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# Tungsten Carbide-Silicon Carbide Nanocomposite Fibers Prepared from Tungsten Nanoparticle Dispersed Polycarbosilane by Electrospinning

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W<sub>2</sub>C–SiC nanocomposite fibers were fabricated by electrospinning and pyrolysis using tungsten nanoparticle (nW; diameter, 3-5 nm) dispersed polycarbosilane solution. The nW was uniformly dispersed in the electrospun polycarbosilane fibers and transformed into  $\alpha$ -W<sub>2</sub>C during pyrolysis at 1200 °C, where the polycarbosilane-derived SiC fibers acted as a source of carbon and as an effective support for the  $\alpha$ -W<sub>2</sub>C nanoparticles, preventing them from converting into another phase at 1200 °C. A part of the nW dispersed on the fiber surface is considered to transform into  $\alpha$ -W<sub>2</sub>C at the early stages of pyrolysis by carburization with the gases evolved during the pyrolytic decomposition of poly carbosilane, such as CH<sub>4</sub>.

Key words: Tungsten carbide (W<sub>2</sub>C), Catalyst, Tungsten nanopowder (nW), Electrospinning, Polycarbosilane, SiC fiber, Catalytic support materials (CSMs).

# Introduction

Group IV and VI metal carbides have catalytic properties similar to those of noble metals such as platinum and have been studied for their physicochemical properties [1-3]. Among them, tungsten carbides are considered promising materials for catalytic anodes in portable devices or fuel cells because of their high chemical inertness, oxidation resistance, and low price compared with noble metal catalysts [3-6]. Especially, the catalytic activity of nano-sized W<sub>2</sub>C is better than WC [7], furthermore, when W<sub>2</sub>C was combined with platinum, it showed an excellent catalytic activity compared to a commercial Pt-Ru catalyst and it would be interesting to explore the application of nano-sized tungsten carbide as a catalyst [3, 8].

Catalyst-support materials (CSMs) are required to have several properties: (1) high thermal stability; (2) high oxidation resistance, especially at high temperature; (3) high chemical inertness; and (4) high surface area, in the range 20-200 m<sup>2</sup>/g [9]. Fine SiC fibers would make a very useful catalytic supports owing that it can have large specific surface areas and have very high temperature oxidation resistances [9, 10, 13-15].

Electrospinning is a very simple and effective process

for producing web type ceramic fibers with diameters from several nanometers to several micrometers [16, 17]. Recently, various ceramic nanofibers have been prepared by electrospinning [14-17]. We have reported on the preparation of a SiC fiber (more exactly, carbon-rich silicon oxycarbide fiber) with a diameter of 1-3  $\mu$ m and specific surface area of about 100-300 m<sup>2</sup>/g by electrospinning a polymer precursor and some other studies also reported [18]. Such a fiber could well satisfy the abovementioned requirements of a CSM for SiC.

We have extended the electrospinning process to the production of composite fibers with special functional properties, made from SiC and other useful elements, especially transition and noble metals such as iron, nickel, tungsten, platinum, and palladium. These metalceramic fiber nanocomposites are expected to have potential applications as high-temperature catalysts or catalytic filters and in various types of gas membranes or sensors [3-5, 19, 20]. Another interesting point is that these metals (except the noble metals) can be easily transformed into compounds under suitable environmental conditions. Tungsten, for example, usually forms compounds such as tungsten carbides under carbon-rich environments above the specific temperature. And tungsten nanoparticle (nW) having several nanometers, in particular, can be easily melted at a relatively low temperature below 1,000 °C and transformed into tungsten carbide [21, 23], and are therefore considered a good starting material for the production of a W<sub>2</sub>C-

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SiC nanocomposite fibers.

In this study, we fabricated the  $W_2$ C-SiC nanocomposite fibers in which tungsten nanoparticles (nW) were uniformly dispersed and transformed into  $W_2$ C in the SiOC matrix and investigated thermal behavior during pyrolysis.

# **Experimental Procedure**

Polycarbosilane (PCS) was used as the polymer precursor for the preparation of the SiC fibers. PCS was synthesized from the Kumada rearrangement of polydimethylsilane (PDMS) under normal pressure in the presence of zeolite catalyst [23]. The weight-average molecular weight ( $M_w$ ) of PCS after additional polymerization was 3640 and the ceramic yield was 49 wt%. The nW having diameter under 10 nm was synthesized by a simple process comprising the thermal decomposition of W(CO)<sub>6</sub> vapor [21]. The W(CO)<sub>6</sub> was decomposed and transformed into nW in the resistive heating vessel at a filament voltage of 20-25VAC.

