



***PREPARATION AND CHARACTERIZATION OF
POROUS ALUMINO-SILICATE BONDED SILICON
CARBIDE REFRACTORIES***

Thesis Submitted by

Noha Ahmed Ali Ajiba

(M. Sc. in Chemistry)

Assistant Researcher-National Research Centre

For Fulfillment of the Degree of Ph. D. Of Science
(Inorganic Chemistry)

Supervisors

Prof. Dr. Ebtissam A. Saad

Professor of Inorganic Chemistry,
Department of Chemistry, Faculty of
Science, Ain Shams University.

Prof. Dr. Samir B. Hanna

Professor of Chemistry and Technology of
Refractories, Department of Refractories,
ceramics and Building Materials, National
Research Centre.

Prof. Dr. Mohamed Awaad

Professor of Chemistry and Technology of ceramics,
Department of Refractories, ceramics and Building
Materials, National Research Centre

**Chemistry Department
Faculty of Science
Ain Shams University
Cairo, Egypt
2017**

Acknowledgement

Thanks to Allah for granting me the chance and ability to successfully complete this work,

*I would like to express my deep gratitude to **Prof. Dr. Ebtissam A. Saad**, Professor of Inorganic Chemistry, Department of Chemistry, Faculty of Science, Ain Shams University for her kind supervision, continuous encouragement, valuable advice, critical reading of the manuscript. The guidance and support especially during the latest phase of the present work,*

*I also want to express my sincere appreciation and gratitude to **Prof. Dr. Samir B. Hanna**, Professor of Chemistry and Technology of Refractories, Department of Refractories, Ceramics and Building Materials, National Research Centre, for kind supervision, valuable advice, and continuous guidance throughout the research. I am indebted to Dr. Samir for his helpful and invaluable criticism and lively discussions that guided me during the preparation of this thesis, which made it possible in its present work,*

*I wish also to thank **Prof. Dr. Mohamed Awaad Ahmed**, Professor of Chemistry and Technology of ceramics, Department of Refractories, Ceramics and Building Materials, National Research Centre, for sound supervision, kind help, valuable advice and critical reading of the manuscript.*

*Finally, I am particularly grateful to my father **Prof. Dr. Ahmed Ali Ajiba**, my mother **Dr. Hanan Barakat**, my husband **Dr. Asem Metwally**, my sisters, my brother, my daughter and son for encouraging and assisting me in all the stages of this work,*

CONTENTS

	<u>Page</u>
- List of figures	
- List of tables	
- Abstract	

CHAPTER I

- Introduction	1
- Silicon Carbide	1
- Oxidation of SiC	3
- Porous Silicon Carbide	5
- Processing strategies	6
- Replica method	8
- Sacrificial template method	14
- Direct foaming method	22
- Bonding technique	25
- Objectives of the present work	30

CHAPTER II

- Materials and Experimental Methods	32
- Main starting materials	32
- Particle size distribution of the used SiC grades	35
- Secondary starting materials:	36
- Thermal gravitation analysis of the used pore former agent	37
- Particle size distribution and surface area of the used pore former agents	40
- Test-specimens preparation	42
- Porous SiC specimens prepared by foaming method	44
- Porous SiC specimens prepared by sacrificial template method	46
- Testing methods of investigation	47
- X-ray Diffraction Analysis	47
- Thermal Gravitation Analysis	48

- Particle Size Distribution Analysis	48
- Measurement of Physical Properties	48
- Compressive Strength	49
- Scanning Electron Microscopy	49
- Oxidation Resistivity	49
- Pore Size, Pore Surface Area and Pore Volume	49
- Thermal Shock Resistivity	50

CHAPTER III

- <u>Part 1:</u> Porous SiC specimens prepared by foaming method	51
- The mechanism of used foaming method	51
- Physical properties	53
- Different factors affecting the physical properties of specimens	56
(a) Effect of CaC_2/Al ratio	57
(b) Effect of temperature	59
(c) Effect of water addition	62
(d) Effect of stabilizer addition	65
- Microstructure characteristics	69
(a) Effect of chemical composition	69
(b) Effect of firing temperature	72
(c) Effect of water addition	74
(d) Effect of stabilizer	76
- Mineral composition	78
(a) Effect of chemical composition	78
(b) Effect of firing temperature	80
- <u>Part 2:</u> Porous SiC specimens prepared by sacrificial template method	84
-Without using additive	84
(a) Physical properties	84
(b) Compressive Strength	87
(c) Oxidation resistivity	89
(d) Mineral composition	90
(e) Microstructure evolution	95

