitride Fibers from Titania/PVP/Carbon Black Composite Fibers.

To study the effect of another type of carbon source, carbon black was added into the spinning solution. The Ti-to-C molar ratio of carbon black in the mixture was 1:2. As mentioned early, PVP was also added to the spinning solution, as the aid for spinability. Amount of PVP ($M_w \sim 1,300,000$) added was 13 wt.%. When carbon black is added, viscosity of the spinning solution is higher than that of the solution with PVP only. Since, in this study, the spinning solution is form at the tip of the needle by gravity, the increase in viscosity reduces amount of spinning solution that is drawn away from the needle tip. This causes diameter of as-spun fibers to be smaller than the fibers obtained from the spinning solution without carbon black. The SEM micrograph of the as-spun fibers is shown in Figure 4.23. From this Figure, it can be seen that surface of the fiber is not as smooth as previously observed from the titania/PVP composite fiber. Close observation suggests that the rough feature on the surface of the fiber is a result from the lumping of carbon black particles.

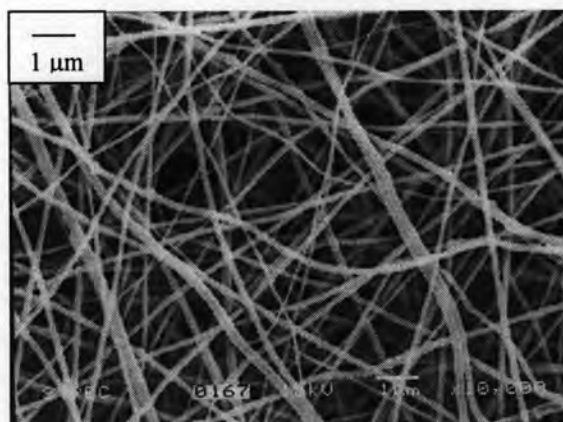


Figure 4.23 SEM micrographs of the as-spun fibers of titania/PVP/carbon black composite.

These as-spun fibers were pyrolyzed at 600°C for 3 h in argon atmosphere. The resulting fibers are similar to those mentioned earlier in the previous context. SEM image in Figure 4.24 shows that the pyrolyzed product is still in the form of fiber. The titania fibers obtained after pyrolysis in this case still exhibit significant shrinkage as well as a reduction in fiber diameter due to the evaporation of solvent and the decomposition of PVP. Crystallization, of titania also takes place during the pyrolysis process, as witnessed from well-aligned crystal fringes in the high-magnification TEM image. The sharp circular pattern in SAED image indicates that, although the fiber is polycrystalline, it has very high crystallinity. It is suggested that each particle observed in TEM image is in fact single-crystal particle. From TEM image in Figure 4.24(c), the fiber appears to be consisted of linked particles or crystallites surrounded in amorphous matrix. It is suggested that the amorphous part is free carbon, while the crystalline particles are titania in anatase phase.

In this case, the pyrolyzed fibers were calcined at 400°C for 5 min in a box furnace to remove residual PVP. Since the temperature at which PVP can be removed by oxidation is about 350°C, while carbon black starts to be oxidized at about 500°C (shown in Appendix D), it is expected that carbon black remains in the sample after calcination. After calcination, the color of fibers changes from black to grey. However, the products are still in the form of fiber as shown in Figure 4.25(a). The calcined fiber appears to be more distorted and its surface becomes rougher. TEM image in Figure 4.25(c) illustrated the growth of crystallite grains within the fiber. Size of these grains is about 20 nm. Nevertheless, the calcined fibers have much higher crystallinity than the pyrolyzed fibers as witnessed from the clear rings in the SAED pattern, as well as the distinct lattice fringes observed in Figure 4.25(b).