A mixture of nW and a PCS solution (nW-PCS) was prepared by the following simple method: nW (1-5 wt%) was dispersed in a 30% *N*,*N*-dimethylformamide (DMF)/70% toluene co-solvent by mechanical stirring. PCS was dissolved in the co-solvent at concentrations between 1.1 and 1.3 g/ml and stirred for 24 hrs at room temperature to afford a uniform solution.

The electrospinning system is described elsewhere [16-18] and basically comprised three parts: a spinning part, collecting part, and power supply. The nW-PCS solution was loaded into a 5 ml-capacity syringe and subjected to electrospinning using a metallic needle (diameter, 0.5 mm) at a rate of 0.5 mm/hr under an applied voltage in the range 15-20 kV. Samples with a dimension of  $50 \times 50$  mm<sup>2</sup> were taken from the electrospun fibers and subjected to the thermal curing at 200 °C for 1 hr in a muffle furnace and then sintered at a temperature between 1200 and 1400 °C for 1 hr under a

Table 1. Summary of the materials and samples in the experiments.

mark	Description	preparation method
PCS	polycarbosilane	Kumada rearrangement of PDMS using zeolite catalyst
nW	tungsten nanopowder	thermal decomposition
ESP	electrospun web	electrospinning
ESP-nW	tungsten nanopowder contained electrospun web	electrospinning
ESP-C	ESP cured at 200 °C	thermal oxidation
ESP-C- nW	ESP-nW cured at 200 °C	thermal oxidation
ESP-P- nW	ESP-nW-C pyrolyzed at the target temperature (1200, 1400 °C)	pyrolysis

flowing argon atmosphere in a graphite furnace. Samples were summarized in Table 1.

A thermogravimetric analyzer (TGA; TGA/SDTA 851, Mettler Toledo, USA) was used to analyze the pyrolysis behavior of the electrospun nW particle polycarbosilane precursor fibers. A sample (10 mg) of the cured fibers was roughly chopped and loaded into an alumina crucible and slowly heated (5 °C/min) to 1200 °C in a furnace under an argon atmosphere. During the heating process, the weight change was continuously monitored. The microstructure and morphology of the asspun and pyrolyzed nanocomposite fibers were observed using a field-emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL, Japan) operating at 15 kV. Samples were placed horizontally and against the holder, carefully fixed using carbon tape, and then dried at 50 °C in a vacuum oven for 1 day. Then, after applying a platinum coating, the holder was loaded into the FE-SEM and observed at several magnifications. The structural changes under different pyrolysis conditions were characterized by X-ray diffraction (XRD; FR-150, Enraf-Nonius Co, Netherlands). The nanostructure was studied using a high-resolution transmission electron microscope (HR-TEM; JEM-4010, JEOL, Japan). Samples were ground into fine powder using an alumina crucible and then dispersed into alcohol (high purity grade) by ultrasonic treatment for 10 min. The sample floating in the alcohol was dropped onto a carboncoated copper grid and dried for 1 hr in the oven.

### **Results and Discussion**

Thermal analysis was conducted to determine the behavior of the electrospun fiber during pyrolysis. Fig. 1 showed the thermo-gravimetry analysis (TGA) results of (a) ESP, (b) ESP-nW, (c) ESP-C and (d) ESP-nW-C. The weight of ESP was declined to approximately 61% at the temperature between 400 and 700 °C, and there were three major reductions at around 400, 530, and 650 °C due to



**Fig. 1.** Comparison of TGA curves of (a) ESP-nW, (c) ESP-C and (d) ESP-C-nW where sample (b) contained 5 wt% tungsten nanoparticle.



Fig. 2. DTA curves for (a) tungsten nanoparticle (nW) and (b) ESP-C-nW having 5 wt% of tungsten nanoparticle.

the decomposition of PCS into CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub> and other gases [18, 24, 255]. A similar behavior was observed in ESP-nW except for some weight loss in the initial stage that might be caused by the evaporation of the solvent that remained after electrospinning. In contrast, there was the only one weight loss at above 600 °C in the ESP-C shown as Fig. 1(c) and showed a high ceramic yield above 90% at 1000 °C. This is closely related to the H<sub>2</sub> or O<sub>2</sub> evolution instead of the CH<sub>4</sub> by the cross-link among polymer chains at the thermal curing step which oxygen act as cross-linker [24, 25]. In case of ESP-C-nW in Fig. 1(d), the weight slightly increased at over 700 °C. The reason why the weight of ESP-C-nW increased during pyrolysis is not clear but can be assumed that the oxygen introduced during curing step was attributed to have some reaction with nW.