- Porous SiC specimens prepared using sacrificial template	100
- Effect of saw-dust addition	100
- Effect of preparation method	103
- Effect of type and content of starch	105
- Microstructure Characteristics	111
(a) Effect of saw-dust	111
(b) Effect of starch type	115
- Pore size distribution	118
- Oxidation Resistivity, Compressive strength and Thermal shock resistivity	121
- Sacrificial template specimens	121
- Foamed specimens	124
- Thermal Shock Resistivity	129
- General Consideration and Applications	132

CHAPTER IV

- Summary and Conclusions	136
- References	143
- Arabic Summary	

List of Figures

<u>Fig.No.</u>		<u>Page</u>
Fig. (1)	Schematic of processing methods	7
Fig. (2)	Typical microstructures of macroporous SiC ceramics produced via the replica technique	11
Fig. (3)	Typical microstructures of macroporous SiC ceramics produced via the sacrificial template technique	16
Fig. (4)	Schematic illustration of the preparation of porous ceramics with oriented cylindrical pores by the extrusion method	20
Fig. (5)	SEM micrographs of the cross-sections of porous ceramics prepared by extruding alumina with Nylon 66 fibers (30 vol%) as the pore former.	22
Fig. (6)	Typical microstructures of macroporous SiC ceramics produced via the direct foaming technique	24
Fig. (7)	Typical microstructures of macroporous SiC ceramics produced via the bonding technique	26
Fig. (8)	X-ray diffraction pattern of Klabsha kaolin, calcined alumina and silicon carbide	35
Fig.(9)	Particle size distribution of used fine SiC grade.	36
Fig.(10)	TG and DTG curves of saw-dust during heating up to 1000 °C	38
Fig.(11)	TG and DTG curves of corn starch during heating up to 1000 °C	39

List of Figures

Fig.(12)	TG and DTG curves of potato starch during heating up to 1000 °C.	40
Fig.(13)	The particle size distribution of used pore formers.	41
Fig.(14)	A schematic sketch of homemade extruder.	47
Fig.(15)	Flow-chart of the mechanism of the reaction.	51
Fig.(16)	Relationship between physical properties of SiC specimens fired at 1450°C and their SiC content	55
Fig(17)	Effect of CaC_2/Al mass ratio on physical properties of 80 mass% SiC specimens fired at 1450°C.	59
Fig.(18)	Effect of firing temperature on physical properties of 80 mass% SiC specimens	61
Fig.(19)	Effect of water addition on physical properties of 80 mass% SiC foamed specimens fired at 1350°C	64
Fig.(20)	Effect of stabilizer addition on physical properties of 80 mass% SiC specimens fired at 1450°C for 2hr.	67
Fig.(21)	SEM micrographs of fracture surface of specimens No.1 and 2 fired at 1450°C for 2 hr.	70
Fig.(22)	SEM micrographs of fracture surface of specimens No. 3 and 4 fired at 1450°C for 2hr.	70
Fig.(23)	SEM micrographs of fracture surface of specimens No. 5 and 6 fired at 1450°C for 2hr.	71
Fig.(24)	SEM micrographs of fracture specimens No. 6 and 7 fired at 1450 and 1350°C, for 2 hr. respectively	73

Fig.(25)	SEM micrographs of fracture surface of specimens No. 7 and 8 fired at 1350°C for 2hr.	75
Fig.(26)	SEM micrographs of fracture surface of specimens No. 8 and 9 fired at 1350°C for 2hr.	77
Fig(27)	XRD patterns of 80 mass% SiC containing specimens foamed using CaC ₂ /Al mass ratio of 3.3 and fired for 2hr. at temperature of 1450°C	78
Fig(28)	XRD patterns of 80 mass% SiC containing specimens foamed using CaC ₂ /Al mass ratio of 1.43 and fired for 2hr. at temperature of 1450°C	79
Fig(29)	XRD patterns of 80 mass% SiC containing specimens fired for 2hr. at temperature of 1350°C.	81
Fig(30)	XRD patterns of 80 mass% SiC containing specimens fired for 2hr. at temperature of 1400°C.	81
Fig(31)	XRD patterns of 80 mass% SiC containing specimens fired for 2hr at temperature of 1450°C.	82
Fig.(32)	Relationship between physical properties of coarse and fine SiC containing specimens, fired at 1450°C for 2hr and their SiC content.	86
Fig(33)	Relationship between compressive strength and SiC content of specimens fired at 1450°C for 2hr.	88
Fig.(34)	Relationship between oxidation resistivity of investigated specimens and their SiC content.	90

