

FORMATION OF INORGANIC NANOFIBERS BY HEAT-TREATMENT OF POLY(VINYL ALCOHOL)-ZIRCONIUM COMPOUND HYBRID NANOFIBERS

K. Nakane^{a,*}, S. Matsuoka^a, S. Gao^a, S. Yonezawa^a, J.H. Kim^a, N. Ogata^a

^a *Department of Materials Science and Engineering, University of Fukui, Bunkyo, Fukui, Japan*

(Received 01 November 2012; accepted 19 June 2013)

Abstract

Poly(vinyl alcohol)-zirconium compound hybrid nanofibers (precursors) were formed by electrospinning employing water as a solvent for the spinning solution. The precursors were converted into oxide (ZrO₂), carbide (ZrC) or nitride (ZrN) nanofibers by heating them in air, Ar or N₂ atmospheres. Monoclinic ZrO₂ nanofibers with high-specific surface area were obtained by heat-treatment of the precursors in air. ZrC and ZrN nanofibers could be obtained below theoretical temperatures calculated from thermodynamics data.

Key words: *Electrospinning; Nanofiber; Poly(vinyl alcohol); Zirconium oxide; Zirconium carbide; Zirconium nitride*

1. Introduction

Technical progress in electrospinning (ES) has made it possible to form a wide variety of nanofibers [1-5], and many kinds of inorganic nanofibers have been obtained by heat-treatment of organic-inorganic hybrid precursor nanofibers formed by ES [4,6]. Almost all of the inorganic nanofibers obtained from the precursors are metal oxide nanofibers [7-10], but the reports of metal carbide or nitride nanofibers have increased gradually in recent years. Qiao et al. reported the formation of crystalline SiC nanofiber by the pyrolysis of polycarbomethylsilane-coated platelet carbon nanofiber as the precursor [11], and Hwang et al. formed boron nitride (BN) nanofiber by the thermal decomposition of poly(vinyl alcohol) (PVA)/BN nanoparticles composite precursor nanofiber at 1000°C for 5 h in Ar atmosphere [13].

Most transition metals of the fourth (Ti, Zr, Hf) and fifth (V, Nb, Ta) rows of the periodic table form metal carbides and nitrides with extremely high melting points (3000-4000°C), excellent high temperature strength, good corrosion and good hardness [12,13]. There are some reports about the formation of transition metal carbide and nitride nanofibers using ES. Park et al. reported the formation of ZrC nanofibers by the heat-treatment of the precursor nanofibers of zirconium acetyl acetonate/phenolic resins (or cellulose acetate) [14, 15]. The formation of ZrN nanofibers by the heat-treatment of the poly(vinyl pyrrolidone) (PVP)/zirconium oxychloride precursor nanofibers

have also been reported by Li et al. [16]. These precursors were formed by ES using (2,4-pentanedione) or ethanol/water mixture as solvents.

In a previous paper, we reported the formation of TiC and TiN nanofibers by the heat-treatment of PVA-Ti lactate (TL) hybrid precursor nanofibers [17]. The PVA-TL mixed aqueous solution was used as the spinning solution to form the precursor nanofibers. It is the convenient and safety technique to use water as a solvent of a spinning solution on ES. In this study, we formed PVA-zirconium compound hybrid nanofibers by ES using water as a solvent of the spinning solution and used the hybrid nanofibers as a new precursor to form ZrO₂, ZrC and ZrN nanofibers.

Shao et al. reported the formation of ZrO₂ nanofibers by the heat-treatment (800°C, 10 h) of PVA-zirconium oxychloride composite nanofibers prepared by using the sol-gel process and ES [18]. The nanofibers of tetragonal phase ZrO₂ with diameters of 50-200 nm were obtained by this method, but further detailed investigations, such as the effect of heating temperatures on the productivity of ZrO₂ nanofibers, were not described in this report. ZrO₂ nanofibers have also been formed by the heat-treatment of PVP-ZrO₂ precursor nanofibers [19-21], and these precursor nanofibers were formed using ethanol or ethanol/water mixture.

ZrC and ZrN nanofibers could be applied as a super-refractory filter and a constructional material for nuclear facilities as alternate materials for commercially available SiC microfibers.