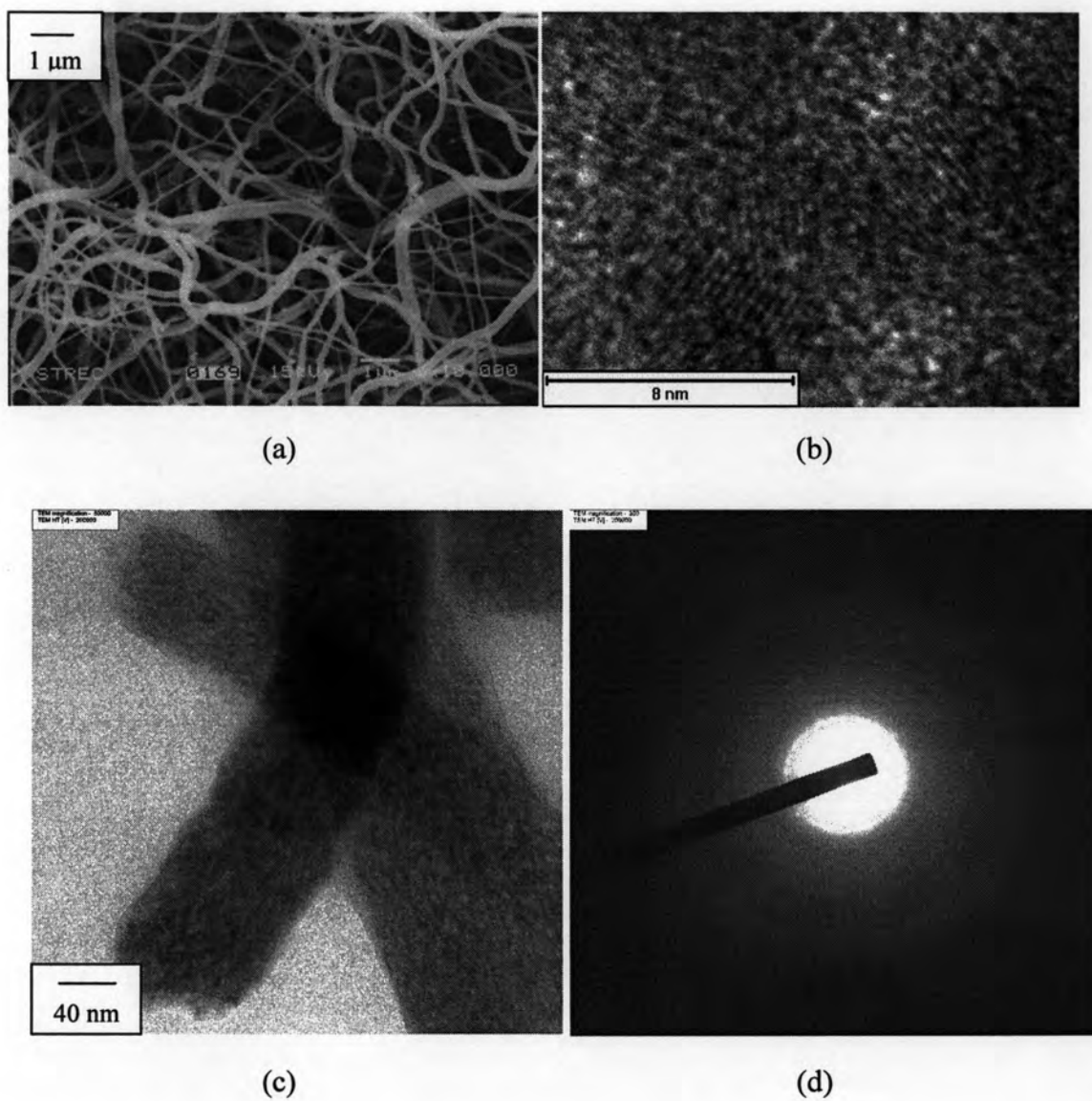


Figure 4.24 SEM and TEM micrographs of the titania/PVP/carbon black composite fibers after pyrolysis at 600°C for 3 h: (a) SEM image, (b) - (c) TEM images and (d) SAED pattern.

