

Order Number 9423355

Processing silicon carbide fibers from organosilicon precursors

Zhang, Zhi-Fan, Ph.D.

The University of Michigan, 1994

U·M·I

300 N. Zeeb Rd.
Ann Arbor, MI 48106

Order Number 9423355

Processing silicon carbide fibers from organosilicon precursors

Zhang, Zhi-Fan, Ph.D.

The University of Michigan, 1994



U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

This is an authorized facsimile, made from the microfilm master copy of the original dissertation or master thesis published by UMI.

The bibliographic information for this thesis is contained in UMI's Dissertation Abstracts database, the only central source for accessing almost every doctoral dissertation accepted in North America since 1861.

UMI[®] Dissertation
Services

From:ProQuest
COMPANY

300 North Zeeb Road
P.O. Box 1346
Ann Arbor, Michigan 48106-1346 USA
800.521.0600 734.761.4700
web www.il.proquest.com

Printed in 2007 by digital xerographic process
on acid-free paper

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

**PROCESSING SILICON CARBIDE FIBERS FROM
ORGANOSILICON PRECURSORS**

by

Zhi-Fan Zhang

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Materials Science and Engineering)
in The University of Michigan
1994

Doctoral Committee:

Associate Professor Richard M. Laine, Chair
Professor John W. Halloran
Associate Professor John W. Holmes
Professor Tseng Y. Tien

© Zhi-Fan Zhang 1994
All Rights Reserved

In presenting this Ph.D. dissertation in partial fulfillment of the requirements for a Ph.D. degree at the University of Michigan, I agree that the Library shall make its copies freely available for inspection. I further agree that extensive copying of this dissertation is allowed only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Any other reproduction for any purposes or by any means shall not be allowed without my written permission.

Signature ZF. Zhang
Date April 5, 1994

***This dissertation is dedicated to
my parents,
Mr. Xin Zhang and Mrs. Hua-Ze Zhu,
and my sister,
Ms. Zhi-Wen Zhang***

ACKNOWLEDGMENTS

I wish to express sincere appreciation to Professor Richard M. Laine, my academic advisor and chair of supervisory committee, for his assistance and direction. I would also like to acknowledge the other members of my supervisory committee, Prof. John W. Halloran, Prof. Tseng. Y. Tien, and Prof. John W. Holmes for their suggestions and advice.

Special thanks must go to all the group members of Materials Chemistry Laboratory, especially Dr. Cathy Scotto for her valuable discussion and help. I would also like to thank Dr. Florence Babonneau for doing solid state NMR experiments.

The financial support was provided by U.S. Army Advanced Materials and Technology Laboratory through contract No. DOD-C-DAAL 04-91-C-0068 and Army Research Office through ASSERT Grant No. DAAH 04-93-G-0107.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
LIST OF SCHEMES	viii
LIST OF FIGURES	ix
CHAPTER	
1. INTRODUCTION	1
2. WORKING PRINCIPLES AND BACKGROUND	4
2.1. Methods used for processing ceramic fibers	4
2.2. Criteria for processing ceramic fibers via polymer precursor route	8
2.2.1. Preceramic polymer fiber processing	8
2.2.2. Pyrolysis processing	10
2.2.3. Parameter refinement processing	14
2.2.4. Summary	15
2.3. Commercial methods used to produce polymer-derived	
SiC based fiber	15
2.3.1. Nicalon TM fiber	15
2.3.2. Tyranno TM fiber	18
2.4. Other approaches to polymer-derived SiC fibers	19
2.4.1. Substituted PDMS-Polysilastyrene $[-(\text{Me}_2\text{Si})_x(\text{PhMeSi})_{1-x}]$	19
2.4.2. Catalytic redistribution of disilanes	20
2.4.3. Synthesis of precursors with high latent reactivity	
and controlled Si to C ratio	21
2.4.4. Low oxygen content SiC fibers	25
2.5. Summary	27
2.6. Research objectives	27

3. EXPERIMENTAL PROCEDURES	34
3.1. Synthesis	34
3.1.1. General synthesis procedures	34
3.1.2. Example of catalyst preparation	35
3.1.3. Preparation of methylsilane (MeSiH_3)	35
3.1.4. Synthesis of PMS from MeSiH_3	39
3.1.5. Increasing MW of PMS	40
3.1.6. Incorporation of vinyl chain extender into PMS	40
3.1.7. Boron modification of PMS	41
3.2. Spinning	42
3.2.1. Melting drawing	42
3.2.2. Dry-spinning (fiber extrusion)	43
3.3. Curing	44
3.3.1. Thermal curing	44
3.3.2. Ammonia curing	45
3.3.3. γ -irradiation curing	45
3.3.4. Chemical curing	45
3.4. Pyrolysis	46
3.5. Materials characterization	46
3.5.1. Nuclear magnetic resonance (NMR)	47
3.5.2. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)	47
3.5.3. Thermogravimetric analyses (TGA)	48
3.5.4. Differential thermal analyses (DTA)	48
3.5.5. Chemical analyses	48
3.5.6. Powder X-ray diffraction (XRD)	49
3.5.7. Scanning electron microscopy (SEM)	49
3.5.8. Density (ρ) measurements	50
3.6. Mechanical evaluation	50
4. RESULTS AND DISCUSSION	63
4.1. Synthesis	63
4.1.1. Synthesis of PMS	63
4.1.2. Incorporation of vinylsilane into PMS polymer	65
4.1.3. Incorporation of boron (B) containing compound into precursor system	67

