8

Characteristics and Properties of Silicon Carbide and Boron Carbide

1.0 INTRODUCTION

In the previous chapter, the structure and composition of the two covalent carbides, i.e., silicon carbide and boron carbide, were reviewed. This chapter is an assessment of the properties and a summary of the fabrication processes and applications of these two compounds.

Silicon carbide and boron carbide to a lesser degree are important industrial materials which are produced on a large scale in the form of powders, molded shapes, and thin films.

2.0 CHARACTERISTICS AND PROPERTIES OF SILICON CARBIDE

2.1 Historical Background and Present Status

Silicon carbide was first synthesized in 1891 by Acheson by passing an electric current through a mixture of carbon powder and clay. The material was originally thought to be a mixture of carbon and corundum (aluminum oxide) and trademarked *Carborundum* (CARBOncoRUNDUM).

Acheson soon determined that it was actually silicon carbide. The product was an immediate commercial success as an abrasive.[1][2]

The Acheson process is still the major production process. In the US, over 115,000 metric tons of silicon carbide were produced in 1994 with a value estimated at $40 million, much of which was for abrasives and metallurgical uses.[3]

2.2 Summary of Properties

The characteristics and properties of silicon carbide are summarized in Table 8.1[4]–[10] and reviewed in more detail in Secs. 4–8. Values quoted are for hot-pressed material and are an average of the values reported in the literature.

Table 8.1: Summary of Characteristics and Properties of Silicon Carbide.

Notes: (a) When structure is not indicated, values reported are for βSiC.
(b) Test temperature is 20°C unless otherwise stated.

Composition: SiC (very narrow range)

Molecular Weight (g/mol): 40.097

Color: colorless to yellow if pure, brown if doped with boron, nitrogen or aluminum

X-ray Density (g/cm3):
αSiC(6H) 3.211
βSiC 3.214

Melting Point:
2545°C at 1 atm. (decomposes)
2830°C at 35 atm.
(decomposes to Si, Si_2C, Si_2, and SiC_3)
(see Sec. 4.2)

Specific Heat (J/mol·K) (see Fig. 8.1):
αSiC 27.69
βSiC 28.63

Heat of Formation (-ΔH) (kJ/mol·K at 298.15 K):
αSiC - 25.73 ± 0.63
βSiC - 28.03 ± 2

Thermal Conductivity (W/m·°C) (see Fig. 8.2):
αSiC 41.0
βSiC 25.5

Table 8.1: *(Cont'd)*

Thermal Expansion (× 10^{-6}/°C) (see Fig. 8.3):		
	αSiC	5.12
	βSiC	3.8
Dielectric Constant @ 300 K:		
	αSiC (6H)	9.66–10.03
	βSiC	9.72
Electrical Resistivity (Ω·cm):		
	αSiC	0.0015 to 10^3
	βSiC	10^{-2} to 10^6
Debye Temperature:	αSiC	1200 K
	βSiC	1430 K
Energy Gap (eV):	αSiC (6H)	2.86
	βSiC	2.6
Exiton Energy Gap (eV) @ 4.2 K:		
	αSiC (4H)	3.265
	αSiC (6H)	3.023
	βSiC	2.39
Superconductive Transition Temperature: 5 K		
Refractive Index βSiC, *n*, (Na) 2.48:		
	2.7104 @ 467 μm	2.6916 @ 498 μm
	2.6823 @ 515 μm	2.6600 @ 568 μm
	2.6525 @ 589 μm	2.6446 @ 616 μm
	2.6264 @ 691 μm	
Vickers Hardness (GPa): 24.5–28.2 (varies with crystal face)		
Modulus of Elasticity (GPa):		475 @ 293K
		441 @ 1773K
Shear Modulus (GPa): 192		
Bulk Modulus (GPa): 96.6		
Elastic Constants (dynes/cm^2):		
	αSiC	C11 5.0, C12 0.92, C33 5.64, C44 1.68, C66 2.04
	βSiC	C11 2.89, C12 2.34, C44 0.544
Poisson Ratio: 0.142		
Flexural Strength (MPa): 350–600 (see Fig. 8.4)		
Oxidation Resistance: excellent due to the formation of a layer of SiO_2		
Chemical Resistance: essentially inert at room temperature		