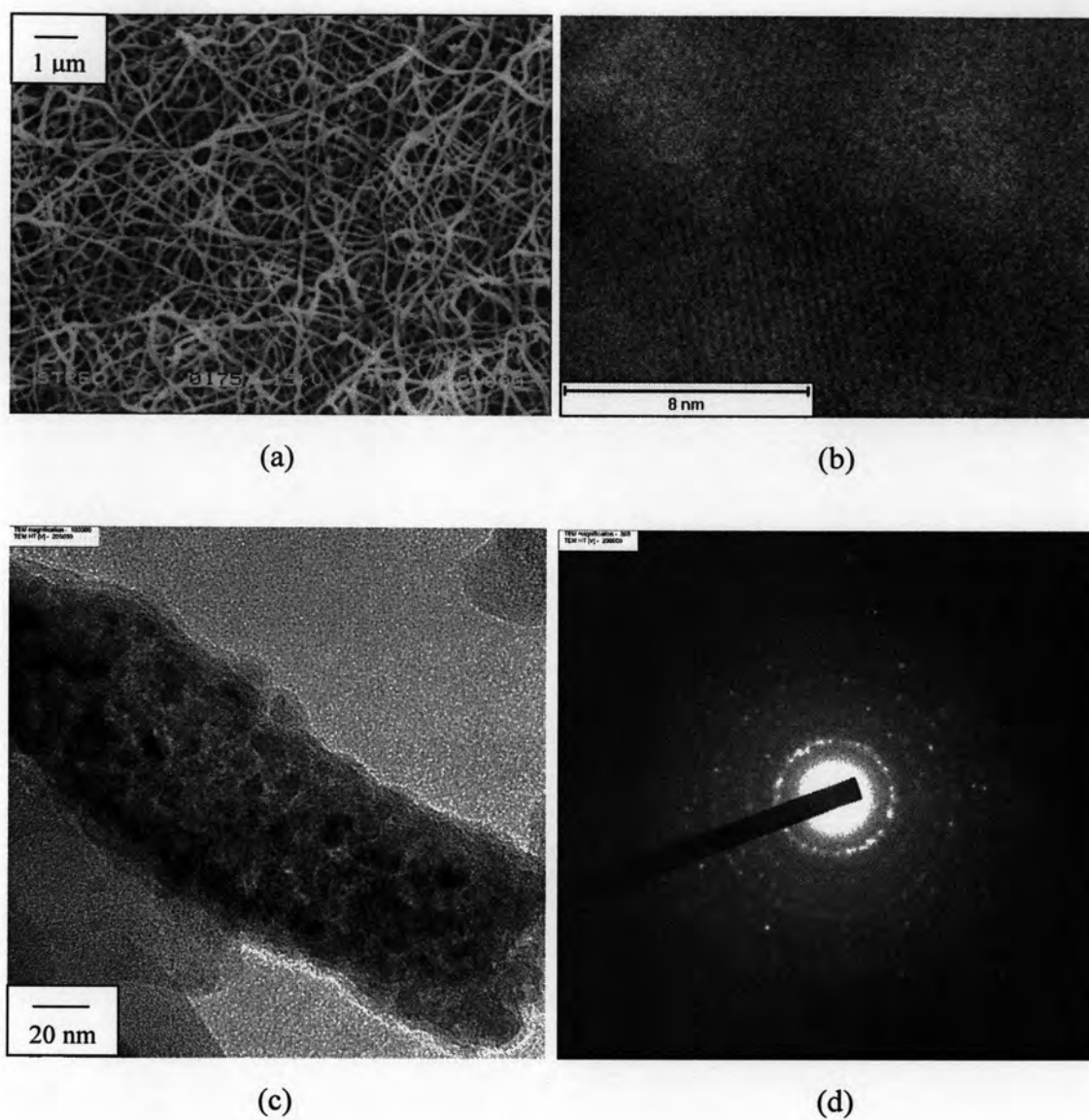


Figure 4.25 SEM and TEM micrographs of the titania/PVP/carbon black composite fibers after calcination at 400°C for 5 min: (a) SEM image, (b) - (c) TEM images and (d) SAED pattern.

After calcination, it is expected that the fibers are composed of carbon black and titania. This is confirmed by TGA-DTA thermodiagram in Figure 4.26. This graph shows that mass of the pyrolyzed sample decreases in two steps at temperature about 300°C and 500°C, respectively. These temperatures are corresponding with the temperature for decomposition (via oxidation) of PVP and carbon black, respectively (see Appendix D.). The mass loss is approximately 35 wt. % in the first step and 30 wt.% in the second step. On the other hand, The thermodiagram of the calcined sample show a decrease in mass only at the temperature about 500°C. This mass loss is approximately 25 wt.%. Therefore, it can be concluded that the organic matters originated from PVP are removed by the calcinations. Only titania and carbon black are present in the calcined fibers.