* Corresponding author: nakane@matse.u-fukui.ac.jp

2. Experimental

2.1. Materials

PVA (degree of polymerization: 1500) was obtained from Wako Pure Chemicals Ind., Ltd., Japan. Water-soluble zirconium compound (ZC) was a kind gift from Matsumoto Fine Chemical Co., Ltd., Japan [ORGATIX® ZB-126, content: zirconyl chloride compound 15-25% (as pure ZrO_2 : ca.15%), aminocarboxylic acid, 5-15%, water: 65-75%].

2.2. Formation of PVA-ZC Hybrid Nanofibers (Precursors) by ES

PVA (10wt%) aqueous solution was prepared. ZC was added to the PVA solution to produce transparent PVA-ZC mixed solution (spinning solution).

The mixed solution was loaded into a plastic syringe (2 ml) equipped with a needle. The solution extrusion rate was 0.5 ml/h. A voltage of 18 kV was applied to the needle, and the PVA-ZC hybrid nanofibers were then deposited on a collector. The collector (copper plate) was grounded, and the distance between the tip of the needle and the collector was 10 cm. The PVA-ZC hybrid nanofibers obtained were used as a precursor to form inorganic nanofibers.

2.3. Formation of Inorganic Nanofibers by Heat-Treatment of Precursors

The PVA-ZC hybrid nanofibers were heated to a given temperature in an alumina tube furnace (Asahi Rika Seisakusyo Co., Ltd., AHRF-30KC-9P, Japan) at 500-1400°C for 5 hours in air, Ar or N_2 , and inorganic nanofibers were obtained. The flow rate of Ar and N_2 gas was 3.8 L/min.

2.4. Apparatus and Procedure

The structure of the nanofibers was observed with a scanning electron microscope (SEM) (Keyence VE-9800, Japan). Using a digitizer on the enlarged SEM images, the fiber diameter and its standard deviations at each nanofiber were estimated. X-ray diffraction (XRD) measurement was taken using $\text{CuK}\alpha$ with a Ni filter (40 kV, 30 mA) (Shimadzu XRD-6100, Japan). X-ray photoelectron (XP) spectra were measured using $\text{MgK}\alpha$ (10 kV, 10 mA) (JEOL JPS-9010MCY, Japan). Nitrogen adsorption isotherms (-196°C) of the nanofibers were measured with Micromeritics TriStar 3000, USA.

3. Results and Discussion

3.1. Formation of PVA-ZC Hybrid Nanofibers (Precursors) by ES

The viscosity of the transparent PVA/ZC [PVA/ ZrO_2 = 60/40 wt% (calculated content)]

spinning solution was 147 mPa·s at 23°C, and it had not changed after 2 weeks (143 mPa·s), indicating that the interaction between PVA and ZC is very weak. The viscosities decreased with increasing ZC (ZrO_2) content [pure PVA solution = 346 mPa·s, PVA/ ZrO_2 (80/20 wt%) solution = 278 mPa·s, PVA/ ZrO_2 (70/30 wt%) solution = 182 mPa·s, PVA/ ZrO_2 (50/50 wt%) solution = 127 mPa·s (23°C)]. The spinning solutions with greater than 130 mPa·s showed good productivity of nanofibers. Many beads (size: 1-2 μm) were observed in the nanofibers when the spinning solutions with greater than ZrO_2 60 wt% were used. Thus the PVA-ZC hybrid nanofibers (PVA/ ZrO_2 = 60/40 wt%) were selected as the precursor from which to obtain well-formed inorganic nanofibers.

Figure 1 shows SEM image of the PVA-ZC (PVA/ ZrO_2 = 60/40 wt%) hybrid nanofibers obtained by ES. The average fiber diameter and the specific surface area of the nanofibers are 279 nm (standard deviation, 93.3) and 1.06 m²/g. The value of the specific surface area means these nanofibers are nonporous materials.

