SILICON CARBIDE

1. Introduction

Silicon carbide [409-21-2] (SiC) is a technologically important material that is one of the small number of unusual materials that were first created synthetically and then subsequently discovered in nature. Silicon carbide was first observed in its natural form in 1905 by the Nobel-prize-winning chemist Henri Moissan, who discovered it in the meteor that created the Diablo Canyon in Arizona. The transparent mineral, now known as moissanite [12125-94-9], is almost as brilliant and as hard as diamond and is therefore often used as a gemstone. The color of SiC depends strongly on the level of impurities ranging from colorless and transparent for the pure form through pale yellow to dark black for very impure specimens. To date, SiC has been found to occur in nature in only minute quantities, and therefore, for practical purposes, all SiC used today is synthetic.

The first artificial synthesis of SiC in 1891 is usually attributed to Edward Acheson who unexpectedly discovered small black crystals of SiC in an electrically heated melt of carbon and alumina (1). The subsequent refinement of this technique (the so-called Acheson process) led to the commercial production of large volumes of small SiC crystals (ground into powder form) for use as an industrial abrasive (2). The commercial product, which is made in an electric furnace, is usually obtained as an aggregate of iridescent crystals. The iridescence is caused by a thin layer of silica produced by superficial oxidation of the carbide. The loose black or green grain of commerce is prepared from the manufactured product by crushing and grading for size. Although Acheson's 1891 experiments are credited with being the first known synthesis of SiC, work about 10 years earlier had produced tetratomic radicals of silicon ($Si_2C_2O_2$, Si_2C_2N) and some SiC (3).

Techniques to form such SiC powder into shaped ceramic components by the use of various binding agents soon extended the commercial impact of SiC into numerous engineering and scientific applications. Currently, SiC is one of the most widely used materials and plays a critical role in industries as diverse as aerospace, electronics, industrial furnaces, and wear-resistant mechanical parts. Traditionally, the metallurgical, abrasive, and refractory industries are the largest users of silicon carbide. SiC is also used for heating elements in electric furnaces, in electronic devices, and in applications where its resistance to nuclear radiation damage is advantageous. The development of advanced pressureless sintering and complex shape-forming technologies has led to silicon carbide becoming one of the most important structural ceramics. Silicon carbide has found wide acceptance in wear-, erosion-, and corrosion-resistant applications; it has demonstrated excellent performance as a material in a wide range of high temperature applications (such as has turbine blades).

2. Properties

The term “silicon carbide” is commonly used to describe a range of materials that are in fact distinct; eg, from the point of view of mechanical engineers, it may be used to describe ceramics (fabricated from relatively impure SiC crystallites bonded together with various binders under temperature and/or pressure), whereas electrical engineers may use the term to describe high purity single crystal wafers of SiC. In this review, a strict nomenclature will be used—the term “silicon carbide” or “SiC” will be used in the strict scientific sense for high purity crystals, whereas manufactured ceramic materials will be described by the composite term SiC-ceramic.

The properties of both SiC and SiC-ceramics (4–6) depend on purity, polytype, and method of formation. Measurements made on commercial, polycrystalline SiC-ceramic products should not be interpreted as being representative of single-crystal SiC. In addition, the pressureless-sintered SiC-ceramics, being essentially single-phase, fine-grained, and polycrystalline, have properties distinct from direct-bonded SiC-ceramics, which may contain a wider range of crystallite sizes and polytypes. Table 1 shows a comparison of the properties of the fully compacted, high purity material SiC ceramics with various polytypes of SiC single-crystal.

2.1. Crystal Structure. Silicon carbide is composed of carbon and silicon in equal amounts with each atom bonded to four atoms of the opposite type in a tetrahedral bonding configuration. The crystal structure is composed of hexagonal packed bilayers with each atom type exclusively occupying either the upper or the lower of the bilayers. There are three possible arrangements of atoms in a layer of SiC crystal, and each type has the same layers but a different stacking sequence (28). As a given bilayer may be stacked on top of another bilayer in

Table 1. **Properties of Silicon Carbide**

Property	Value		References
mol wt	40.10		
decomposition temperature,[a] °C			
α-form	2825 ± 40		7
β-form	2985		
sp gr, g/mL at 20°C			
β-form	3.210		
6H polytype[b]	3.211 (3.208)		
commercial	3.16		
refractive index			
β-form	2.48		8
α-form[b]	ε	Ω	4
4H	2.712	2.659	
6H	2.690	2.647	
15R	2.687	2.650	
free energy of formation, $\Delta G^\circ{}_f$, kJ/mol[c]			
α-form	504.1		9
β-form	506.2		
heat of formation, $\Delta H^\circ{}_{f,298}$, kJ/mol[c]			
α-form	−25.73 ± 0.63		
β-form	−28.03 ± 2		
thermal conductivity at 25°C, W/(m·K)			10
commercial, high density	125.6		
reaction bonded	129.7		
emissivity[d]			10–15
spectra (3–5 μm)	0.9		
total (0–1600°C)	0.9		
coefficient of thermal expansion,[d] per °C			15–21
25–200°C	2.97×10^{-6}		
25–600°C	4.27×10^{-6}		
700–1500°C	6.08×10^{-6}		
Young's modulus, GPa[e]			22,23
α-form, hot-pressed	440		
α-form, sintered	410		24
β-form, sintered	410		22,23
shear modulus, GPa[e]			
reaction-bonded	167.3		25
α-form, sintered	177		26
β-form, sintered	140–190		22
sublime	19		27

[a] The decomposition products are Si, Si_2C, Si_2, SiC, and Si_3.

[b] H = hexagonal, R = rhombohedral.

[c] To convert J to cal, divide by 4.184.

[d] Of the sintered α-form.