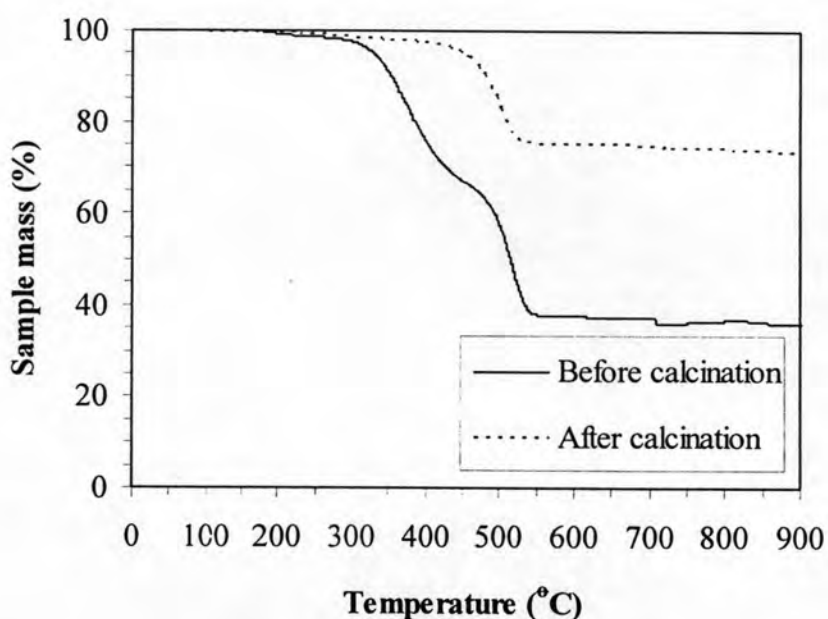
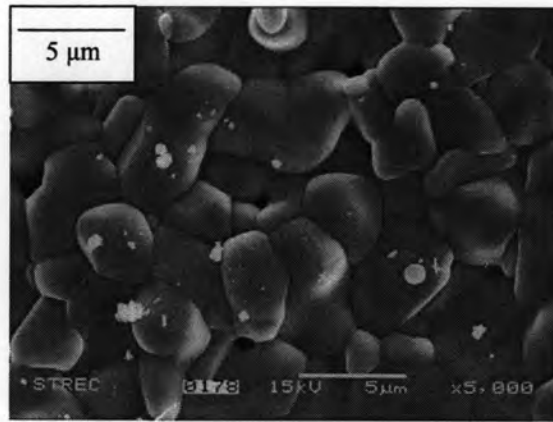
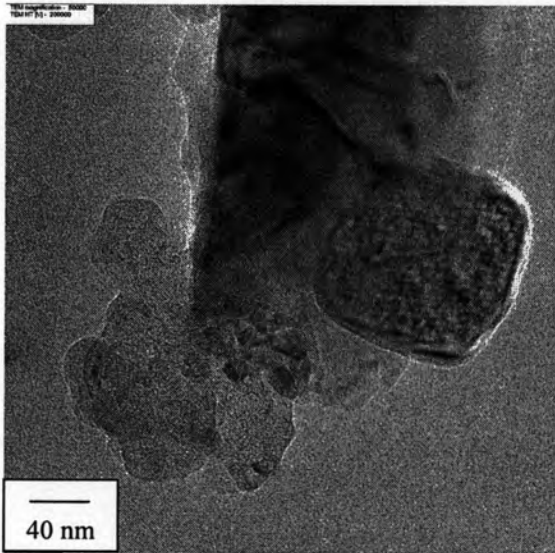


Figure 4.26 TGA-DTA thermodiagrams of the pyrolyzed titania/PVP/carbon black composite fibers before and after calcination at 400°C for 5 min.