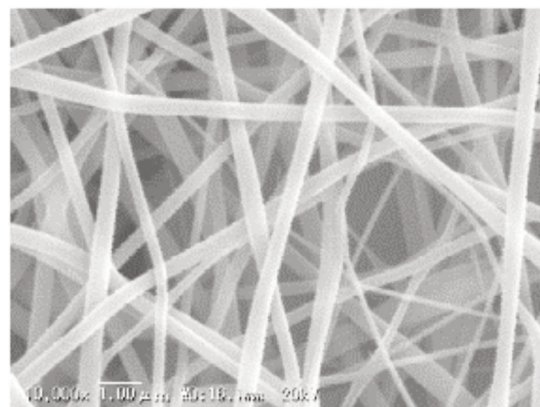


Figure 1. SEM image of PVA-ZC (PVA/ ZrO_2 = 60/40 wt%) hybrid nanofibers (precursors) obtained by ES.

3.2. Formation of Inorganic (ZrO_2) Nanofibers by Heat-Treatment of Precursors

White residues were obtained after heat-treatment of PVA-ZC hybrid nanofiber fabrics at 500-1100°C for 5 h in air. Figure 2 shows the XRD curves for the residues heated at various temperatures. Monoclinic ZrO_2 is formed at 500-600°C. Tetragonal ZrO_2 appears at 700°C (but it consists of monoclinic-tetragonal mixed crystals at this temperature). The peak intensity of the tetragonal crystal increases with heating temperature, and almost all the peaks of the monoclinic crystal disappear at 1000°C.

Figure 3 shows the SEM images of the residues after heat-treatment of the precursor nanofibers at

500°C, 800°C or 1000°C for 5 h in air. From these images and Fig. 2, we see that the ZrO_2 nanofibers are formed after the heat-treatment of the precursors. The specific surface area and the pore volume of the ZrO_2 nanofibers heated at 500°C were 36.3 m^2/g and 0.0647 cm^3/g , respectively, showing that highly porous ZrO_2 nanofibers were obtained due to the thermal decomposition of PVA. Therefore, the porosity of the nanofibers decreased with increasing heating temperature due to the sintering. The specific surface area and the pore volume of the ZrO_2 nanofibers heated at 800°C were 6.98 m^2/g and 0.0102 cm^3/g , respectively, and it is likely that the nanofibers became nonporous material. Figure 4 shows the effect of heating temperature on the average fiber diameter of the ZrO_2 nanofibers. The fiber diameters are distributed from 150 to 200 nm. The diameters of the ZrO_2 nanofibers are smaller than that of the precursor nanofiber (279 nm), because of the shrinkage of the fibers due to the thermal decomposition of PVA.

3.3. Formation of Inorganic (ZrC and ZrN) Nanofibers by Heat-Treatment of Precursors

The precursor nanofibers were heated at 1000–1300°C in Ar gas flow for 5 h or at 1000–1400°C in N_2 gas flow for 5 h. Figures 5 (a) and (b) show the SEM images after the heat-treatment at 1200°C in Ar and at 1300°C in N_2 , respectively. The nanofibers were retained after each heating condition. Figure 6 shows the effect of heating temperature on the average fiber diameter of each resultant nanofiber. The diameters of the resultant

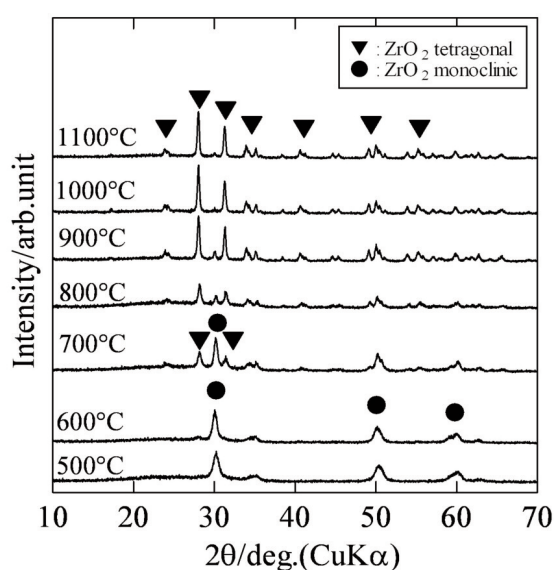


Figure 2. XRD curves of residues obtained after heat-treatment of PVA-ZC hybrid nanofibers at various temperatures for 5 h in air.