[e] To convert GPa to psi, multiply by 145,000.

a variety of orientations (with both lateral translations and rotations being feasible energetically), silicon carbide may occur in a wide variety of stacking sequences—each unique stacking sequence generating a different polytype (cubic, hexagonal, and rhombohedral structures can all occur). The hexagonal and rhombohedral structure designated as the α-form (noncubic) may crystallize in a large number of polytypes, whereas to date only one form of cubic structure (designated as the β-form has been recorded). Designation (29) is by the number of layers in the sequence, followed by H, R, or C to indicate whether the type belongs to the hexagonal, rhombohedral, or cubic class. To date, over 215 polytypes have been recorded, although only a limited number are of interest technologically (principally the 4H and 6H hexagonal plus the 3C cubic forms).

Several theories have been put forth to explain the mechanism of polytype formation (29–35), such as the generation of steps by screw dislocations on single-crystal surfaces that could account for the large number of polytypes formed (29,34,35). The growth of crystals via the vapor phase is believed to occur by surface nucleation and ledge movement by face-specific reactions (36). The solid-state transformation from one polytype to another is believed to occur by a layer-displacement mechanism (37) caused by nucleation and expansion of stacking faults in close-packed double layers of Si and C.

A progressive etching technique (38,39), combined with x-ray diffraction analysis, revealed the presence of several α polytypes within a single crystal of silicon carbide. Work using lattice imaging techniques via transmission electron microscopy has shown that α-silicon carbide formed by transformation from the β-phase (cubic) can consist of many α polytypes in a syntactic array (40).

A phase diagram for the carbon−silicon system and for the relationship between temperature and solubility of carbon in silicon has been determined (41).

2.2. Mechanical Properties. Until the recent emergence of silicon carbide as a significant material for electronics, the mechanical properties of SiC-ceramics were the dominant commercial interest. All forms of silicon carbide are well known as hard materials occupying a relative position on Mohs' scale between alumina at 9 and diamond at 10. The average values for Knoop hardness under a load of 100 g are shown in Table 2.

Because of high thermal conductivity and low thermal expansion, silicon carbide is resistant to thermal shock as compared with other refractory materials.

Silicon carbide ceramics are leading candidate materials for rotating and static components in many gas turbine engine applications. As is the case for other ceramics, silicon carbide ceramics are brittle in nature. They are characterized by low fracture toughness and limited strain-to-failure as compared with metals. The strength of a silicon carbide ceramic component is generally determined by preexisting flaws introduced into the material during processing. The type, size, shape, and location of the flaws vary considerably and, consequently,

Table 2. **Knoop Hardness Values for Forms of Silicon Carbide**

Material	Knoop hardness
sapphire [1317-82-4]	2013
SiC, dense, direct-bonded	2740
SiC, sintered alpha	2800
SiC, black single crystal	2839
SiC, green single crystal	2875
boron carbide	3491

Table 3. **Flexure Strength and Fracture Toughness**[a]

	Young's modulus, GPa[b]		Fracture toughness MPa·m$^{1/2}$[c]	Flexural strength, MPa[b,d]	
	20°C	1400°C		20°C	1400°C
hot-pressed SiC	440	380	3.9	650	500
range	430–450		3–4	300–800	175–575
sintered SiC	410	372	4.6	460	460
range	375–420	300–400	3.5–5.5	345–485	345–485
reaction-bonded SiC	380	275	4.9	310	190
range	360–400	200–320	3.5–6	175–450	70–450

[a] Refs. 10 and 42.
[b] To convert Pa to psi, multiply by 1.45×10^{-4}.
[c] For a single-edged notched beam (SENB) test.
[d] Corresponding to a 4 pt. bend.

so does the strength. Therefore, designing with silicon carbide ceramics requires a probabilistic treatment of strength and component life. The strength, a statistical entity, can be described by the specification of at least two parameters, σ_0, the characteristic strength, and m, the Weibull modulus. These parameters are most commonly obtained from flexural strength data.

Silicon carbide ceramics made by different techniques also have distinct mechanical properties. Sintered silicon carbide ceramic retains its strength at elevated temperatures and shows excellent time-dependent properties such as creep and slow crack growth resistance. Reaction-bonded SiC ceramic, because of the presence of free silicon in its microstructure, exhibits slightly inferior elevated temperature properties as compared with sintered silicon carbide ceramic. Table 3 and Table 4 show selected mechanical properties of silicon carbide at room and elevated temperatures.

2.3. Electrical Properties. The electrical properties of both silicon carbide and silicon carbide ceramics are highly sensitive to purity, density, and even to the electrical and thermal history of the sample.

Resistivity. Due to the difficult manufacturing conditions, no pure sillicon carbide material has ever been made, and thus, no data are available on the electrical conduction of ultra-pure crystals. Typical commercial semiconductor epitaxial layers (44) are available at doping levels from 9×10^{14} carriers cm^{-3} to 1×10^{19} carriers cm^{-3}, and such material is well characterized.

Resistivity measurements of doped, alpha-silicon carbide single crystals from −195°C to 725°C showed a negative coefficient of resistivity below room temperature, which gradually changed to positive above room temperature (45). The temperature at which the changeover occurred increased as the ionization of the donor impurity increased.