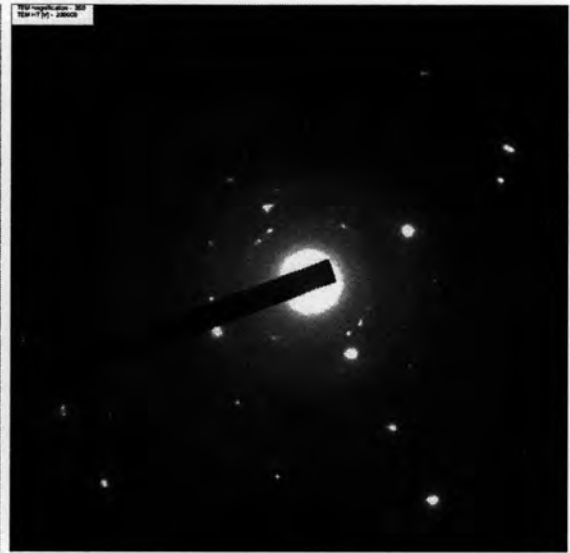




(a)

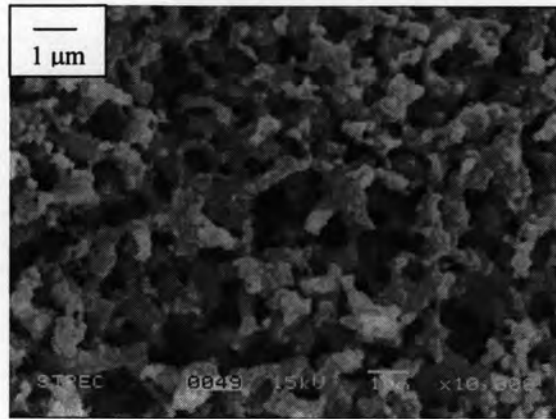


(b)

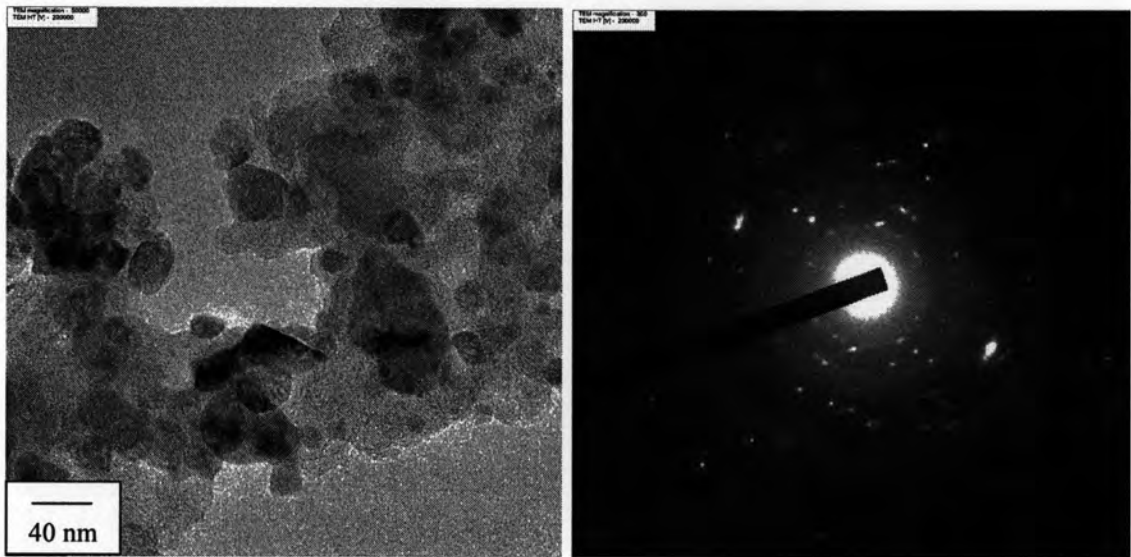


(c)

Figure 4.27 SEM and TEM micrographs of upper layer of the nitrated product, using titania/PVP/carbon black composite fibers as starting material: (a) SEM image, (b) TEM image and (c) SEAD pattern.



(a)



(b)

(c)

Figure 4.28 SEM and TEM micrographs of lower layer of the nitrated product, using titania/PVP/carbon black composite fibers as starting material: (a) SEM image, (b) TEM image and (c) SEAD pattern.

The calcined fibers were subsequently nitrided at 1400°C for 3 h. The final products can be easily categorized into two parts, similar to the product synthesized without carbon black as mentioned earlier. SEM images of the upper parts of the product in Figure 4.27(a) shows that it is not in the form of fiber. Similar to what has been discussed in the proceeding section, it is densely packed titania which are formed from particles sintering together. On the other hand, the lower portion of the product looks like network of joined fibers. The surface is rough and particulate.