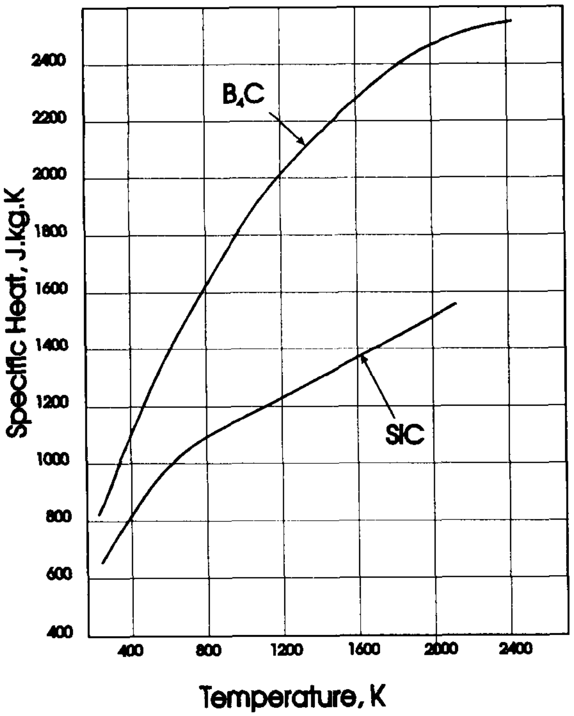

Figure 8.1: Specific heats of the covalent carbides as a function of temperature.

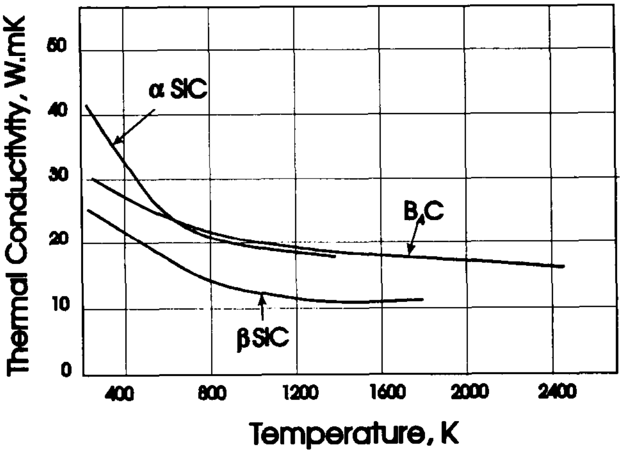

Figure 8.2: Linear thermal expansions of the covalent carbides as a function of temperature.

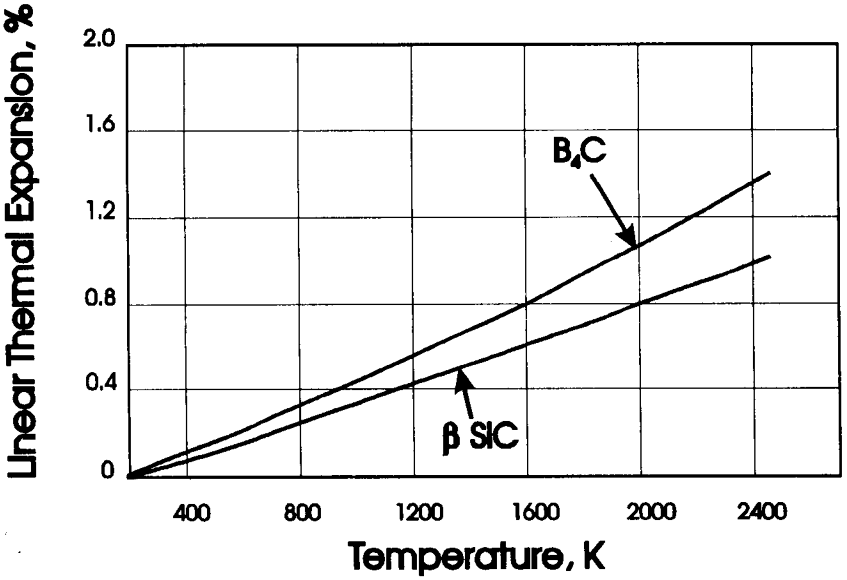

Figure 8.3: Linear thermal conductivities of the covalent carbides as a function of temperature.[15][16]