The temperature coefficient of electrical resistivity of commercial silicon carbide ceramics at room temperature is generally negative. No data are given for

Table 4. **Steady-State Creep for Alpha-Silicon Carbides**[a]

Density, g/mL	Temperature, K	Stress, MPa[b]	Creep rate, s^{-1}	Deformation, μm	Test duration, 10^3 s
3.155	1820	138	1.06×10^{-9}	4.5	492.7
	1820	207	1.73×10^{-9}	6.0	356.2
	1820	276	2.23×10^{-9}	7.2	349.1
	1820	345	4.14×10^{-9}	7.7	271.9
	1820	414	5.10×10^{-9}	10.0	253.3
3.151	1923	69	[c]	6.5	360.5
	1923	138	6.37×10^{-9}	15.0	260.4
	1923	207	1.02×10^{-8}	27.0	319.3
	1923	276	1.68×10^{-8}	23.7	175.1
	1923	345	2.25×10^{-8}	34.0	181.7
	1923	414	3.18×10^{-8}	62.0	238.4
3.160	2020	69	2.75×10^{-8}	66.9	263.3
	2020	138	8.91×10^{-8}	105.9	152.2
	2020	207	1.16×10^{-7}	122.7	99.7
	2020	276	2.96×10^{-7}	51.6	31.2
	2020	345	3.90×10^{-7}	127.3	45.0
	2020	414	6.33×10^{-7}	117.0	26.0
3.152	1823	179	[c]	14.5	117.4
	1873	179	6.55×10^{-9}	19.5	378.2
	1923	179	1.46×10^{-8}	70.0	356.3
	1973	179	5.56×10^{-8}	64.0	161.5
	2023	179	2.00×10^{-7}	128.0	89.3
	2073	179	6.33×10^{-7}	47.0	14.8
3.153	1670	345	[c]	2.0	163.7
	1720	345	1.50×10^{-9}	4.5	255.5
	1770	345	1.88×10^{-9}	7.0	340.2
	1820	345	3.82×10^{-9}	18.0	433.9
	1870	345	1.29×10^{-8}	38.0	333.9
	1920	345	2.83×10^{-8}	43.0	181.9
	1970	345	1.19×10^{-7}	131.0	147.7
	2020	345	3.85×10^{-7}	113.0	39.8
3.162	1670	414	3.68×10^{-10}	2.0	492.4
	1720	414	9.75×10^{-10}	4.2	351.4
	1770	414	2.52×10^{-9}	8.6	346.8
	1820	414	5.09×10^{-9}	16.0	325.9
	1870	414	1.14×10^{-8}	25.0	354.8
	1920	414	3.11×10^{-8}	67.0	264.1
	1970	414	1.28×10^{-7}	160.4	165.4
	2020	414	5.34×10^{-7}	143.7	36.0

[a] Ref. 43.

[b] To convert MPa to psi, multiply by 145.

[c] Steady-state creep did not occur at these experimental conditions.

refractory materials because resistivity is greatly influenced by the manufacturing method and the amount and type of bond. Manufacturers should be consulted for specific product information.

A common application of silicon carbide ceramic material is as heating elements for furnaces. The resistivity of heating elements made from recrystallized silicon carbide ceramic varies with raw material grain size, purity, and porosity.

Typical resistivity is 0.1 ohm·cm at room temperature. Resistivity decreases with rising temperature to a minimum at 400°C and then gradually increases to about 0.13 ohm·cm at 1500°C. This result has the effect of reducing the total power input used to heat a furnace up to temperature while preventing the heating element from overheating after the operating temperature has been reached. This resistivity–temperature characteristic is also beneficial in other devices such as gas igniters.

Semiconducting Properties. In recent years, there has been a great deal of interest in the semiconducting properties of silicon carbide for potential use in a range of specialized applications (4,12,46,47). The electronic band gaps of the different polytypes range from 2.4 eV to 3.3 eV, and thus silicon carbide is considered a wide band gap material (c.f. silicon with a band gap of 1.1 eV). In some respects, such a wide range of band gaps is unexpected, particularly when the crystal structures of the polytypes differ only in the stacking sequence of otherwise identical bilayers (see above). Extensive research, however, has generated considerable knowledge of the technologies required to modify the properties of the basic semiconductor in ways suitable for the formation of complex electronic devices.

Because of the thermal stability of its electronic structure, silicon carbide has been studied for uses at high (>500°C) temperature. The Hall mobility in silicon carbide is a function of polytype (48,49), temperature (40,41,45–50), impurity, and concentration (49). It is now well understand how to increase the conductivity of both n-type and p-type silicon carbide by the inclusion of doping elements such as nitrogen or phosphorous (n-type) and/or aluminium or boron (p-type). Such doping can be achieved either during crystal growth or by established semiconductor industry techniques such as ion implantation.

In n-type crystals, the activation energy for ionization of nitrogen impurity varies with polytype (50,51). Resistivity is strongly dependent on crystal structure and impurities. It is generally accepted that boron and nitrogen can substitute for carbon in the SiC lattice (52,53), and aluminum is thought to substitute for silicon (49). In addition, high resistivity substrates of silicon carbides with resistivities as high as 10^{11} ohm·cm have been prepared, either by compensation doping using additional vanadium doping or by increased purity (54). Such wafers have the potential for use as semiconductor substrates in high frequency electronic devices, because the SiC has higher thermal conductivity than substrates needed for competing materials such as GaN, allowing better thermal dissipation (54).

Radiation Effects. Alpha silicon carbide exhibits a small degree of anisotropy in radiation-induced expansions along the optical axis and perpendicular to it (55). When diodes of silicon carbide were compared with silicon diodes in exposure to irradiation with fast neutrons (56), an increase in forward resistance was noted only at a flux about 10 times that at which the increase occurs in a silicon diode. In general, it seems that silicon carbide, having the more tightly bound lattice, is less damaged by radiation than silicon.

2.4. Optical Properties. The optical properties of silicon carbide crystals have been the subject of a great deal of research in recent years—both as a source of information about the basic properties of the material and as a part of potential commercial opto-electronic devices (such as blue LEDS).

Optical absorption measurements give band-gap data for cubic silicon carbide as 2.2 eV and for the α-form as 2.86 eV at 300 K (57). In the region of low absorption coefficients, optical transitions are indirect, whereas direct transitions predominate for quantum energies above 6 eV. The electron affinity is about 4 eV. The electronic bonding in silicon carbide is considered to be predominantly covalent in nature, but with some ionic character (57). In a Raman scattering study of valley-orbit transitions in 6H-silicon carbide, three electron transitions were observed, one for each of the inequivalent nitrogen donor sites in the silicon carbide lattice (58). The donor ionization energy for the three sites had values of 0.105, 0.140, and 0.143 eV (59).