The grain boundary of the product in the upper portion cannot be clearly seen from TEM image since the grains are heavily aggregated and sintered into very large particle (Figure 4.27(b)). On the contrary, for the lower part of the product, Figure 4.28(b) clearly shows that the structure observed in the TEM micrograph is in fact consisted of many nanoparticles. Size of these particles is less than 40 nm. SAED patterns in Figure 4.27(c) and 4.28(c) clearly illustrate the single crystalline nature of both parts of the product. Nevertheless, crystallinity of the upper product is much higher than the lower part.

XRD patterns of the samples obtained after each synthesis step are shown in Figure 4.29. The pattern of the as-spun fibers indicates that they are amorphous. After pyrolysis process, the crystalline peaks corresponding to anatase phase appear. Peaks for anatase become sharper, i.e. anatase crystallites grow bigger, as the fibers are calcined at 400°C for 5 min, to removed organic residue of PVP. Moreover, small peaks corresponding to rutile are also observed, since oxygen in calcination atmosphere assists rearrangement of titania structure, even when the temperature is not high. Finally, the XRD analysis reveals that the nitrided fibers are consisted of titanium nitride and the residual unreacted titania in rutile phase. The conversion of the final product can be calculated from XRD pattern of titanium nitride and it is found to be about 0.77. It should be noted that the XRD analysis was done on both upper and lower portions of the product combined, since amount of the synthesized sample was not large enough for separated analysis.

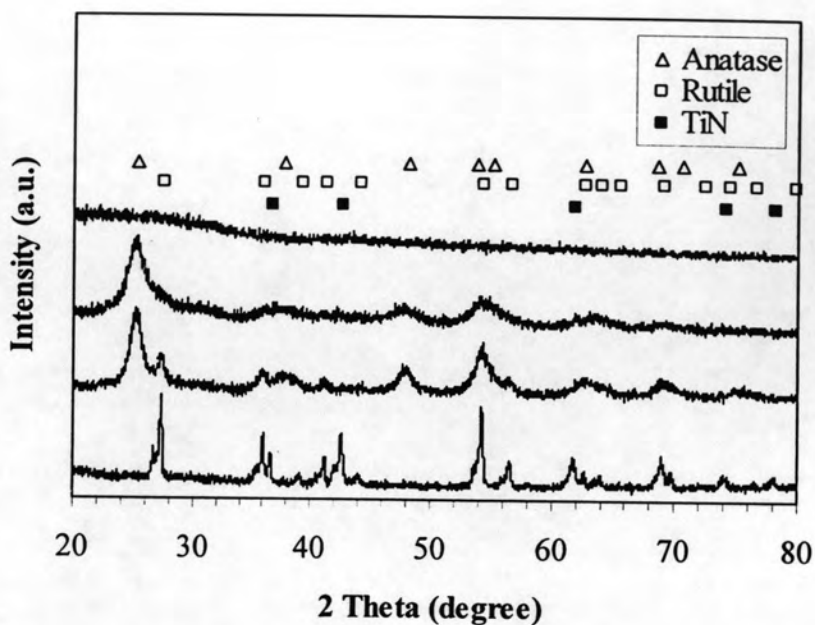


Figure 4.29 XRD patterns of titania/PVP/carbon black composite fibers: (a) as-spun fibers, (b) pyrolyzed fibers, (c) calcined fibers and (d) nitrified fibers.

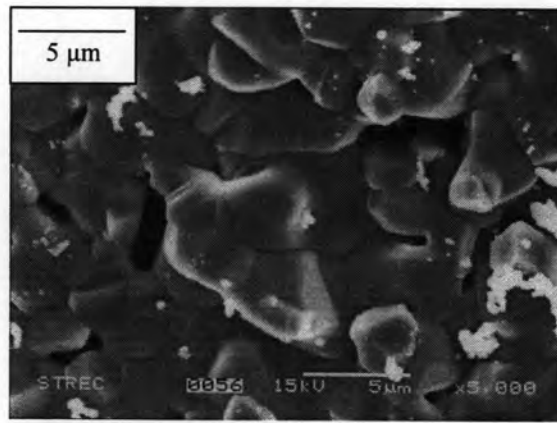
Although morphology of the product is altered when source of carbon is changed, changing carbon source does not affect the conversion of the reaction. There are many factors that influence the reaction such as reaction temperature and reaction time. The flow rate of nitrogen is another factor that is interesting and it is easy to practice. Such effect will be described in the following section.