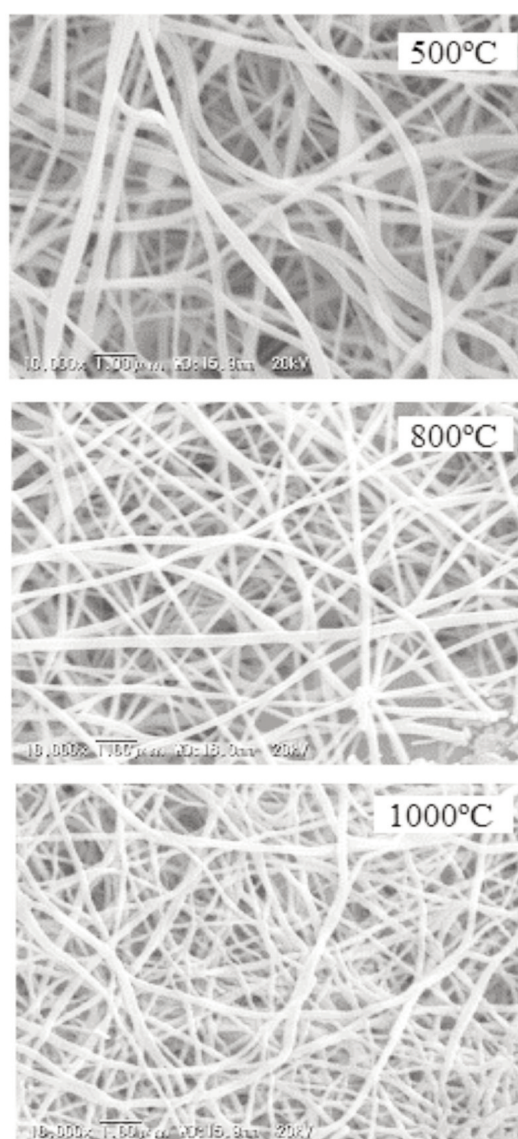


Figure 3. SEM images of residues obtained after heat-treatment of PVA-ZC hybrid nanofibers at 500, 800 or 1000°C for 5 h in air.

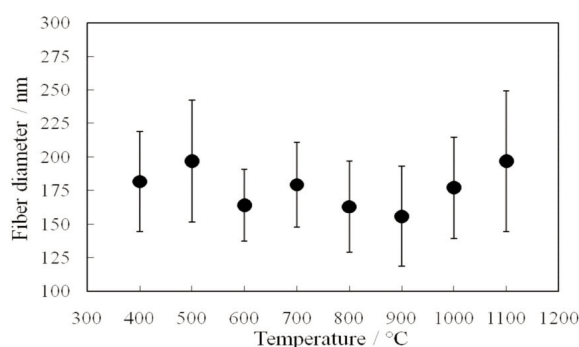


Figure 4. Effect of heating temperature of the precursors on the average fiber diameter of the ZrO_2 nanofibers.

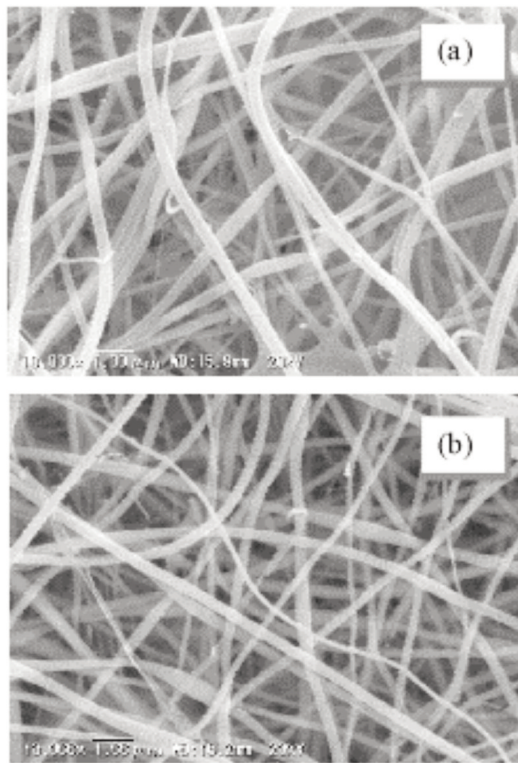


Figure 5. SEM images of residues after heat-treatment (a) at 1200°C in Ar or (b) at 1300°C in N₂.

