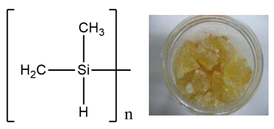
High-temperature Performance SiC-HfC Nanocomposite Fiber Derived from Modified Polycarbosilane

***Seong-Gun Bae[1†], Yoonjoo Lee[2], and Dong-Geun Shin[1†]**

[1]Aerospace & Convergence Materials Center, Korea Institute of Ceramic Engineering & Technology, Jinju 52851, Republic of Korea
[2]Semiconductor Materials Center, Korea Institute of Ceramic Engineering & Technology, Jinju 52851, Republic of Korea
† Corresponding author: sg0329@kicet.re.kr, dgshin73@kicet.re.kr

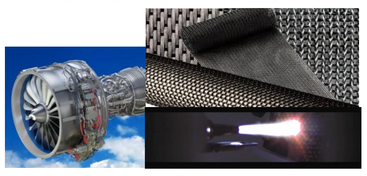
Introduction

✓Polycarbosilane



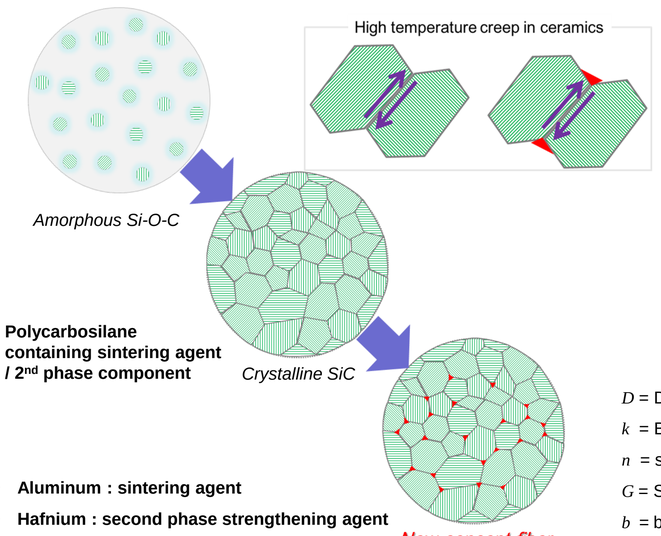
- Si-C backbone structure
- major intermolecular bonding : $Si\text{-}CH_3$, $Si\text{-}CH_2$, Si-C, Si-H
- *C/Si ratio : 2 (carbon excess structure)*

✓Silicon carbide fiber



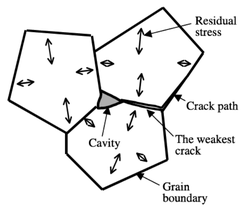
- Reinforcement of Ceramic matrix composites(CMCs)
- Excellent physical & chemical properties
- *Applications : aerospace, nuclear. military*

✓Microstructure of SiC-HfC Nanocomposite fiber



- Polycarbosilane containing sintering agent / 2nd phase component
- Aluminum : sintering agent
- Hafnium : second phase strengthening agent

✓Expected effect of hafnium carbide



Monolithic ceramics

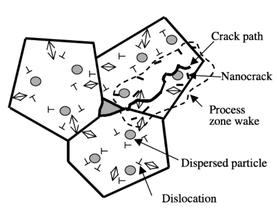
Normal creep mechanism

$$\dot{\varepsilon} = A' \frac{DGb}{kT}\left(\frac{\sigma}{G}\right)^n$$

D = Diffusion coefficient
k = Boltzmann's constant
n = stress exponent (fine ceramics, n=1)
G = Shear modulus
b = burgers vector