4.5 The Effect of Nitrogen Flow Rate

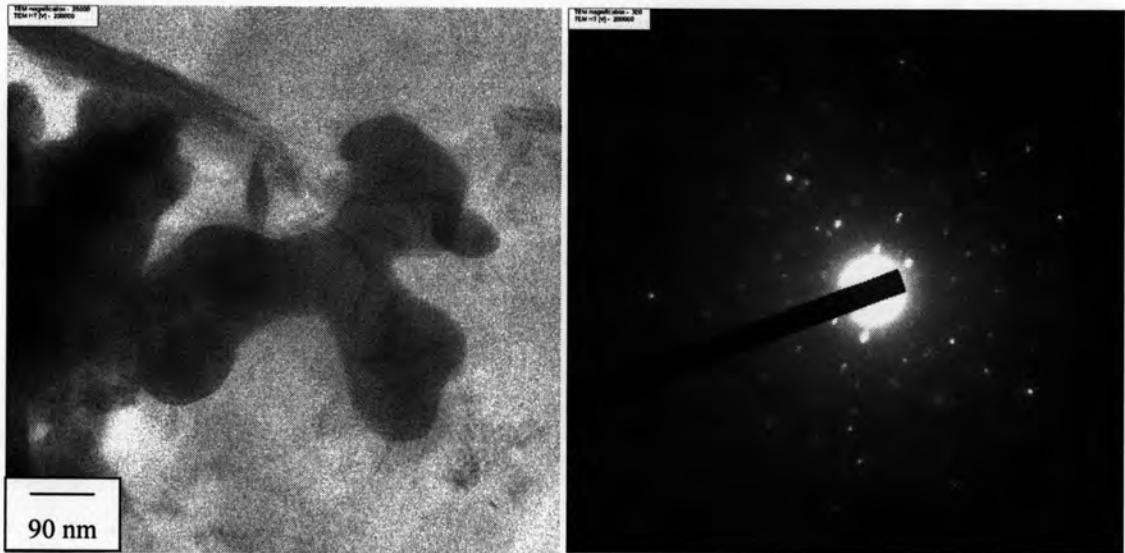
Although it has been proved that titanium nitride synthesis is possible, the conversion in early experiments is not satisfied. To increase the conversion of titanium nitride, effect of nitrogen flow rate is investigated. In this study, the titania/PVP/carbon black composite fibers, after pyrolyzed and calcined, were nitrated at 1400°C for 3 h with the nitrogen flow rate of 1.8 l/h, which is twice of that used in the previous studies.

Morphology of the product, on both upper and lower part, is very similar to that observed earlier, as shown in Figure 4.30 and 4.31. However, when the flow rate of nitrogen is increased, the upper portion of the product becomes thinner. The high flow rate immediately removes any gaseous intermediates product from the top layer of the stacking fibers. On the other hand, the lower product still looks like structure forming from the joining of the particulate fibers.

TEM images reveal that the grain size of the upper product is still much larger than that of the lower product. SAED pattern clearly suggests the single-crystalline nature of those grains. However, the crystallinity of these products are lower than those obtained from regular flow rate. Again, crystallinity of the upper part is higher than the lower part of the product.



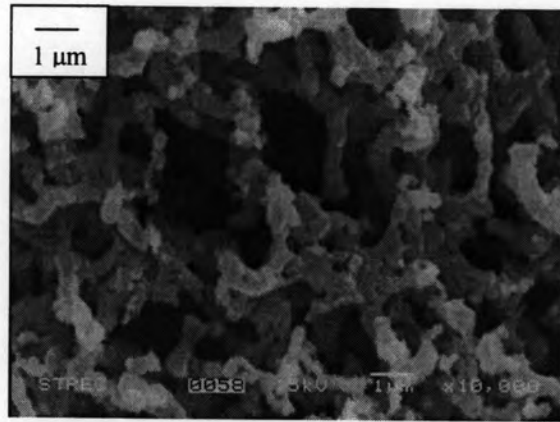
(a)