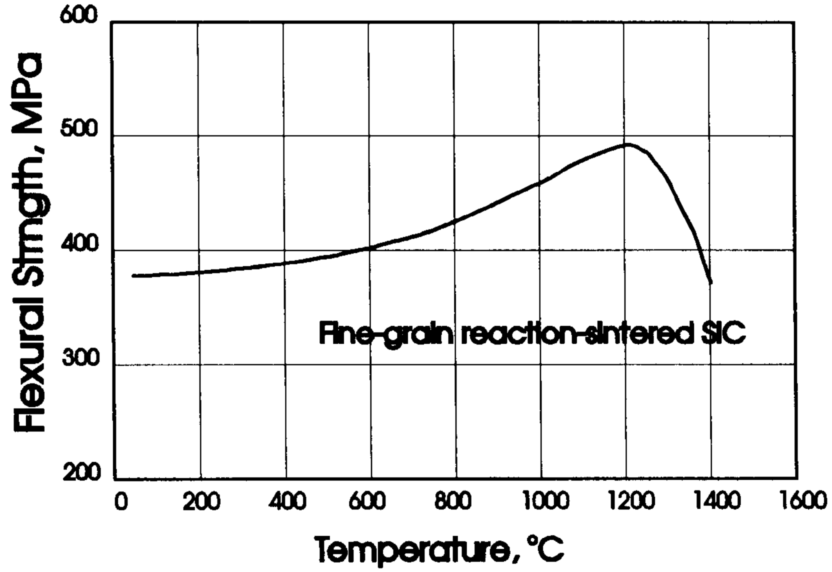

Figure 8.4: Flexural strength of silicon carbide as a function of temperature.

3.0 CHARACTERISTICS AND PROPERTIES OF BORON CARBIDE

3.1 Historical Background and Present Status

Boron carbide was first produced and identified at the end of the nineteenth century and for many years remained a laboratory curiosity. The structure and composition were tentatively determined in 1934.[11] It was not until the end of World War II that the first major applications were developed particularly in the nuclear industry. Production was estimated to reach $40 million in 1994.[12]

3.2 Summary of Properties

The characteristics and properties of boron carbide are summarized in Table 8.2 (for structural data, see Table 7.5 of Ch. 7). They are reviewed in more detail in Secs. 4–8. The material has outstanding hardness and excellent nuclear properties (see Sec. 7.0).

Table 8.2: Summary of Characteristics and Properties of Boron Carbide.

Note: Test temperature is 20°C unless otherwise stated.

Composition: $(B_{11}C)CBC$
Molecular Weight (g/mol): 55.26
Color: black (pure crystal is transparent and colorless)
X-ray Density (g/cm$^{3)}$: 2.52

Melting Point: ≈2400°C (does not decompose)
Specific Heat (J/mole·K): 50.88 (see Fig. 8.1)
Heat of Formation (-ΔH) (kJ/mol·K at 298.15 K): 57.8 ± 11.3
Thermal Conductivity (W/m·°C): 30 (see Fig. 8.2)
Thermal Expansion (10^{-6}/°C): 4.3 (see Fig. 8.3)

Electrical Resistivity (Ω·cm): 0.1–10 (Fig. 8.5)
Seebeck Coefficient (μV/K): 200–300 @ 1250 (Fig. 8.6)

Vickers Hardness (GPa): 27.4–34.3

Modulus of Elasticity (GPa): 290–450

Shear Modulus (GPa): 165–200

Bulk Modulus (GPa): 190–250

Poisson's Ratio: 0.18

Flexural Strength (MPa): 323–430

Compressive Strength (MPa): 2750

Oxidation Resistance: in air up to 600°C. Formation of a film of B_2O_3 retards oxidation.

Chemical Resistance: generally excellent. Reacts with halogens at high temperature.