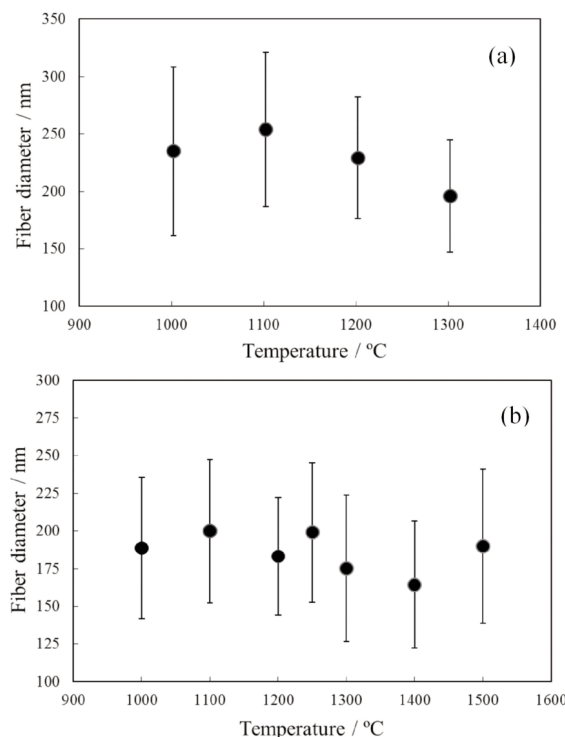


Figure 6. Effect of heating temperature of the precursors in Ar or N₂ for 5 h on the average fiber diameter of inorganic nanofibers.

nanofibers are less than or equal to that of the precursor nanofibers (279 nm). No difference was observed in the diameters between the heating in Ar and in N₂.

Figures 7 and 8 show the XRD curves of the residues after the heat-treatment in Ar and N₂ gas flow, respectively. In Fig. 7, ZrO₂ is formed by heat-treatment of precursors up to 1100°C, and the peaks of ZrC are observed at 1200°C. Oxygen and carbon would be supplied from thermal decomposition of PVA and ZC. A similar tendency can be observed in Fig. 8. XRD peaks of ZrN are observed at 1250°C. The peaks of ZrO₂ disappeared at this temperature. The average lattice constants of the residues obtained after the heat-treatment at 1300°C in Ar and at 1300°C in N₂ were 0.4684 nm and 0.4593 nm, respectively. The theoretical lattice constants of ZrC and ZrN are 0.4698 and 0.4585 nm, respectively [22, 23]. The experimental values are close to the theoretical ones. Thus we confirmed that ZrC and ZrN nanofibers were obtained by our methods.

Figure 9 shows the XP spectra of N 1s orbital for the samples heated under N₂ gas flow (1300°C, 5 and 10 h) or in air (800°C, 5 h). The peak is observed for the samples heated under N₂ gas flow. This means that a nitrogen atom was introduced on the nanofibers. The results shown in Fig. 9 confirm that the nitride (ZrN) was formed by the heat-treatment of the precursors in N₂ gas flow. To form metal nitride, the heat-treatment of precursors using N₂ gas has advantages such as high safety for handling, simplified equipment and low running cost compared to the conventional method using NH₃ gas.