List of Figures

Fig.(35)	XRD patterns of fine 40 mass% SiC specimens fired at 1450°C for 2hr.	91
Fig.(36)	XRD patterns of fine 60 mass% SiC specimens fired at 1450°C for 2hr.	92
Fig.(37)	XRD patterns of fine 80 mass% SiC specimens fired at 1450°C for 2hr.	93
Fig.(38)	SEM micrographs of fracture surface of 80 mass% SiC containing specimens fired at 1450°C.	97
Fig.(39)	SEM micrographs of fracture surface of 80 mass% SiC containing specimens fired at 1450°C, for 2hr.	98
Fig.(40)	Relationship between physical properties of fired 80 mass% SiC containing specimens and saw-dust content.	102
Fig.(41)	Relationship between physical properties of 80 mass% SiC containing specimens prepared by the two methods and saw-dust content.	105
Fig.(42)	Relationship between physical properties of hand pressed 80 mass% SiC containing specimens fired at 1450°C for 2hr. and starch content.	107
Fig.(43)	Relationship between physical properties of extruded 80 mass% SiC containing specimens fired at 1450°C for 2hr. and added starch content.	109
Fig.(44)	SEM micrographs of fracture surfaces of 80 mass% SiC containing specimens fired at 1450C for 2hr.	111

List of Figures

Fig.(45)	SEM micrographs of fracture surface of 80 mass% SiC prepared using 7.5 mass% saw-dust and fired at 1450 °C for 2hr.	114
Fig.(46)	SEM of fracture surface of 80 mass% SiC containing specimens fired at 1450 °C, 2h.	116
Fig.(47)	SEM of fracture surface of 80 mass% SiC containing specimens fired at 1450 °C, 2h.	117
Fig.(48)	Pore size distribution of 80 mass% SiC containing specimens prepared using 15 mass% starch and fired at 1450°C for 2h.	118
Fig.(49)	Pore size distribution of 80 mass% SiC containing specimens prepared using 10 mass% saw-dust and fired at 1450 °C for 2hrs.	119
Fig.(50)	Relationship between specific mass gain and oxidation time at temperature of 1100 °C for specimens prepared by sacrificial template method.	123
Fig.(51)	Relationship between specific mass gain and oxidation time at temperature of 1100 °C for foamed specimens	126

List of Table

Table No.		Page
Table (1)	Chemical composition of main starting materials	33
Table (2):	Specific surface area of used raw materials.	35
Table (3)	Sieve analysis of the used coarse SiC grade	36
Table (4)	Some properties of 163M admixture	37
Table (5)	Specific surface area of pore former agents	42
Table (6)	Chemical composition of fired kaolin-alumina mixture	42
Table (7)	Chemical composition of fired 40 mass% SiC containing mixtures	43
Table (8)	Chemical composition of fired 60 mass% SiC containing mixtures	43
Table (9)	Chemical composition of fired 80 mass% SiC containing mixtures	43
Table(10)	The change in physical properties of SiC specimens fired at 1450°C with increasing their SiC content	53
Table(11)	Different preparation conditions of prepared specimens	56

List of Tables

Table(12)	The change in physical properties with increasing the CaC_2/Al mass ratio for 80 mass% SiC specimens fired at 1450°C .	57
Table(13)	The change in physical properties with increasing firing temperature for 80 mass% SiC specimens	60
Table(14)	The change in physical properties of specimens prepared using different water contents	62
Table(15)	The change in the values of physical properties of specimens with the increase of stabilizer addition	65
Table(16)	Preparation conditions and physical properties of the selected specimens	69
Table(17)	Preparation conditions and physical properties of the specimens No. 6 and 7.	73
Table(18)	Preparation conditions and physical properties of the specimens No. 7 and 8	74
Table(19)	Preparation conditions and physical properties of the specimens No. 8 and 9	76
Table(20)	The change in physical properties of coarse and fine SiC containing specimens with their SiC content	85
Table(21)	Compressive strength values of different SiC containing specimens.	88
Table(22)	The mass change of specimens with different SiC content fired at 1450°C	89

List of Tables

Table(23)	The change in physical properties of 80 mass% SiC containing specimens with different saw-dust content	100
Table(24)	Change in physical properties of 80 mass% SiC containing specimens, prepared by the two methods, with different saw-dust contents.	103
Table(25)	The change in physical properties of hand pressed 80 mass% SiC containing specimens with starch content.	106
Table(26)	The change in physical properties of extruded 80 mass% SiC containing specimens with starch content.	108
Table(27)	The preparation conditions and physical properties of specimens No. 13 and 14.	112
Table(28)	The preparation conditions and physical properties of specimen No. 12	113
Table(29)	Preparation conditions and physical properties of the selected specimens.	115
Table(30)	Mean pore diameter and pore surface area of specimens	119
Table(31)	The preparation conditions and physico-mechanical properties of specimens prepared by sacrificial template method	121
Table(32)	Preparation conditions and physico-mechanical properties of foamed specimens	125