Absorption Cross Sec. for Thermal Neutrons (barn): 755 (see Sec. 7.0)

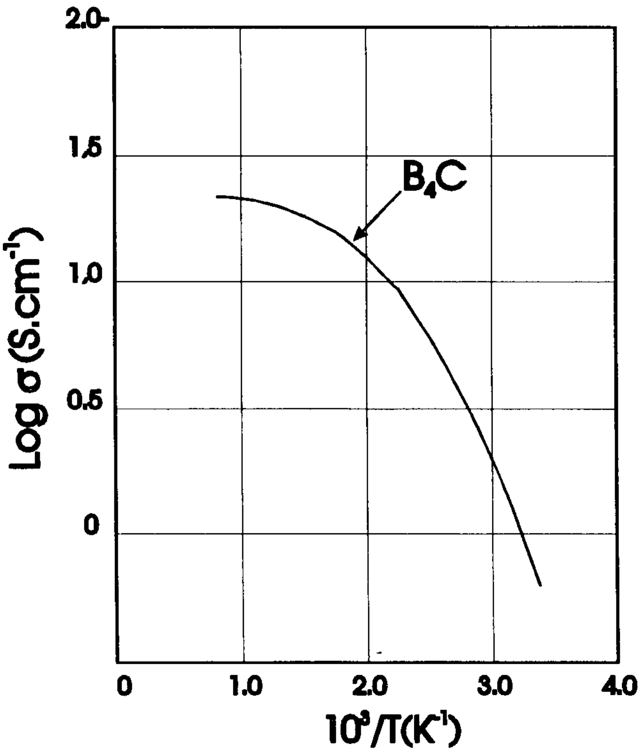

Figure 8.5: Electrical conductivity of boron carbide as a function of temperature.[23]

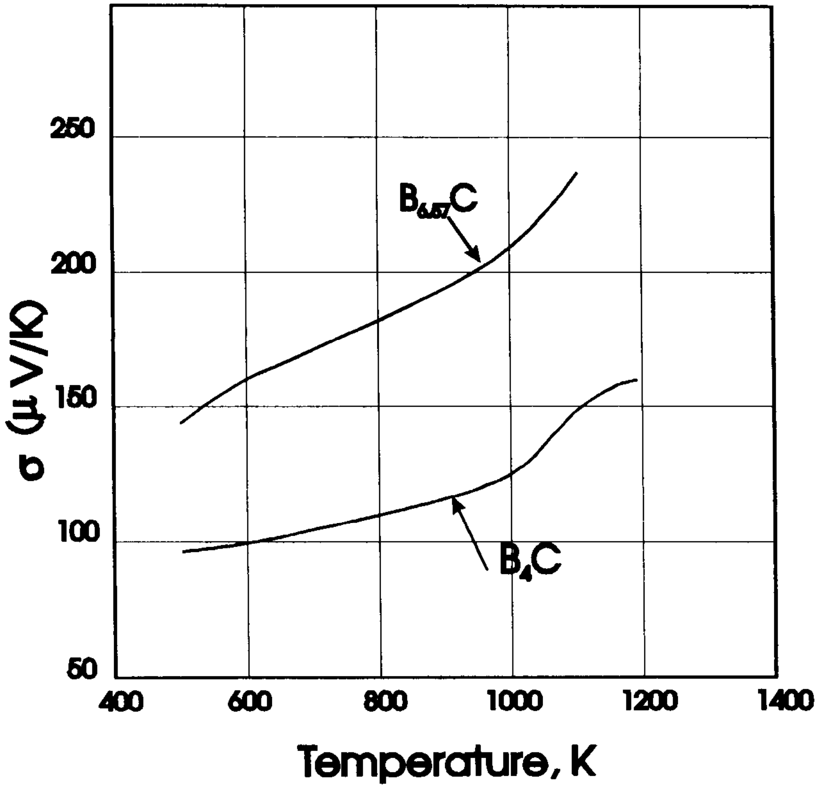

Figure 8.6: Seebeck coefficient of boron carbide as a function of temperature.

4.0 PHYSICAL AND THERMAL PROPERTIES OF THE COVALENT CARBIDES

4.1 Discussion and Comparison

In this section and the next three, the properties and characteristics of the covalent carbides are reviewed and compared whenever appropriate with those of the parent elements and of the refractory compounds of titanium. For comparison with other carbides, nitrides, or borides, see the appropriate tables in Chs. 4–6. Reported property values often vary considerably and the values given here are a general average.

4.2 Physical Properties

Physical properties are shown in Table 8.3.

Table 8.3: Density and Melting Point of Covalent Carbides and Other Refractory Compounds.