Silicon carbide is now well established as a material for opto-electronic devices, in particular for blue LEDS and blue LASER devices. This market has now become the dominant commercial driver for the development of silicon carbide wafer technology, and fabricated devices are now entering a variety of industrial and consumer products (44).

3. Reactions

Silicon carbide is comparatively stable. The only violent reaction occurs when SiC is heated with a mixture of potassium dichromate and lead chromate. Chemical reactions do, however, take place between silicon carbide and a variety of compounds at relatively high temperatures. Sodium silicate attacks SiC above 1300°C, and SiC reacts with calcium and magnesium oxides above 1000°C and with copper oxide at 800°C to form the metal silicide. Silicon carbide decomposes in fused alkalies such as potassium chromate or sodium chromate and in fused borax or cryolite, and it reacts with carbon dioxide, hydrogen, air, and steam. Silicon carbide, resistant to chlorine below 700°C, reacts to form carbon and silicon tetrachloride at high temperature. SiC dissociates in molten iron, and the silicon reacts with oxides present in the melt, a reaction of use in the metallurgy of iron and steel. The dense, self-bonded type of SiC ceramic has good resistance to aluminum up to about 800°C, to bismuth and zinc at 600°C, and to tin up to 400°C; a new silicon nitride-bonded type exhibits improved resistance to cryolite.

In a study of oxidation resistance over the range 1200–1500°C, an activation energy of 276 kJ/mol (66 kcal/mol) was determined (60). The rate law is of the form $\delta^2 = kT + C$; the rate-controlling step is probably the diffusion of oxygen inward to the $SiC{-}SiO_2$ interface while CO diffuses outward. The oxidation rate of granular silicon carbide ceramics in dry oxygen at 900–1600°C was studied, and an equation for the effect of particle size was derived (61). Small changes in impurity content did not affect this rate, but the presence of water vapor and changes in partial pressure of oxygen were critical (61,62). Steam and various impurities and binders in ceramics also affect the oxidation of silicon carbide (63). Differences have been observed in oxygen adsorption on the different SiC crystal faces (64).

At high temperature, silicon carbide exhibits either active or passive oxidation behavior depending on the ambient oxygen potential (65,66). When the partial pressure of oxygen is high, passive oxidation occurs and a protective layer of SiO_2 is formed on the surface.

$$2\,\mathrm{SiC(s)} + 3\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{SiO_2(s)} + 2\,\mathrm{CO(g)}$$

Active oxidation occurs where the oxygen partial pressure is low and gaseous oxidation products are formed.

$$\mathrm{SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g)}$$
$$\mathrm{SiC(s) + 2\,SiO_2(s) \rightarrow 3\,SiO(g) + CO(g)}$$

A fresh surface of silicon carbide is thus constantly being exposed to the oxidizing atmosphere. Active oxidation takes place at and below approximately 30 Pa (0.23 mm Hg) oxygen pressure at 1400°C (66). Passive oxidation is determined primarily by the nature and concentration of impurities (67).

4. Manufacture and Processing

4.1. Generation of Different Physical Forms. The technologies needed for the manufacture of different physical states of silicon carbide are distinct and are usually specific to that form.

High Purity Single Crystal Manufacture. The commercial manufacture of electronic-grade high purity silicon carbide was revolutionized by the development of the so-called modifed Lely process in 1978 (68). This method is essentially a form of physical vapor transport growth in which silicon and carbon containing molecules (typically Si2C, SiC2, Si2, and Si) are transported at high temperatures across a specialized reactor to a growing seed crystal. Usually a temperature gradient is used to keep the seed crystal at a lower temperature than the carbon/silicon source, and this the vapor condenses onto the SiC seed. The source of the silicon and carbon atoms is usually a key element of the process—in traditional systems, such atoms are provided by a high temperature mass of silicon carbide (from which silicon and carbon containing molecules sublime), whereas in recent years, there has been substantial interest in using gas sources. The interest in using gas phase sources has been fuelled by the problems of ensuring the purity of a high temperature melt system—in particular, the difficulties of keeping down the level of impurties (such as atmospheric nitrogen) that affect the electrical properties of the silicon carbide wafer. Regardless of the type of source used, it is of crucial importance to reduce the density of crystal defects in the growing silicon carbide ingot. Several common defects have been identified, in particular, so-called micropipes (long-range hollow cylinders that can propagate through the ingot and a variety of stacking faults). Techniques for reducing both the frequency and the size of such defects have been developed, and the quality and size of commercial wafers have improved markedly in recent years. Currently, wafers up to 100 mm in diameter are available and further developments should drive wafer size and decrease wafer cost in the near future.

Methods of SiC Powder Generation. This is an essential prerequisite to the manufacture of many types of ceramic article (subsequently formed by forming the manufactured silicon carbide powder into the required shape). There are several routes to preparing SiC powders having variable purity levels, crystal structure, particle size, shape, and distribution. Methods that have been examined include growth by sublimation carbothermic reduction (the Acheson Process), conversion from polymers, and gas-phase chemical reactions.

Silicon carbide is usually commercially produced by the electrochemical reaction of high-grade silica sand (quartz) and carbon in an electric resistance furnace (the Acheson Process). The carbon is in the form of petroleum coke or anthracite coal. The overall reaction is

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

Sawdust may be added to increase the porosity of the furnace charge, thus increasing the circulation of the reacting gases and facilitating the removal of CO. The process has been reviewed (69). The substitution of anthracite coal for coke was advocated in the 1950s (70). The addition of a small percentage of common salt (typically 3%) to the melt introduces chlorine gas into the reaction zone to remove impurities (71). Also, addition of small amounts of boron, titanium, or zircon to the furnace charge reduces the product sensitivity to oxidation at 900–1100°C (72). In the Acheson process, the reduction of silica is carried out at temperatures in excess of 2100°C, resulting in α-SiC grains. The product produces crystals with a color that varies from pale yellow or green to black, depending on the amount of impurities. The manufactured product is usually crushed and graded for size. In such a furnace, considerable variation in reaction conditions exist within the furnace and different polytypes are usually found (73). In addition, it is common to find larger platelets (that may be of high quality) formed in voids within the reactor or on the walls.