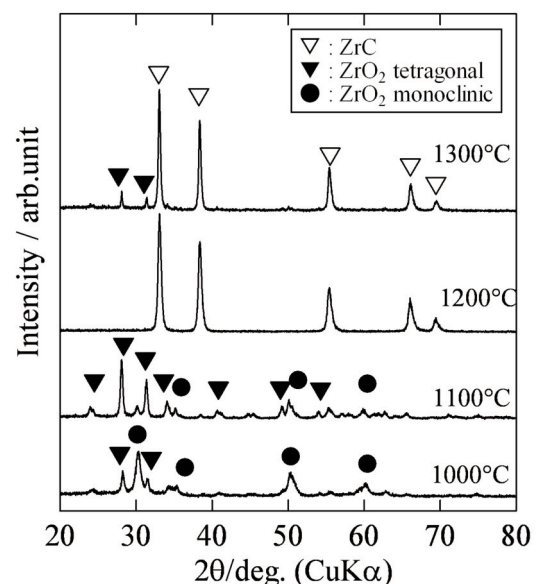


Figure 7. XRD curves of inorganic nanofibers after the heat-treatment at various temperatures for 5 h in Ar.

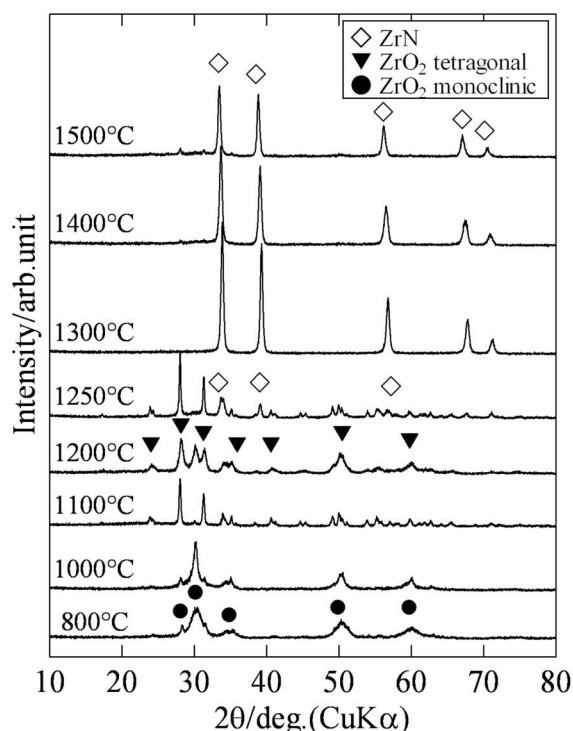


Figure 8. XRD curves of inorganic nanofibers after the heat-treatment at various temperatures for 5 h in

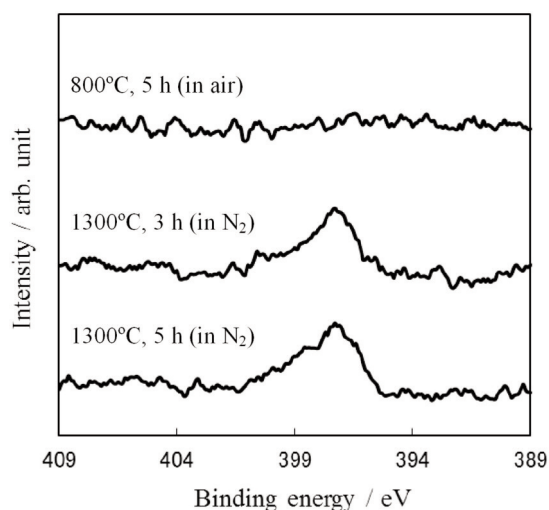


Figure 9. XP spectra of N 1s orbital for residues heated in N_2 (1300°C, 5 and 10 h) or in air (800°C, 5h).

The carbonization and the nitridation will typically proceed as follows [13, 24]:



The Gibbs free energy change, ΔG° , for the

reaction was given using the available thermodynamic data [25]. If the $\Delta G^\circ < 0$, the reaction will proceed. The initial carbonization (ZrC) and nitridation (ZrN) temperatures calculated from thermodynamics data are 1656°C and 1626°C, respectively. These temperatures are higher than observed temperatures, 1200°C and 1250°C (as shown in Figs. 7 and 8), indicating that the precursor nanofiber is a molecular-scale mixture of metal and carbon sources, and thus the reaction formulae (1) and (2) would proceed effectively, or another reaction route might be created.