Material	Density (g/cm^3)	Melting Point °C
βSiC	3.214	2545 (decomposes)
αSiC(6H)	3.211	-
B_4C	2.52	2450
Si	2.329	1414
βB	2.35	2050
C (graphite)	2.26	3730 (sublimes)
C (diamond)	3.51	~1000 (graphitizes)
TiC	4.91	3067
TiN	5.40	2950
TiB_2	4.52	2980

Both covalent carbides have high melting points which are slightly lower than the titanium compounds but higher than silicon and boron. Under most conditions, the thermal decomposition of SiC may occur well below its intrinsic melting point[13] and decomposition can become significant at approximately 1700°C (see Sec. 3.7 and Fig. 7.8 of Ch. 7). The density of SiC is closer to that of diamond than it is to graphite, which can be expected since SiC has the structure of diamond.

Boron carbide does not appear to decompose up to its melting point. It vaporizes by the preferential loss of gaseous boron.[14]

4.3 Thermal Properties

The thermal properties of the covalent carbides are shown in Table 8.4.[15][16]

Table 8.4: Thermal Properties of Covalent Carbides and Other Refractory Materials at 20°C

Material	Specific Heat (J/mole·K)	Specific Heat (J/g·K)	Thermal Conductivity (W/m,K)	Thermal Expansion (× 10^{-6}/°C)
αSiC	27.69	0.691	41.0	5.12
βSiC	28.63	0.714	43–145	3.8
B_4C	50.88	0.921	20–35	4.3
Si	18.58	0.405	150	2.6
B(β)	11.16	1.032	60	4.8
C(diamond)	6.19	0.515	600–2100	0.8
TiC	33.8	0.563	21.0	7.4
TiN	33.74	0.545	19.2? 29.1	9.3 9.4
TiB_2	44.29	0.744	24.3	6.6

Specific Heat. The specific heat (C_p) of the covalent carbides as a function of temperature is shown in Fig. 8.1.[10] On a weight basis (J/g·K), the specific heat of silicon carbide and particularly boron carbide is higher than that of the other refractory carbides and nitrides listed in Table 8.2

Thermal Conductivity. The thermal conductivity or *k* (i.e., the time rate of transfer of heat by conduction) of covalent carbides, unlike that of the interstitial carbides, decreases with increasing temperature as shown in Fig. 8.2.[10] It is highly dependent on the method of formation which is reflected by the large spread in values. The thermal conductivity of silicon carbide (particularly αSiC) is high yet considerably lower than that of the best conductors such as Type II diamond (2000 W/m·K), silver (420 W/m·K), copper (385 W/m·K), beryllium oxide (260 W/m·K), and aluminum nitride (220 W/m·K).[17]

Thermal Expansion. As shown in Fig. 8.3, thermal expansion of the covalent carbides is low and increases with increasing temperature but this increase is not entirely linear and is slightly more rapid at high temperature.[10] For discussion of thermal expansion, see Sec. 2.5 of Ch. 4.

5.0 ELECTRICAL AND SEMICONDUCTOR PROPERTIES

5.1 Electrical Properties

For discussion of electrical conductivity, see Sec. 3.1 of Ch. 4. As opposed to the transition metal carbides, the covalent carbides are considered electrical insulators since they have no metallic bonding and their electrons are strongly bonded to the nucleus and are not free to move.

Silicon carbide has self-heating and beta-emitting glow characteristics and as such is a standard material for heating elements (see Ch. 15). The anisotropy of the electrical conductivity of boron carbide is low, between 70 and 700 K.[18]

5.2 Semiconductor Properties

In a semiconductor material, the forbidden-energy gap is such that electrons in usable quantities are able to jump across it from the filled valence band to the empty conduction band.[19] The three elements that form the covalent carbides, i.e., boron, silicon, and carbon (in the form of doped diamond) are semiconductors and one would expect to find semiconductor properties in their compounds.

This is indeed the case and the semiconductor properties of βSiC have long been recognized but it is only recently, with the development of high-quality thin film techniques, that it is possible to consider it as a practical semiconductor material. βSiC is an indirect bandgap semiconductor with properties that promise significant improvements over existing materials in high power, high-frequency devices as shown in Table 8.5.