4.1.4. Summary of synthetic processing	70
4.2. Spinning	70
4.2.1. Melt-drawing	71
4.2.2. Dry-spinning	71
4.2.3. Stabilization of PMS	72
4.2.4. Effect of TVS/BH ₃ -adduct on spinnability	73
4.2.5. Air-sensitivity in TVS-PMS precursor fibers	74
4.3. Curing and pyrolysis	74
4.3.1. Curing	74
4.3.2. Pyrolysis	81
4.4. Bulk materials characterization of unmodified PMS and TVS-PMS	83
4.4.1. Thermogravimetric analyses (TGA) of unmodified PMS and TVS-PMS	83
4.4.2. Differential thermal analyses (DTA) of unmodified PMS and TVS-PMS	85
4.4.3 ²⁹ Si nuclear magnetic resonance (NMR) of unmodified PMS	88
4.4.4. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) of unmodified PMS and TVS-PMS	90
4.4.5. Powder X-ray diffraction (XRD) of unmodified PMS and TVS-PMS	93
4.4.6. Chemical analyses of TVS-PMS derived SiC	96
4.5. Fiber materials characterization	
4.5.1. Thermogravimetric analyses (TGA) of TVS-PMS fibers	96
4.5.2. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) of TVS-PMS fibers	96
4.5.3. Scanning electron microscopy (SEM) of TVS-PMS/B-TVS-PMS derived SiC fibers	96
4.5.4. Density of B-TVS-PMS derived SiC fibers	97
4.5.5. Bending experiments	98

5. CONCLUSIONS	138
6. FUTURE EFFORTS	142
REFERENCES	144

LIST OF SCHEMES

Scheme

2.1.	Parameters for preceramic fiber processing	30
2.2.	Parameters for fiber pyrolysis processing	31
2.3.	Parameters for fiber properties optimization processing	32
2.4.	Processing steps used in Nicalon Process.	33
4.1.	Possible reactions occurring during the polymerization of MeSiH ₃	102
5.1.	University of Michigan SiC fiber processing chart	141

LIST OF FIGURES

Figures

3.1.	Schematic diagram of synthesis apparatus for synthesis of MeSiH_3 from MeSiCl_3	53
3.2.	Schematic diagram of synthesis apparatus for synthesis of MeSiH_3 from polymethylsilsesquioxane reaction	54
3.3	Schematic diagram of synthesis apparatus for polymerization reaction of MeSiH_3	55
3.4.	Schematic diagram of fiber spinning	56
3.5.	SEM micrograph of an as-spun PMS precursor fiber	57
3.6.	Schematic diagram for curing/pyrolysis	58
3.7.	Schematic diagram for mounting SEM samples	59
3.8.	Schematic representation of room temperature bend test	60
3.9.	SEM micrographs of typical fracture cross-sections of fibers broken via bending	61
3.10.	Schematic representation of fractured fiber	62
4.1.	Polymerization reaction pressure vs. reaction time at 55°C	104
4.2.	^1H NMR spectrum of PMS polymer	105
4.3.	Proposed molecular structure of PMS	106
4.4.	^1H NMR spectrum of PMS polymer with addition of 20 weight percent of TVS	107
4.5.	^{13}C NMR spectrum of PMS polymer with addition of 5 weight percent of TVS	108
4.6.	Plot of integration ratio of Si-H/Si-CH_3 and $=\text{CH}_2/\text{Si-CH}_3$ as a function of added TVS	109
4.7.	Proposed molecular structure of TVS-PMS	110
4.8.	DRIFT spectra of as-synthesized PMS with addition of 0, 5, 10, and 20 weight percent of TVS	111
4.9.	Proposed B-TVS-PMS molecular structure	112