4. Conclusions

PVA-ZC hybrid precursor nanofibers were formed by ES using PVA-ZC aqueous solution as a spinning solution. Monoclinic and tetragonal ZrO_2 nanofibers were easily obtained by heat-treatment of the precursors in air. The monoclinic ZrO_2 nanofibers obtained were highly porous materials. ZrC and ZrN nanofibers could be formed at low temperatures by heating the precursors under Ar and N_2 gas flow, respectively. Highly pure and highly crystalline inorganic nanofibers will be formed by optimizing the heating conditions of the precursors in the next step.

References

- [1] J. Doshi, D. H. Reneker, J. Electrostatics, 35 (1995) 151-160.
- [2] C. J. Buchko, L. C. Chen, Y. Shen, D. C. Martin, Polymer, 40 (1999) 7397-7407.
- [3] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, Comp. Sci. Tech., 63 (2003) 2223-2253.
- [4] S. Ramakrishna, K. Fujihara, W. E. Teo, T. C. Lim, Z. Ma, An Introduction to Electrospinning and Nanofibers, World Scientific Publishing Co. Pte. Ltd., Singapore, 2005, p.22-62.
- [5] A. Kumar, (Ed.), Nanofibres, Intech, Vukovar, Croatia, 2010, p.121-138, 179-188, 213-226.
- [6] I. S. Chronakis, J. Mater. Proc. Tech., 167 (2005) 283-293.
- [7] D. Li, Y. Xia, Nano Lett., 3 (2003) 555-560.
- [8] H. Guan, C. Shao, Y. Liu, N. Yu, X. Yang, Solid State Commun., 131 (2004) 107-109.
- [9] M. Krissanasraanee, T. Vongsetskul, R. Rangkupan, P. Supaphol, S. Wongkasemjit, J. Am. Ceram. Soc., 91 (2008) 2830-2835.
- [10] K. Nakane, M. Seto, S. Irie, T. Ogihara, N. Ogata, J. Appl. Polym. Sci., 121 (2011) 1774-1779.
- [11] W. M. Qiao, S. Y. Lim, S. H. Yoon, I. Mochida, L. C. Ling, J. H. Yang, Appl. Surf. Sci., 253 (2007) 4467-4471.
- [12] H. O. Pierson, Handbook of Refractory Carbides and Nitrides, Noyes Publications, New Jersey, 1996, p.55-98, 181-207.
- [13] S. T. Oyama, (Ed.), The Chemistry of Transition Metal Carbides and Nitrides, Blackie Academic & Professional, London, 1996, p.1-31.

- [14] X. M. Cui, Y. S. Nam, J. Y. Lee, W. H. Park, *Mater. Lett.*, 62 (2008) 1961-1964.
- [15] Y. S. Nam, X. M. Cui, L. Jeong, J. Y. Lee, W. H. Park, *Thin Solid Films*, 517 (2009) 6531-6538.
- [16] J.Y. Li, Y. Sun, Y. Tan, F.M. Xu, X.L. Shi, N. Ren, *Chem Eng J*, 144 (2008) 149-152.
- [17] K. Nakane, K. Nakanishi, J.-H. Kim, S. Yonezawa, T. Ogihara, N. Ogata, *Sen'i Gakkaishi*, 67 (2011) 261-265.
- [18] C. Shao, H. Guan, Y. Liu, J. Gong, N. Yu, X. Yang, *J. Cryst. Growth*, 267 (2004) 380-384.
- [19] N. Jing, M. Wang, J. Kameoka, *J. Photopolym. Sci. Technol.*, 18 (2005) 503-506.
- [20] M. Panapoy, B.Ksapabutr, *Adv. Mater. Res.*, 55-57 (2008) 605-608.
- [21] L. Li, P. Zhang, J. Liang, S. M. Guo, *Ceram. Int.*, 36 (2010) 589-594.
- [22] A. N. Christensen, *Acta Chem. Scand.*, 44 (1990) 851-852.
- [23] A. N. Christensen, *Acta Chem. Scand.*, A 29 (1975) 563-568.
- [24] Y. Kurokawa, S. Kobayashi, M. Suzuki, M. Shimazaki, M. Takahashi, *J. Mater. Res.*, 13 (1998) 760-765.
- [25] I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim, Germany, 1993, p.210, 271, 935, 1714, 1732, 1734.