Table 8.5: Semiconductor Properties of βSiC and Other Materials

Property and Unit	Silicon	GaAs	βSiC	Diamond
Bandgap at 300K (eV)	1.12	1.43	2.35	5.45
Thermal Conductivity at RT (W/cm·K)	1.5	0.5	5	20
Saturated Drift Velocity (em/sec)	1.0×10^7	2.0×10^7	2.5×10^7	2.7×10^7
Drift Mobility, Electrons (em/V·sec)	1500	8500	1385	1800
Drift Mobility, Holes (em/V·sec)	450	400	100	1200
Breakdown Electric Field (V/cm)	3×10^5	4×10^5	5×10^6	1×10^7
Dielectric constant	11.8	12.8	9.7	5.5
Max. Junction Temperature (°C)	$\approx$250	$\approx$300	$\approx$1000	$\approx$1000

The table shows that βSiC is potentially more effective than silicon or gallium arsenide particularly in microwave and millimeter-wave devices and in high-voltage power devices (see Ch. 16).[20]

Boron carbide is a p-type semiconductor with a bandgap varying from 2.5 eV at the center of the Brillouin zone to about 1 eV at the zone boundary in the direction of the (111) wave vector.[21] It is considered a degenerate semiconductor with charge carriers (holes) of low mobility (< 1 cm/V sec) forming small polarons and moving through the material by phonon-assisted hopping.[22]

5.3 Boron Carbide as a Thermoelectric Material

Boron carbide is characterized by a relatively wide gap in its forbidden band, a low thermal conductivity, and a high thermoelectric power. These properties make it a potentially useful material for high-temperature thermoelectric energy conversion.[23] Electrical conductivity and Seebeck coefficient as a function of temperature and composition are shown in Figs. 8.5 and 8.6.

6.0 MECHANICAL PROPERTIES

6.1 Property Variables

For a discussion of mechanical properties and variables see Sec. 4.1 of Ch. 4. The mechanical properties of the covalent carbides often show a large spread in the reported values mostly due to differences in the fabrication processes. In addition, the following factors influence mechanical testing[6][24]:

- Density and porosity
- Presence of impurities
- Grain size and morphology
- Grain orientation
- Structural defects (vacancies, dislocations)
- Testing methods (3 points vs. points, Weibull statistics etc.)

6.2 Summary of Mechanical Properties

The mechanical properties of the covalent carbides are summarized in Table 8.6. The values are average values reported in the recent literature.[1][7][17][25]

6.3 Strength

Covalent carbides are strong materials especially at high temperature. However, like the transition-metal carbides and most other ceramics, they are intrinsically brittle (for discussion, see Sec. 4.3 of Ch. 4). Silicon carbide retains its strength at high temperature up to 1200°C as shown in Fig. 8.6. This is also true for boron carbide but to a lesser degree.[6]

The covalent carbides, like the transition-metal carbides, have the ability to deform plastically above the ductile-to-brittle transition temperature. Below that temperature, the carbides fail in a brittle manner while above they show ductile behavior and undergo plastic deformation

Table 8.6: Mechanical Properties of Covalent Carbides and Other Refractory Compounds at 20°C

Compound	Vickers Hardness (GPa)	Young's Modulus of Elasticity (GPa)	Shear Modulus (GPa)	Flexural Strength (MPa)
βSiC	24.5–28.2	475	192	350–600
B_4C	up to 48	290–450	165–200	323–430
B	25.3	up to 480		
C (diamond)	up to 100	910–1250		
TiC	28–35	410–510	186	240–390
TiN	18–21	250		
TiB_2	33	575	400	

Hot-isostatic pressing and high firing temperature (2100°C) significantly increase the strength of boron carbide. Flexural strength as high as 429 MPa and Young's modulus as high as 433 GPa are observed.[26][27]

6.4 Hardness

It is significant that two of the hardest materials contain boron (cubic boron nitride and boron carbide), boron itself being a very hard material.[26]

Boron carbide is the hardest material after diamond and cubic boron nitride, and it maintains its hardness to 1800°C.[21] For discussion on hardness, see Sec. 4.4 of Ch. 4.