4.10.	TGA of TVS-PMS (10 weight percent of TVS added) precursor fibers isothermed at 30°C in air for 24 h	113
4.11.	TVS-PMS precursor fibers (100 µm in diameter, 10 weight percent of TVS added) heated to 1000°C for 1 h in Ar	114
4.12.	TGA's of two batches of PMS with selected amounts of TVS added (Samples were heated at 10°C/min to 1000°C in Ar)	115
4.13.	DTA's of PMS with selected amounts of TVS added (Samples were heated at 10°C/min to 1000°C in Ar)	116
4.14.	²⁹ Si solid state NMR of unmodified PMS heated at 5°C/min to selected temperatures (≤ 1000°C) for 0.5 h in N ₂	117
4.15.	²⁹ Si solid state NMR of unmodified PMS heated at 5°C/min to 900°C for selected times, and to 1000° and 1100°C for 1 h in N ₂	118
4.16.	²⁹ Si solid state NMR of pure PMS heated at 5°C/min to selected temperatures (≥ 1000°C) for 0.5 h in N ₂	119
4.17.	DRIFT spectra of unmodified PMS heated at 5°C/min to selected temperatures (≤ 1000°C) for 1 h in Ar	120
4.18.	DRIFT spectra of unmodified PMS heated at 5°C/min to selected temperatures (≥ 1000°C) for 1 h in Ar	121
4.19.	DRIFT spectra of TVS-PMS (5 weight percent TVS added) heated at 5°C/min to selected temperatures for 1 h in Ar	122
4.20.	DRIFT spectra of TVS-PMS (10 weight percent TVS addition) heated at 5°C/min to selected temperatures for 1 h in Ar	123
4.21.	DRIFT spectra of TVS-PMS (20 weight percent TVS addition) heated at 5°C/min to selected temperatures for 1 h in Ar	124
4.22.	XRD of unmodified PMS heated to selected temperatures for 1 h in Ar	125
4.23.	XRD of TVS-PMS with selected amounts of TVS added, heated to selected temperatures for 1 h in Ar	126

4.24. Plots of grain size as a function of added TVS for PMS heated to selected temperatures	127
4.25. Plot of grain size as a function of pyrolysis temperatures for PMS with selected amounts of TVS addition	128
4.26. TGA of TVS-PMS precursor fibers (10 weight percent TVS added). Sample was heated at 10°C/min to 1000°C in Ar)	129
4.27. DRIFT spectra of TVS-PMS fibers (10 weight percent of TVS added) heated to selected temperatures for 1 h in Ar	130
4.28. SEM micrograph of a TVS-PMS fiber heated to 1000°C for 1 h in Ar	131
4.29. SEM micrograph of a TVS-PMS fiber heated to 1600°C for 1 h in Ar	132
4.30. SEM micrograph of a TVS-PMS fiber heated to 1800°C for 1 h in Ar	133
4.31. SEM micrograph of a B-TVS-PMS fiber (10 weight percent of TVS added) heated to 1800°C for 1 h in Ar	134
4.32. Density of B-TVS-PMS fibers (10 weight percent of TVS added) as a function of pyrolysis temperature	135
4.33. Room temperature bending strain (at fracture) of B-TVS-PMS fibers as a function of pyrolysis temperature	136
4.34. Room temperature strength of B-TVS-PMS fibers as a function of pyrolysis temperature	137

CHAPTER 1

INTRODUCTION

Continuous, high temperature stable ceramic fibers, when incorporated into ceramic matrices, provide composites with high temperature mechanical properties that are superior to the unreinforced matrix materials.¹⁻⁴ The first reinforcing fibers produced on a commercial basis in large quantities were silica-alumina glass fibers.³ Although these fibers provided superior polymer composite materials, their low elastic moduli (<100 GPa) made them unsuitable for reinforcement in ceramic matrices.¹⁻³ Furthermore, their tensile strength decreases from 3 to 4 GPa, at ambient temperature, to ≈ 1 GPa at 600°C ,² an additional disadvantage for use in ceramic matrices.

Carbon fibers, with elastic moduli of 200 to 500 GPa and tensile strengths of 1.5 to 3 GPa, were the second type of inorganic reinforcing fibers commercialized. However, except in special cases, their application temperatures are limited to $< 500^{\circ}\text{C}$ due to carbon's poor oxidation resistance.¹⁻³ The need for better high temperature structural materials has motivated materials scientists to develop alternative methods of producing ceramic based reinforcing fibers which exhibit high elastic moduli and tensile strengths at temperatures above 1200°C .

During the last 15 years, several varieties of these high temperature ceramic fibers have been developed.⁵⁻²⁸ Among these, SiC fibers, with their potential high temperature stability ($> 1500^{\circ}\text{C}$), high modulus (> 300 GPa) and high strength (> 3 GPa), have received a great deal of attention for applications in high temperature composite materials. Two commercial approaches have been developed to produce these SiC-based continuous fibers. One approach is the Textron (originally AVCO) chemical vapor deposition process