diffusion coefficient HfC < SiC

✓ *High temperature Creep strain ↓*



Ceramics dispersed Nano particles

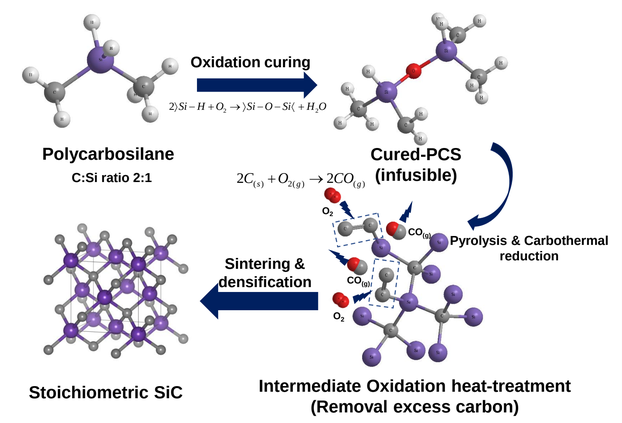
Zener-pinning effect

$$\frac{dD_\alpha}{dt} = K\left(\frac{3\gamma_\alpha}{D_\alpha} - \frac{9}{8}\cdot\gamma_\alpha\cdot\frac{D_\alpha}{P_\beta^2}\cdot\frac{f_\beta}{1-f_\beta}\right)$$

D_α = mean matrix grain size
γ_α = grain-boundary energy of the matrix phase
P_β = particle size of the second phase
f_β = volume fraction of the second phase particles
K = constant.

✓ *SiC grain coarsening control*

✓*Carbon control by intermediate oxidation*



✓**Intermediate oxidation heat-treatment**

→ ***Remove excess carbon directly reaction with oxygen***

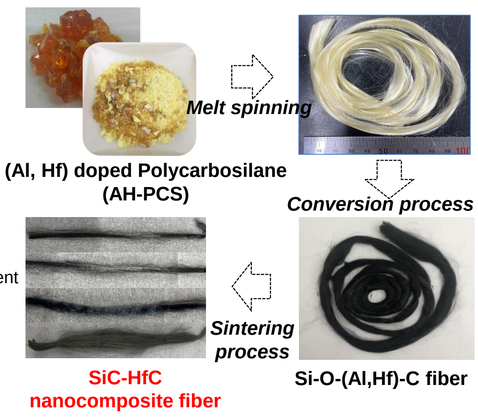
→ **Densification & Increasing the high-temperature properties**

Experiment / Results & Discussion

Experiment

✓*Fabrication process of SiC-HfC nanocomposite fibers*

Poly(Al,Hf)carbosilane
↓ Melt spinning
Poly(Al,Hf)carbosilane fiber
↓ Oxidation curing ~200 ℃ in Air
Cured AH-PCS fiber
↓ Pyrolysis ~1600 ℃ in Ar
Porous SiC-HfC nanocomposite fiber
↓ Oxidation heat treatment 700 ℃
Carbon controlled SiC-HfC fiber
↓ Sintering 1800 / 2000 ºC in Ar
Stoichiometric SiC-HfC fiber