The polymer conversion method consists of heating an organosilicon polymer, thereby obtaining a skeleton that contains carbon and silicon, to produce silicon carbide (74–78). Polycarbosilanes and polyborosiloxanes have been used. Some precursors for the organic polymer are polydimethylsilane obtained by a dechlorination condensation reaction of dimethyldichlorosilane [75-78-5], $C_2H_6Cl_2Si$. In many of these conversions, complete SiC formation is never achieved and beta silicon carbide coexists with graphite microcrystals. The material also has high (>10 wt%) oxygen content and hydrogen (0.02–8 wt%) content. Of the various thermal decomposition products of organosilicon polymers, the β-SiC ultrafine powder from polyborosiloxane was found to have the best sinterability. Polymer conversion routes have been successful in fabricating high strength SiC fiber such as Nicalon fiber, which are widely used to reinforce a range of metal-matrix composites.

A gas-phase synthesis route to making fine, pure SiC having controllable properties has been described (79,80). Methane was used as a carbon source if required, and the plasma decomposition of three feedstocks, silicon tetrachloride [10026-04-7], $SiCl_4$, dimethyldichlorosilane, and methyltrichlorosilane [75-79-6], CH_3Cl_3Si, into fine SiC powders was investigated. Another method of manufacturing SiC by the decomposition of a gas mixture containing silane, propane, and hydrogen, and hydrogen chloride has been described (81). With such a mixture, it was possible to work at a relatively lower (1200°C) temperature, and it was claimed that compact, homogeneous β-SiC crystals were obtained. In a variation of this gas-phase synthesis theme, SiC has been produced from the reaction of $SiCl_4$ and methane (82). SiC precipitates from 1000 to 3000°C.

Whiskers. Silicon carbide whiskers are all grown from the gas phase in one fashion or another. Those grown at the relatively low temperatures of

1200°C to 1800°C are composed of mostly β-SiC, those grown above 2000°C of α-SiC. Ribbonlike crystals are formed by sublimation (recrystallization) techniques similar to the Lely process. Hairlike crystals are mostly formed by a variety of chemical vapor deposition processes: from gaseous silicon–carbon compounds in the low temperature range, giving either α- or β-SiC; by reaction of gaseous carbon compounds with $SiCl_4$, usually at heated filaments such as *W* or on graphite surfaces, forming β-SiC; by reaction of hydrocarbons or other gaseous carbon species and silica at 1300°C to 1500°C, for example, $3\,CH_4 + SiO_2 \rightarrow SiC + 2\,CO + 6\,H_2$.

The hydrocarbon is carried in a stream of H_2 or Ar, and β-SiC is formed; or β-SiC is formed by reaction in the gas phase, under static conditions, of compounds such as SiO or CO formed *in situ* during the process. In this latter case, the important reaction seems to be $SiO + 3\,CO \rightarrow SiC + 2\,CO_2$. It takes place in some regions of the commercial Acheson furnace and in the Lely-type furnace.

In all of these processes, it is possible to increase the yield of whiskers by adding metallic impurities, and the sublimation process requires such additions. The vapor–liquid–solid (VLS) growth mechanism is often thought to be involved.

Silicon carbide whiskers typically have diameters of a few micrometers and lengths up to 5 cm. They may be composed of either β-SiC or α-SiC, the latter in one or more polytypes, and occur mostly as hair- or ribbonlike crystals. Despite many attempts to produce SiC whiskers on a large scale at low cost, they have never acquired a wide importance. SiC whiskers have been reviewed (83–92).

Fiber Manufacture. Silicon carbide is also a prime candidate material for high temperature fibers, particulary if they can be produced in long lengths. These fibers can be produced by three main approaches: polymer pyrolysis, chemical vapor deposition (CVD), and sintering. Whereas fiber from the former two approaches are already available as commercial products, the sintered SiC fiber is still under development. Because of its relatively simple process, the sintered α-SiC fiber approach offers the potential of high performance and extreme temperature stability at a relatively low cost. A comparison of the manufacturing methods and properties of various SiC fibers is presented in Table 5.

Table 5. **SiC Fiber Manufacturing Methods and Properties**[a]

Manufacturing method	Trade name	Manufacturer	Strength, GPa[b]	Maximum use temperature, °C	Modulus, GPa[b]	Diameter, μm
Sintering	[c]	Carborundum	0.93–1.24	>1550	414	30–100
		DuPont[d]	0.76	na	414	30–100
Polymer Pyrolysis	HPZ	Dow Corning	2.76	1300	193	10–12
	Nicalon	Nippon Carbon	2.62	1200	193	10
	Tyranno	Ube	2.76	1300	193	10
CVD coating	Sigma	BP/Carborundum	3.45–4.14	1250	414	100
	SCS-6	Avco	3.45–4.14	1400	414	140

[a] Ref. 93.

[b] To convert GPa to psi, multiply by 145,000.

[c] Sintered SiC fibers are still experimental.

[d] Ref. 94.

Platelet Formation. Alpha-SiC can also be synthesized in the form of platelets, a form that is often preferred because it poses fewer health risks than whiskers and is easier to process. The platelets are bounded top and bottom by a basal plane. They are grown by reaction of carbon and silica at high temperatures or by recrystallization of β-SiC, the low temperature structure of SiC, to α-SiC (95,96). When the basal planes are deactivated, commonly by the presence of B or Al compounds, the platelet is forced to grow in the planes perpendicular to the basal plane (97–99). Aspect ratios, the ratio of maximum length to minimum dimension, of 10 or greater are possible by appropriate choice of shape control additives. Various grades have been marketed. Average maximum dimensions range from 15 μm to over 100 μm (100–102). The platelets are mostly single crystals with 6H structure, but mixed polytypes can occur within a single platelet. The single-crystal character and the highly stable structure lead to the maximum stability possible in a SiC reinforcement. Platelets are being used mostly in Al-based metal matrix composites (MMC) but have been studied as reinforcements for ceramics also.