Fig. 2 showed the differential thermal analysis (DTA) curves for (a) tungsten nanopowder (nW) and (b) ESP-C-nW. The sharp endothermic peak at around 900 °C in Fig. 2(a) corresponded to the melting point of nW [23]. However, this peak wasn't observed at ESP-C-nW but a new exothermic peak was evolved between 690 and 880 °C as shown in Fig. 2(b). This result makes it possible to be assumed that nW in the fiber had previously reacted with the oxygen introduced in the fiber during curing step because we have introduced only oxygen during the process and tungsten nanoparticle can be transformed to oxide form at low temperature around 700 °C [27].

The XRD data for the ESP-C-nW pyrolyzed at different temperatures from 600 to 1400 °C, respectively, are compared to that of tungsten nanopowder (nW) in Fig. 3. The diffraction peaks at 37.4 ° (111), 43.5 ° (200), 63.0 ° (220), and 75.5 ° (311) were assigned to nW (Fig. 3 (a)) [21]. No peaks were detected for ESP-C-nW pyrolyzed at 800 °C, except the broad peak at around 23 ° and the sharp peaks corresponding to nW. At 1000 °C, new peaks related to  $\alpha$ -W<sub>2</sub>C phase were appeared with the annihilation of the peaks for nW [2, 3, 27]. Major peak at 39.4 ° was assigned to  $\alpha$ -W<sub>2</sub>C (101) corresponding to JCPDS card number 02-1134. At



**Fig. 3.** XRD patterns of (a) nW, (b) ESP-C-nW having 5 wt% of tungsten nanoparticle, and ESP-P-nW pyrolyzed at (c) 600, (d) 800, (e) 1000, (f) 1200 and (g) 1400  $^{\circ}$ C.

1200 °C, the peak for (111) β-SiC was appeared at around 35 ° even if broad and weak in its intensity. The (100) plane of WC is also observed as a minor peak at 35.7 °. According to the W-C binary phase diagram, two tungsten carbide phases,  $\alpha$ -W<sub>2</sub>C and WC, are stable at 1200 °C and W<sub>2</sub>C is the major phase [22].

The broad peak appeared at around 23 ° is corresponded to  $\alpha$ -cristobalite [23]. However, tungsten oxides are also observed between 22 and 26 ° and it is difficult to distinguish the peaks exactly but possibly considered that tungsten oxides would be formed at this temperature range from these results.

SiC fiber derived from PCS usually contains a large amount of excess carbon and oxygen that is sufficient to react with nW. This suggests that when nW interacts with a Si-C-O amorphous matrix, it reacts with the excess carbon and oxygen as follow equations:

$2W + C = W_2C$ (major reaction) T > 1000 °C	(1)
$3W + 2C = W_2C + WC$ (minor reaction) $T > 1000 \text{ °C}$	(2)
$2W + 3O_2 = 2WO_3T \sim 600 \ ^{\circ}C$	(3)
$4WO_3 + 14C = 2W_2C + 12CO(g) T > 1000$	(4)

A part of nW in the fiber surrounded by the amorphous Si-C-O matrix were considered to react with carbon to form  $\alpha$ -W<sub>2</sub>C before melting [22]. Rest of nW were considered to be oxidized to WO<sub>3</sub> at around 800 °C due to residual oxygen and decomposed to W<sub>2</sub>C again at the temperature up to 1000 °C by the equation (3) and (4) [28]. Actually, nW begin to be oxidized at around 600 °C under free oxidation atmosphere, but residual oxygen in the fiber are not free due to cross-link and can be the cause of delayed oxidation.