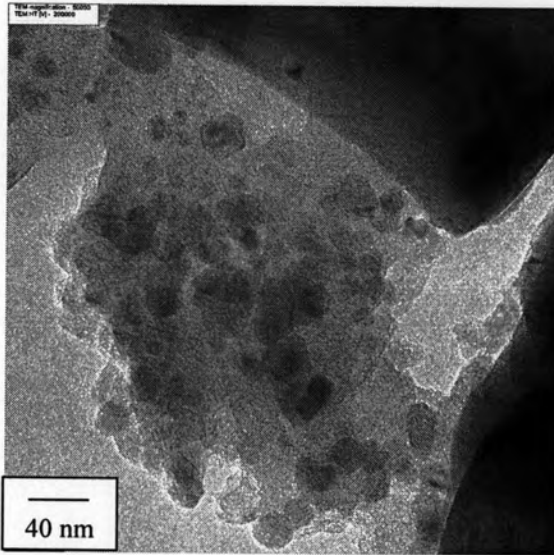
(b)

(c)

Figure 4.30 SEM and TEM micrographs of upper layer of the product nitrided at 1400°C for 3h with double nitrogen flow rate: (a) SEM image, (b) TEM image and (c) SEAD pattern.



(a)



(b)



(c)

Figure 4.31 SEM and TEM micrographs of lower layer of the product nitrided at 1400°C for 3h with double nitrogen flow rate: (a) SEM image, (b) TEM image and (c) SEAD pattern.

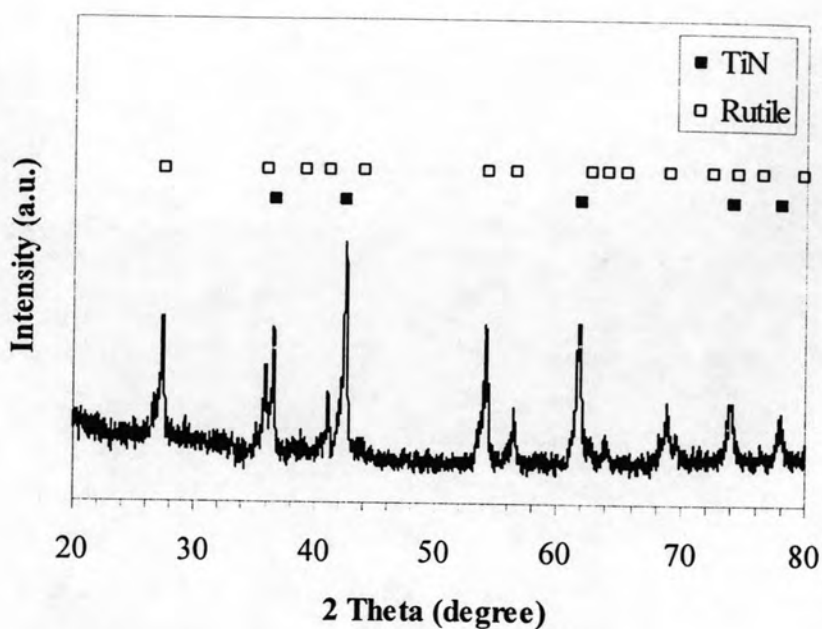
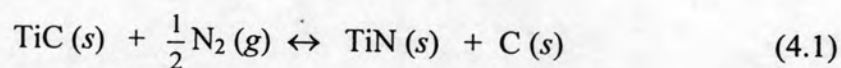


Figure 4.32 XRD patterns of fibers nitrified at 1400°C for 3 h, using double nitrogen flow rate.

XRD pattern of the nitrified fibers are shown in Figure 4.32. This graph shows that the final product is the mixture of titania in rutile phase and titanium nitride. The calculated conversion from the XRD pattern of the product is found to be 0.78. From this result, the conversion is only slightly higher than that in the previous experiment because higher amount of nitrogen is supplied to the reaction. Moreover, since titanium carbide is already formed in the sample before nitrogen is fed into the reactor (see section 4.2), formation of titanium nitride from titanium carbide is enhanced according to reaction (Yu and Lin 1998)



When the amount of nitrogen is increased, the reaction is shifted toward the formation of titanium nitride.