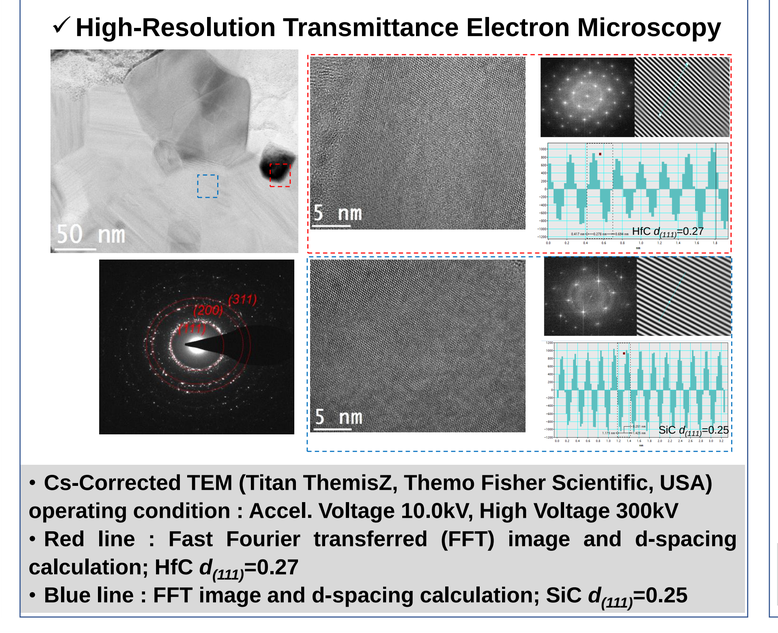


Sample	Oxidation curing	Pyrolysis condition	Intermediate oxidation	Sintering condition
SiC-HfC1	200 ºC / Air	-	-	1800 ℃/Ar
SiC-HfC2		1600 ℃/Ar	700 ℃ / Air	
SiC-HfC3				2000 ℃/Ar

- Near-stoichiometric SiC-HfC nanocomposite fibers were fabricated using Al-Hf modified polycarbosilane

Microstructure

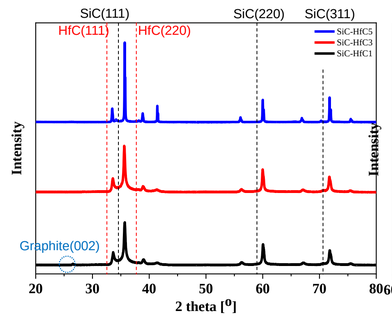
✓*Field Emission – Scanning Electron Microscopy*



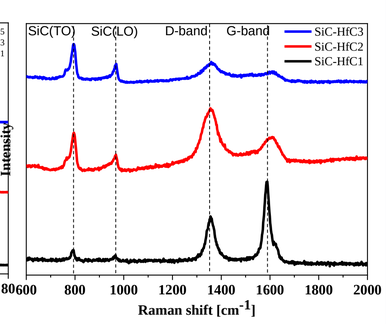
- FE-SEM (JEOL-JSM7610E, JEOL, Japan)
operating condition: accelerate Voltage 30kV, current charge 30uA / Secondary Electron Imaging (SEI), Back scattered electron imaging (BSE) mode

Phase & Carbon analysis

✓*X-ray Diffraction*



✓*Raman spectroscopy*

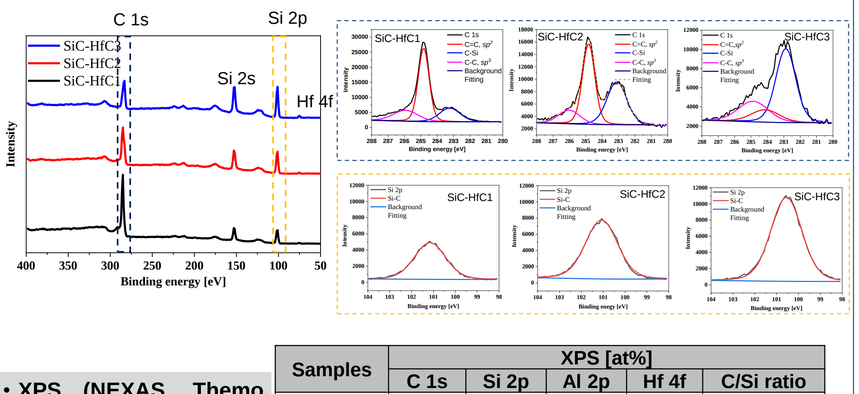


Samples	Phase analysis	Crystallite size, D (nm) SiC (111)	Crystallite size, D (nm) HfC (111)	I_D/I_G
SiC-HfC1	Carbon 3C-SiC HfC	21.4	18.2	0.63
SiC-HfC2	3C-SiC HfC	23.8	22.3	0.39
SiC-HfC3	3C-SiC HfC	93.2	48.8	1.28

- XRD (D8Advance, Bruker , USA)
operating condition : CuK_α, 0.02º step, 20~80º, 0.02º step, scan time 0.4s
- Raman Spectroscopy (LabRAM ARAMIS, Horiba Jobin Yvon, France) operating condition λ=532nm, 400~2000cm^{-1}