In Fig. 3(g), the intensity of the peak assigned to  $\alpha$ -W<sub>2</sub>C slightly decreased with increasing pyrolysis temperature

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**Fig. 4.** FE-SEM images of ESP-P-nW web pyrolyzed at (a) 1200 and (b) 1400 °C, and (c, d) their single fibers.

because  $\alpha$ -W<sub>2</sub>C is highly metastable and easily decomposed at higher temperature [22]. A new peak appeared at 42.5 ° was assigned to W<sub>5</sub>Si<sub>3</sub> (411) [30, 31]. ESP-C-nW pyrolyzed at 1400 °C showed strong peaks for  $\beta$ -SiC at around 35.7 ° (111), 60 ° (220) and 71.8 ° (311)

The weak and broad shoulder at around 35.7 ° was observed in the ESP-C-nW pyrolyzed at 1200 °C and became stronger at 1400 °C, the diffraction peaks at around 35.7 ° (111), 60 ° (220), and 71.8 ° (311) were assigned to  $\beta$ -SiC. It was caused by the decomposition and crystal growth of the nanocrystalline  $\beta$ -SiC having amorphous characteristics among Si-C-O matrix [18]. The weak peak at 33.5 ° is attributed to the polymorphic  $\alpha$  phase produced due to extended line defects such as stacking faults [32, 33].

Figs 4(a) and 4(b) showed the overall images of the ESP-P-nW pyrolyzed at (a) 1200 and (b) 1400 °C. Fibers were uniformly distributed and have a broad range of diameters with an average about 2 µm after pyrolysis. In Figs. 4(c) and 4(d), FE-SEM images of the single fiber including the cross-section showed a porous surface and inside. In case of Fig. 4(c), pores were arranged in a fixed direction on the surface contrary to dense inside and it was accorded with a stretching direction of green fiber during electrospinning. This arrayed pore structure is come from the difference of evaporation rate of co-solvent [34]. For electrospinning of polycarbosilane, 30% N,N-dimethylformamide (DMF)/ 70% toluene co-solvent was used for effective spinning with the elimination of beads in the fiber web. At this time, each solvent have a different evaporation rate, and DMF which have lower evaporation rate remains in the fiber after electrospinning and can evaporate during drying or curing step [30].

Fig. 5 showed 200 kV TEM images of ESP-P-nW pyrolyzed at 1200 °C and 1400 °C. The nanoparticles with diameters of 3-5 nm were uniformly dispersed in the amorphous matrix and seemed to maintain their



**Fig. 5.** TEM images (200 kV) of a single fiber of ESP-P-nW pyrolyzed at (a) 1200 °C and (b) 1400 °C.



Fig. 6. High-resolution TEM images (400 kV) of (a)  $\alpha$ -W<sub>2</sub>C nanoparticle inside ESP-P-nW pyrolyzed at 1400 °C.

spherical shape and grain size at 1200 °C. However, these nanoparticles partially lost their shape and grew out of the matrix at 1400 °C. The selected-area electron diffraction pattern (SAED) in the inset to Fig. 5(a) showed ring patterns with discrete spots caused by the complex mixtures of polycrystalline phase. Polycrystalline ring patterns were assigned as the {101} and {110} plane of the  $\alpha$ -W<sub>2</sub>C phase with other spot of {101} of WC and {002} of C. The other extra circles observed around {101}  $\alpha$ -W<sub>2</sub>C was due to the double diffraction from the thick fiber. The SADE in Fig. 5 (b) shows an intense spot attributed to the {111} planes of  $\beta$ -SiC and a weak spot attributed to the {411} planes of W<sub>5</sub>Si<sub>3</sub>. Fig. 6 showed high-resolution bright-field TEM image

(400 kV) of the  $\alpha$ -W<sub>2</sub>C nanoparticles existed in the nanocomposite fiber pyrolyzed at 1400 °C. The d-space was calculated to be 0.23 nm.

#### Conclusions

W<sub>2</sub>C-SiC nanocomposite fibers were successfully fabricated by electrospinning and pyrolysis of a polycarbosilane solution mixed with tungsten nanoparticles. The tungsten nanoparticles were transformed into  $\alpha$ -W<sub>2</sub>C with a minor amount of WC during pyrolysis at 1200 °C and were uniformly dispersed over the whole of the fibers maintaining their size and shape. The Si-O-C matrix in the fiber acted as an excellent catalystsupport material for W<sub>2</sub>C because the rigid matrix suppressed the coarsening and phase transformation of W<sub>2</sub>C nanoparticle. This type of SiC composite fibers would be a possible alternative to noble metals as a catalytic material for fuel cell, electronic devices, and catalytic diesel particulate filters.

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