4.2. Formation of Silicon Carbide Ceramics Objects. In 1973, it was demonstrated that the simultaneous presence of boron and carbon is required to densify, without pressure, a green compacted body of beta silicon carbide (103). Pressureless sintering techniques were subsequently established (104–107) for α-SiC powder made by inexpensive methods such as the Acheson process. In either case, a density above 98% theoretical is reported. The SiC powder used plays the most decisive role in obtaining high sintered densities and uniform microstructures. Essential characteristics are the kind and quantity of impurities, grain size, and the specific surface area (108,109). A densification mechanism by volume or grain boundary diffusion in the solid state has been reported for boron- and carbon-doped SiC (110–114). Various ceramic-forming methodologies such as dry pressing, slip casting, and extrusion and injection molding can be used to produce both simple and complex shapes using the pressureless sintering process.

This boron- and carbon-doped SiC exhibits excellent strength and stiffness, extreme hardness, and thermal and chemical resistance. The strength of this system is not affected by temperatures up to 1650°C. Creep is virtually nonexistent up to 1400°C. Cyclic durability testing conducted at 1370°C in air showed no deterioration of strength after 3500 h (115).

Pressureless sintering of α- and β-SiC powders can also be achieved by the addition of aluminum and/or aluminum compounds together with carbon or rare-earth elements (116–126). Boron-free, aluminum-containing sintering aids inhibit grain growth (116,125). Aluminum oxide together with yttrium oxide as additives yield a fine and unique microstructure (125). A liquid-phase sintering mechanism has been reported in this aluminum oxide and rare-earth oxide-doped SiC system (125,127). Fine microstructure, good chipping resistance, and over 800-MPa (116,000 psi) room temperature strength have been reported (118,125). Creep resistance and other high temperature related properties are not as good as the boron- and carbon-doped SiC, in general.

Other types of sintering additives such as Be, P, N, and nitrogen compounds have been used (128–131) to modify the electrical properties of SiC, which is intrinsically a semiconductive material. Beryllium and its compounds increased the electrical resistivity dramatically, while maintaining good thermal conductivity, and provided a feasible route to make SiC substrates for electronic applications; however, the potential health hazard of beryllium compounds has become an issue. Nitrogen and P together with Al and B, on the other hand, reduce the electrical resistivity of SiC. This electrically conductive SiC and its good oxidation resistance make SiC an attractive material for heating element and igniter applications.

The high modulus, high intrinsic strength, and temperature stability make SiC, in the form of whiskers, platelets, and fibers, a promising candidate reinforcement material for metal, polymer, and ceramic matrix composites.

5. Economic Aspects

Silicon carbide was first manufactured on a large scale in 1892, but production did not reach 8200 t/year until 1918. World production capacity of silicon carbide was estimated to be 2010×10^3 t in 2005 (Table 6). The average value per ton of all grades of SiC was $388.

Table 7 shows the production and other salient statistics for abrasive silicon carbide in the United States and Canada. In 2005 two firms were producing crude silicon carbide in the United States. U. S. production had an estimated value of $\$22.4 \times 10^6$.

One of the first important uses of silicon carbide was as an abrasive. Additional markets in refractories, electrical devices, and metallurgy have since been developed.

Table 6. **World Production Capacity of Silicon Carbide, $\times 10^3$ t**[a]

	Capacity	
Country	2004	2005[b]
United States and Canada	42.6	42.6
Argentina	5	5
Australia		
Austria		
Brazil	43	43
China	455	455
France	16	16
Germany	36	36
India	5	5
Japan	60	60
Mexico	45	45
Norway	80	80
Venezuela	30	30
Other countries	190	190
World total (rounded)	*1010*	*1010*

[a] Ref. 132.

[b] Estimated.

Table 7. **Salient Statistics for Silicon Carbide: United States and Canada**[a]

Salient Statistics	2001	2002	2003	2004	2005[b]
production, United States and Canada (crude)					
Silicon carbide	40,000	30,000	35,000	35,000	35,000
imports for consumption (U.S.)					
Silicon carbide	133,000	165,000	169,000	209,000	199,000
exports (U.S.)					
Silicon carbide	10,500	13,600	13,200	13,900	12,200
consumption, apparent (U.S.)					
Silicon carbide	NA	181,000	189,000	230,000	222,000
price, dollars per ton United States and Canada					
Silicon carbide	603	532	529	614	600
net import reliance as a percentage of apparent consumption (U.S.)					
silicon carbide	NA[c]	83	82	85	84

[a] Ref. 132.

[b] Estimated.

[c] NA = not available.

6. Specifications and Standards

In the United States, the test methods, specifications, and standards for abrasive grain products are established by the Abrasive Grain Association (AGA) (133), the Grinding Wheel Institute (GWI) (134), and the Coated Abrasive Manufacturing Institute (CAMI) (135). These associations publish standards and specifications through the American National Standard Institute, Inc. (ANSI), New York. In Europe, the International Standards Organization (ISO) issues standards in cooperation with corresponding associations in Austria, France, Germany, Great Britain, Italy, Norway, Spain, Sweden, and Switzerland. The Japanese Standards Association (136) issues standards and methods for Japan. In addition, principal silicon carbide producers have tests, processes, and product specifications for internal use, usually for products not covered by industry standards.

7. Analytical and Test Methods

The analysis of silicon carbide involves identification, chemical analysis, and physical testing. For identification, x-ray diffraction, optical microscopy, and electron microscopy are used (137). Refinement of x-ray data by Rietveld analysis allows more precise determination of polytype levels (138).