7.0 NUCLEAR PROPERTIES

Boron is an important material for nuclear applications due to its high neutron absorption cross section (760 barn at neutron velocity of 2200 m/sec). The cross section of the B^{10} isotope is considerably higher (3840 barn).[24] In addition, boron does not have decay products with long half-life and high-energy secondary radioactive materials. However, pure boron is extremely brittle and difficult to produce in shapes such as control rods. Boron carbide is usually the material of choice since it provides a high concentration of boron atoms in a strong and refractory form and is relatively easy to mold (see Ch. 16).

8.0 SUMMARY OF FABRICATION PROCESSES

The fabrication processes for silicon carbide and boron carbide are also reviewed in Chs. 14 and 15.

8.1 Silicon Carbide

The Acheson process mentioned above is a carbothermic reduction now produced by electrochemical reaction of high purity silica sand and carbon in an electric furnace. The general reaction is:

$$SiO_2 + 3C \rightarrow SiC + 2CO\ (g)$$

The addition of sawdust increases the porosity of the charge and facilitates gas circulation. Chlorine is added to reduce impurities.[4] Alpha SiC is produced above 2100°C and βSiC at 1500–1600°C. Shapes are produced by standard ceramic forming technologies, pressureless sintering, and reaction bonding; coatings are produced by CVD.[6][28]

8.2 Boron Carbide

The major boron carbide production process consists of the reduction of boric oxide (B_2O_3) with carbon (usually in the form of coke) in an electric furnace by resistance heating or arc heating at high temperature (up to 2300°C).[29][30] The material is also produced by the same reduction reaction but in the presence of magnesium and by the direct synthesis of the elements.[21] Monolithic shapes are produced by hot-isostatic pressing.[26] Boron carbide coatings are usually produced by CVD.[28][31]

9.0 SUMMARY OF APPLICATIONS AND INDUSTRIAL IMPORTANCE

The following is a summary of applications of silicon carbide and boron carbide in production or development. More details are given in the Ch. 16.

9.1 Silicon Carbide[1]–[3]

Powder

- Deoxidizer in steel production and other metallurgical processes (largest tonnage use)
- Powder abrasives, bonded abrasives, coated abrasives
- Filler in refractory cements

Shapes

- Refractory products, bricks, kiln furniture, tubes and other shapes[3]
- Electric heating elements and resistors
- Igniters for gas appliances (recrystallized SiC)
- Radiation sensors (amorphous SiC)
- Low-weight, high-strength mirrors
- High-power, high-frequency, and high-temperature semiconductor devices
- Radiation-resistant semiconductors

- Fibers and whiskers
- Matrix in ceramic composites
- Thermocouple sheath
- Lightweight armor

Coatings

- Coatings for susceptors and heating elements for epitaxial silicon deposition
- Coatings for fusion reactor applications
- Nuclear waste container coatings
- Coatings for ceramic heat exchanger tubes
- Oxidation resistant coatings for carbon-carbon composites
- Heteroepitaxial deposit on silicon
- Blue light-emitting diodes (LED)

9.2 Boron Carbide[11][28][32]–[34]

- Shielding and control of nuclear reactors pellets, shapes, and coatings
- Wear parts, sandblast nozzles, seals[25][26]
- Mortar and pestle
- High-grade abrasive and lapping powder
- High-temperature thermocouple
- Lightweight body and airborne armor
- Matrix material for ceramic composites[24]
- Coating for nozzles, dressing sticks for grinding wheels
- Lightweight body armor