Surface elemental analysis

✓X-ray Photoelectron Spectroscopy



- XPS (NEXAS, Themo Fisher Scientific, USA) operating condition : 50.0eV, 5~30scan, 400μm spot size
- Peak distribution: Pseudo-Voigt function

Samples	XPS [at%]				
	C 1s	Si 2p	Al 2p	Hf 4f	C/Si ratio
SiC-HfC1	64.2	32.3	2.9	0.6	1.9
SiC-HfC2	51.0	44.0	4.0	0.9	1.2
SiC-HfC3	50.4	44.9	3.7	0.9	1.1

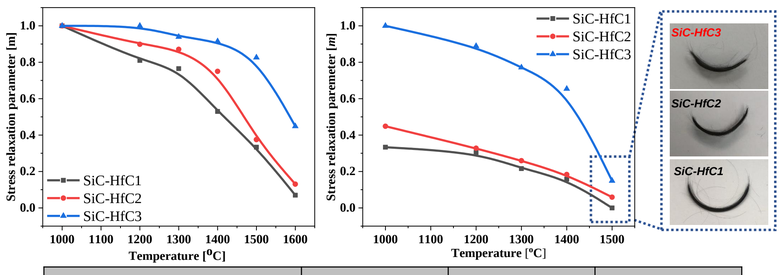
Crystal structure analysis

✓High-Resolution Transmittance Electron Microscopy

- Cs-Corrected TEM (Titan ThemisZ, Themo Fisher Scientific, USA) operating condition : Accel. Voltage 10.0kV, High Voltage 300kV
- Red line : Fast Fourier transferred (FFT) image and d-spacing calculation; HfC $d_{(111)}$=0.27
- Blue line : FFT image and d-spacing calculation; SiC $d_{(111)}$=0.25

Mechanical & Creep properties

✓ Bend Stress Relaxation test



Properties	SiC-HfC1	SiC-HfC2	SiC-HfC3
Tensile strength [GPa]	2.15 ± 0.22	2.34 ± 0.14	1.70 ± 0.10
Tensile modulus [GPa]	347.58 ± 30.03	344.49 ± 18.97	378.83 ± 25.92
Tensile strength after oxidation [GPa]	1.24 ± 0.27	1.45 ± 0.22	1.57 ± 0.17
Creep resistance in Ar[a] [ºC]	1200	1350	1500
Creep resistance in Air[a] [ºC]	< 1000	< 1000	1300

[a]Creep resistance : Stress relaxation parameter [m] <0.8

- Bend stress relaxation test
operating condition : graphite mold / Ar / 1hour each temperature, R_0=8mm

Conclusion

- ✓ The polycrystalline silicon carbide – hafnium carbide nanocomposite fibers were fabricated by polymer derived ceramics (PDCs) method using aluminum, hafnium acetylacetonate modified polycarboisilane
- ✓ During the intermediate oxidation heat-treatment, the excess carbon was eliminated via reaction with oxygen up to 3.2wt%
- ✓ As removing excess carbon, high crystallinity SiC-HfC nanocomposite fiber could be fabricated at the same sintering temperature of 1800℃
- ✓ Near-stoichiometric SiC-HfC nanocomposite fiber (C/Si ratio=1.1) which a lot of removing carbon shows the highest creep & oxidation resistance. however, The RT tensile strength exhibits the lowest as a result of coarsened silicon carbide grain structure.

Reference

[1] Dong-geun Shin, et al. *Key Eng Mater* 2005, 287, 91.
[2] Yoonjoo Lee, et al. *Compos Res.* 30.2.102, (2017)
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[4] Seong-Gun Bae, et al. *Ceramics International* 48.9 (2022): 13295-13303.
[5] Seong-Gun Bae et al. *J. European Ceram. SoC* (2023): 1385-1396