Chemical analysis of abrasive grain and crude in the United States is carried out by using a standard analysis scheme approved by the AGA (133) and issued by the ANSI (139). Grain is usually analyzed for silicon carbide content, free silicon, free carbon, free silica, calcium oxide, magnesium oxide, and oxides of iron, titanium, and aluminum. The standard scheme specified by ANSI uses a combination of gravimetric, volumetric, calorimetric, and atomic absorption techniques. Carbon is usually converted by combustion to carbon dioxide, which is then measured by weighing an absorption bulb (139) or by reading the electrical or thermal conductivity (140). A silicon carbide standard reference material, NBS SRM-112b, is available (141). In Europe and Japan, standard analysis schemes, similar to the ANSI scheme, have been developed by ISO (142) and JSA (143). Instrumental techniques such as x-ray fluorescence, emission spectroscopy, atomic absorption, and neutron activation analysis are used as additional methods of analysis, especially where applications require knowledge of a wide range of trace metals.

In the United States, several physical tests are performed on silicon carbide using standard AGA-approved methods, including particle size (sieve) analysis, bulk density, capillarity (wettability), friability, and sedimentation. Specifications for particle size depend on the use; for example, coated abrasive requirements (135) are different from the requirements for general industrial abrasives. In Europe and Japan, requirements are again set by ISO and JSA, respectively. Standards for industrial grain are approximately the same as in the United States, but sizing standards are different for both coated abrasives and powders.

8. Health and Safety Factors

Silicon carbide has been described as a mild inhalation irritant (144). The threshold limit value for silicon carbide in the atmosphere is 5 mg/m^3. Because of increased interest in SiC whiskers as a reinforcement for composites, the ASTM has established Subcommittee E34.70 on Single-Crystal Ceramic Whiskers to write standards for handling this form of SiC (145).

9. Uses

9.1. Wear Surfaces. The extreme hardness of silicon carbide leads to its use where wear resistance is important as in brake linings or electrical contacts, and for nonslip applications such as floor or stair treads, terrazzo tile, deck-paint formulations, and in road surfaces. SiC is commonly used as a seal face material in mechanical seals used in pumps, compressors, and agitators in a wide variety of demanding environments including highly corrosive ones. More recent applications include the use of silicon carbide in automotive water pump seals and faucet washers. Other uses include blast and atomization nozzles, rocket nozzle inserts, thrust and journal bearings in magnetically driven pumps, pump sleeves, valve seats, and choke inserts.

9.2. Armor. Silicon carbide is used as a candidate in composite armor protection systems. Its high hardness, compressive strength, and elastic modulus provide superior ballistic capability to defeat high velocity projectile threats. In addition, its low specific density makes it suitable for applications where weight requirements are critical (10).

9.3. High Temperature. The low coefficient of thermal expansion and high thermal conductivity of silicon carbide bestow it with excellent thermal shock resistance. Combined with its outstanding corrosion resistance, it is used in heat-transfer components such as recuperator tubes, and furnace components such as thermocouple protection tubes, crucibles, and burner components. Silicon carbide is being used for prototype automotive gas turbine engine components such as transition ducts, combustor baffles, and pilot combustor support (146). It is also being used in the fabrication of rotors, vanes, vortex, and combustor.

9.4. Refractories. Its low coefficient of expansion, high thermal conductivity, and general chemical and physical stability make silicon carbide a valuable material for refractory use. Suitable applications for silicon carbide refractory shapes include boiler furnace walls, checker bricks, mufflers, kiln furniture, furnace skid rails, and trays for zinc purification plants.

9.5. Electrical. Heating elements made from recrystallized silicon carbide, used in electric furnaces, operate up to about 1600°C and represent a significant electrical use of silicon carbide. Heating elements are also used as a source of infrared radiation for drying operations, a light source for mineral determinations, and an ignition source for oil- or gas-fired burners. A more recent use is in ignition devices for gas clothes dryers and cooking ranges. There has been significant development of silicon carbide furnace element technology, in particular, methods for the reduction of heating at the ends (so-called "cold-ends"). This development was originally by the use of larger diameter sections at the ends (and thus less heating occurred in these sections due to lower resistance) but more recently by the use of conductive silicon alloy integrated into pores in the silicon carbide element. Techniques for diffusion bonding have also been applied to the manufacture of complex element shapes and multi-prong elements are now common.

9.6. Electronic. Considerable interest in the solid-state physics of silicon carbide, that is, the relation between its semiconductor characteristics and crystal growth, has resulted from the expectation that SiC would be useful as a high temperature-resistant semiconductor in devices such as point-contact diodes (147), rectifiers (148), and transistors (149,150) for use at temperatures above those where silicon or germanium metals fail. SiC, with its potential for operation at higher voltages, temperatures and power densities than Si, is well poised to revolutionize power electronic technology. Most major classes of the power semiconductor device have been demonstrated at the research level, and SiC is already beginning to penetrate the sector at the commercial level. Indeed, the materials technology has now advanced to the point where large volume commercialization of elementary power device structures, such as Schottky and PIN diodes, is occurring. However, key technological issues must be resolved if the full market potential of SiC is to be realized.

SiC microwave power devices have already achieved considerable maturity with performance, which considerably exceeds that available from other semiconductors. Two basic device variants have been successfully fabricated: the MESFET and the static induction transistor (SIT) (151,152). Both are basically Schottky gate controlled majority carrier devices, with the MESFET having a surface channel for higher frequency use and the SIT a vertically oriented channel.