REFERENCES

1. Parche, M. C., *Fact about Silicon Carbide*, The Carborundum Company, Niagara Falls, NY (1961)
2. Shaffer, P. T., *Handbook of Advanced Ceramic Materials,* Advanced Refractory Technologies Inc., Buffalo, NY (1991)
3. Ault, N. N., and Crowe, J. T., Silicon Carbide, *Ceramic Bulletin*, 70(5) (1991)
4. Divakar, R., et al., Silicon Carbide in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)
5. *Silicon Carbide*, (R. C. Marshall et al., eds.), Univ. of South Carolina Press, Columbia, SC (1973)
6. Srinivasan, M., *The Silicon Carbide Family of Structural Ceramics*, in *Treatise on Materials Science and Technology,* Vol. 29 (Wachtman, J. B., Jr., ed.), Academic Press, Boston (1989)
7. Kosolapova, T. Y., *Carbides*, Plenum Press, New York (1971)
8. Campbell, I. E., and Sherwood, E. M., *High-Temperature Materials and Technology*, John Wiley & Sons, New York (1967)
9. *High Performance Engineered Sintered Silicon Carbide*, Technical Brochure, The Carborundum Co. (1978)
10. *Engineering Property Data on Selected Ceramics,* Vol. 2, *Carbides*, MCIC HB-07-2, Battelle Institute, Columbus, OH (1987)
11. Shaffer, P. T., *Handbook of Advanced Ceramic Materials,* Advanced Refractory Technology, Buffalo, NY (1992)
12. Boron Carbide and Boron Nitride, *Mitchell Market Reports*, Monmouth, Wales (1992)
13. Massalski, T. B., *Binary Alloy Phase Diagrams*, 2d. ed., ASM International, Metals Park, OH (1990)
14. Robson, H. E., and Gilles, P. W., The High Temperature Properties of Boron Carbide and the Heat of Sublimation of Boron, *J. Phys. Chem.*, 68(5):983–989 (1964)
15. Gosset, D., Guery, M., and Kryger, B., *Thermal Properties of Some Boron-rich Compounds*, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds), Am Inst. of Physics, New York (1986)
16. Türkes, P. R., Swartz, E. T., and Pohl, R. O., Thermal Properties of Boron and Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage et al., eds.), Am Inst. of Physics, New York (1986)
17. Pierson, H. O., *Handbook of Carbon, Graphite, Diamond, and Fullerenes*, Noyes Publications, Park Ridge, NJ (1993)

18. Werheit, H., and Rospendowski, S., Anisotropy of the Electrical Conductivity of Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds.), Am Inst. of Physics, New York (1986)
19. Van Vlack, L. H., *Elements of Materials Science and Engineering*, Addison-Wesley Publishing, Reading, MA (1980)
20. Davis, R. F., Silicon Carbide and Diamond Semiconductor Thin Films, *Am. Ceram. Soc. Bull.*, 72(6) (1993)
21. Makarenko, G. N., *Borides of the IVb Group*, in *Boron and Refractory Borides* (V. L. Matkovich, ed.), Springer-Verlag, Berlin (1977)
22. Wood, C., Transport Properties of Boron Carbide, in *Boron-Rich Solids*, AIP Conf. Proc. 140 (D. Aselage, et al., eds.), Am Inst. of Physics, New York (1986)
23. Koumoto, K., Thermoelectric Properties of CVD Boron Carbide, *Am. Ceram. Soc. Bull.*, 73(10):84–87 (1994)
24. Hollenberg, G. W., and Walther, G., The Elastic Modulus and Fracture of Boron Carbide, *J. Am. Ceram. Soc.* 63(11–12):610–613 (1980)
25. Bower. J. G., Elemental Boron, Preparation, Properties and Applications, in *Progress in Boron Chemistry,* (R. Brotherton and H. Steinberg, eds.), Pergamon Press, Oxford, UK (1969)
26. Schwetz, K. A., and Lipp, A., Boron Carbide, Boron Nitride, and Metal Borides, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., Vol. A4, VCH (1985)
27. Tressler, R. E., High-Temperature Stability of Non-Oxide Structural Ceramics, *MRS Bull.*, 58–63 (Sept. 1993)
28. Pierson, H. O., *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge, NJ (1992)
29. Wentorf, R. H., Jr., Refractory Boron Compounds, in *Kirk Othmer, Encyclopedia of Chemical Technology,* John Wiley & Sons, New York (1991)
30. Thomson, R., The Chemistry of Metal Borides and Related Compounds, in *Progress in Boron Chemistry* (R. J. Brotherton and H. Steinberg, eds.), Pergamon Press Ltd., New York (1970)
31. Janson, U., Chemical Vapor Deposition of Boron Carbides, *Materials and Manufacturing Processes*, 6(3):481–500 (1991)
32. Tetrabor Boron Carbide, *Technical Brochure*, ESK, Munich, Germany (1992)
33. Norbide Boron Carbide, *Technical Brochure*, Norton Co., Worcester, MA (1992)
34. Baudis, U., and Fichte, R., Boron and its Alloys, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th. ed., Vol. A4, VCH (1985)