Many groups worldwide have been quick to recognize the potential of SiC Schottky diodes, and with recent improvements in material quality, some impressive practical demonstrations have resulted (153,154). Total yields of over 50% have been obtained for 1.5-mm^2 diodes, and detailed studies of performance and reliability have revealed no significant problems. Such devices are attractive as fast recovery diodes in most power electronic circuits as freewheeling and/or snubber components. Since the introduction of the insulated gate bipolar transistor (IGBT), diodes in many circuits have been subjected to even higher voltage and current levels, and have been required to switch at much higher frequencies (>10 kHz). It is now widely recognized that silicon fast recovery diodes have reached their limit and that they are now the limiting factor in IGBT circuits from 600 V to 2.5 kV and above. SiC Schottky diodes can be based on much thinner, more heavily doped material (on account of the higher breakdown field) than equivalent Si devices and thus exhibit relatively low on-resistance. For example, an ideal SiC Schottky diode might attain a breakdown voltage approaching 1800 V or roughly 10 times higher than that possible in Si, while achieving a lower specific on resistance.

Of the major classes of power semiconductor, the MOSFET probably has the greatest strategic importance in SiC power electronics, largely because it offers a practical solution for majority carrier operation at voltage ratings approaching 5 kV. Although many devices have been demonstrated on 4H-SiC (155,156), the measured on-state performance has been disappointing, largely because of the relatively poor effective channel mobility.

Although it is clear that a substantial market exists for SiC electronics, the rate of commercialization will be limited by the materials technology and, more importantly, cost. Currently, the cost of SiC substrates exceeds those of Si by a factor of nearly 100. Although less SiC is needed to perform an equivalent function (current densities may be up to 10 times higher than in Si), this is not sufficient to offset the additional wafer costs. In addition, the processing costs for SiC are still relatively high, whereas those for Si are falling as the market for power semiconductors continues to expand. The net effect is that something approaching a factor of 10-fold reduction in both the cost of the starting material and the cost of processing is needed before SiC can compete with Si on equal terms. Where a net system advantage can be demonstrated, however (eg, reduced cooling cost outweighs extra die cost), the benefits of SiC may be realized in the shorter term. For more specialist applications, where Si technology cannot compete directly (eg, hostile and high temperature environments), the cost limitation is less relevant; however, the need to recover the full costs on a relatively small initial market may stifle development.

9.7. Abrasives. Silicon carbide is used in loose form for lapping; mixed with a vehicle to form abrasive pastes or sticks; mixed with organic or inorganic binders; shaped and cured to form abrasive wheels, rubs, or tumbling nuggets; bonded to paper or cloth backings to form abrasive sheets, disks, or belts; or incorporated with the fibrous backing material before sheeting. Silicon carbide is harder yet more brittle than abrasives such as aluminum oxide. Because the grains fracture readily and maintain a sharp cutting action, silicon carbide abrasives are generally used for grinding hard, low tensile-strength materials such as chilled iron, marble, and granite, and materials that need sharp cutting action such as fiber, rubber, leather, or copper.

9.8. Metallurgy. Silicon carbide is used extensively in ferrous metallurgy. When added to molten iron, a vigorous exothermic reaction takes place decomposing the silicon carbide and resulting in a hotter melt. The effect is to deoxidize and cleanse the metal and promote fluidity. Thus, a more desirable random distribution of the graphite flakes is achieved and a more machinable product is obtained. Current practice is to add the silicon carbide as briquettes to the cupola or in loose granular form to induction furnaces when producing cast iron. When added as granules to molten steel in the ladle, it reduces the number of undesirable inclusions and leads to better physical properties in the product. When added as granules to steel in a basic oxygen furnace, it extends the capacity of the furnace to melt more scrap as a result of the exothermic reaction.

9.9. Gemstones. Silicon carbide may also be used as a diamond replacement in jewelry and other decorative uses. The color of the material is, however, highly sensitive to the concentration of trace impurities, and thus, high-purity CVD grown material is desirable. Such crystals are clear and can easily be mistaken for true diamond—in fact, some conventional tests for diamond in the jewelry industry are not sensitive to silicon carbide (in particular, those based on crude physical properties such as thermal conductivity, hardness, and/or electrical resistivity). The hardness of silicon carbide is close to that of diamond (9.25 Mohs compared with 10 for diamond), whereas the comparatively large difference in refractive index (typically 2.65 compared with 2.42 for pure diamond) make optical tests more discriminating.

9.10. Other Uses. The special characteristics of silicon carbide give rise to a wide range of applications, including catalyst-carrier nuggets, tower packing, and pebbles for pebble-bed heaters or fluidized-bed reactors. It is used as a raw material for the production of silicon tetrachloride; in welding-rod compositions; as a filler in elastomers; as an additive in other ceramic materials to increase high temperature resistance; and as an ingredient of red glaze. Silicon carbide has been tested as a diluting agent in the coal gasification process.

The ultrafine silicon carbide produced in an electric arc is used as an insulation in cryogenic applications (157). It generally increases the wear resistance of the paint film when added to paint formulations.

Coatings of dense silicon carbide have been applied to materials such as graphite or silicon by various chemical vapor deposition processes. The coatings increase the oxidation and erosion resistance of the substrates for a wide range of applications. A silicon carbide–graphite material has been developed by Carborundum that can serve as a sputtering coating target.

Silicon carbide's relatively low neutron cross section and good resistance to radiation damage make it useful in some of its new forms in nuclear reactors. Silicon carbide temperature-sensing devices and structural shapes fabricated from the new dense types are expected to have increased stability. Silicon carbide coatings may be applied to nuclear fuel elements, especially those of pebble-bed reactors, or silicon carbide may be incorporated as a matrix in these elements (158,159).

A silicon carbide-bonded graphite material in which graphite particles are distributed through the silicon carbide matrix has high thermal shock resistance and is suitable for applications including rocket nose cones and nozzles and other severe thermal shock environments (160). This material has also found use as a disk brake in high performance automobiles.

Materials made of silicon nitride, silicon oxynitride, or sialon-bonded silicon carbide have high thermal shock and corrosion resistance and may be used for pump parts, acid spray nozzles, and in aluminum reduction cells (161–164). A very porous silicon carbide foam has been considered for surface combustion burner plates and filter media. It can also be used as a substrate carrying materials such as boron nitride as planar diffusion source for semiconductor doping applications.

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