

1.1 History

Silicon carbide (SiC) was accidentally discovered in 1890 by Edward G. Acheson, an assistant to Thomas Edison, when he was running an experiment on the synthesis of diamonds. Acheson thought the new material was a compound of carbon and alumina present in the clay, leading him to name it carborundum, a name that is still being used on some occasions. Silicon carbide occurs naturally in meteorites, though very rarely and in very small amounts. Being the discoverer of SiC, Acheson was the first to synthesize SiC by passing an electric current through a mixture of clay and carbon. Today, SiC is still produced via a solid state reaction between sand (silicon dioxide) and petroleum coke (carbon) at very high temperatures in an electric arc furnace.

In the past, the list of ceramics used as industrial materials consisted of alumina and other oxides. In recent years, there have been strong demands for the use of ceramics as structural materials in place of metals and alloys and for use in harsh environments. Consequently, new ceramics such as nitrides, carbides and other covalently bonded materials have received increased attention because of their unique characteristics.

1.2 The Si-C System

The formation of SiC from the reaction between silicon and carbon can take place at temperatures below the melting point of silicon. The phase diagram of the Si-C system is shown in Figure 1.1. It can be seen that SiC is the only compound of silicon and carbon to occur in the condensed state in addition to elemental silicon and carbon. A eutectic point between silicon and SiC exists at 1402°C and 0.75 atom % carbon. The liquidus curve between Si and SiC is shown up to 2600°C and 27 atom % C. A peritectic point is located at 2540°C and 27 atom % C under normal conditions.

There are numerous (~200) polytypes for SiC, but only a few are common. All of the structures may be visualized as being made up of a single basic unit, a layer of tetrahedra, in which each silicon atom is tetrahedrally bonded.
to four carbon atoms and each carbon atom is tetrahedrally bonded to four silicon atoms. The differences among the existing polytypes are the orientational sequences by which such layers of tetrahedra are stacked. Successive layers of tetrahedra may be stacked in only one of two ways or orientations but with many possible sequential combinations, each of which represent a different crystal polytype.

A common system of nomenclature used to describe the different crystalline polytypes assigns a number corresponding to the number of layers in the unit cell followed by a letter suffix designating the crystal symmetry; “C” for cubic, “H” for hexagonal and “R” for rhombohedral. The most common SiC polytypes are the 3C, 4H, 6H, 15R and 9T. The cubic 3C is commonly referred to as beta silicon carbide, β-SiC, which has the zinc blend structure, while all other polytypes are referred to as alpha silicon carbide, α-SiC. In general, α-SiC phase is mainly 6H, which is a wurtzite structure. Figure 1.2 shows an illustration of the two major crystal structures, zinc blend and wurtzite, exhibited by the two SiC phases. Phase transformation of SiC occurs from β-SiC to α-SiC upon heating. Undoped β-SiC transforms to 6H and 15R above 2000°C, with the 15R being a metastable phase that transforms to 6H. Doping β-SiC with boron lowers the transformation temperature and results in the formation of 4H polytype. On the other hand, doping with nitrogen prevents the formation of 4H and stabilizes the 6H. The β→α phase transformation is irreversible under ambient atmosphere. However, under pure nitrogen atmosphere, the transformation can be reversed and β-SiC phase can be stabilized up to 2500°C by applying a nitrogen pressure. Under atmospheric pressure, silicon carbide does not melt when heated to elevated temperatures rather, it sublimes and/or dissociates. In addition, incongruent melting of SiC was reported at 2829°C under >500 psi pressure of argon and is also possible when it is heated rapidly in an arc-image furnace at atmospheric pressure.

Silicon carbide is considered one of the few lightweight covalently bonded ceramics. The theoretical density of β-SiC is only 3.210 g/cm³ and that of α-SiC (6H polytype) is 3.208 g/cm³. Combining it’s lightweight and strong covalency with other properties, such as low thermal expansion coefficient and high thermal conductivity, strength and hardness, make SiC a promising ceramic for the replacement of conventional metals, alloys and ionic-bonded ceramic oxides.

1.3 Production of SiC

The most common forms of SiC include powders, fibers, whiskers, coatings and single crystals. There are several methods to produce SiC depending on the product form desired and its application. Purity of the product imposes certain restrictions on the selection of the method of production.

SiC powders are produced predominantly via the traditional Acheson method where a reaction mixture of green petroleum coke and sand is heated to 2500°C using two large graphite electrodes. Due to the high temperatures, the Acheson process yields the alpha form of SiC, i.e. hexagonal or rhombohedral (α-SiC). The SiC product, usually in the form of a large chunk, is broken, sorted, crushed, milled, and classified into different sizes to yield the commercial grades of SiC powder. To produce ultrafine SiC powder, the finest grade of the Acheson product is further milled, typically for days, and then acid-treated to remove metallic impurities. Fine SiC powder can also be produced using a mixture of fine powders of silica and carbon reacted at lower temperatures for short periods of time followed by quenching to prevent grain growth. The product, however, is agglomerates of SiC and needs to be attrition milled to break up the agglomerates and reduce the particle size to submicron range. SiO₂ powder can be replaced with SiO (silicon monoxide) powder which, when mixed with nano-scale carbon and heated to moderate temperatures, produces nanocrystalline SiC powder with particle size in the range 20-100 nm. The SiC particle characteristics, such as size, shape and surface chemistry, are very important for the subsequent densification processes of the SiC powder. For this reason, some post processes may be needed, such as the addition of certain elements as sintering aids, to achieve high density during hot pressing or pressureless sintering.

SiC fibers are produced via the pyrolysis of organosilicon polymers, such as polysilacarbosilane, and are commercially available. Briefly, the process consists of melt-spinning the polycarbosilane at approximately 300°C, unfusing with thermal oxidation at 110-200°C, and baking at 1000-1500°C under a flow of inert gas. Nicalon fibers are known for their excellent mechanical properties when used as reinforcement in ceramic matrix composites.
SiC whiskers, which are nearly single crystals, are produced (grown) using different methods, including the heating of coked rice hulls, reaction of silanes, reaction of silica and carbon, and the sublimation of SiC powder. In some cases a third element used as a catalyst, such as iron, is added to the reacting materials to facilitate the precipitation of the SiC crystals. In this arrangement, the mechanism for the SiC whisker growth is called the vapor-liquid-solid (VLS) mechanism. SiC whiskers are in the order of microns in diameter and grow several hundred microns in length. The VLS process, developed by the Los Alamos National Laboratory to produce longer SiC whiskers with larger diameters, did not show promise for production due to the extremely low yield. Currently, commercially available SiC whiskers are produced using the rice-hull process with the whisker growth being largely by vapor-solid process with the absence of a catalyst. Because of their excellent mechanical properties, SiC whiskers are very desirable as reinforcements of metal and ceramic matrix composites for structural applications where fracture toughness and strength are significantly improved.

1.4 Fabrication of SiC Products

In addition to the efforts and significant development in the production of different forms of SiC (powders, fibers, whiskers, etc.), more efforts have been devoted to the fabrication of SiC parts as a final product with the desired properties. The densification of the SiC powders has been the largest part of these efforts. Analogous to powder metallurgy techniques, SiC powders have been densified using hot pressing, hot isostatic pressing, and pressureless sintering, in addition to wet processing, such as slip casting of SiC powder slurries. Sintering of SiC powders requires the addition of sintering aids and heating to elevated temperatures. The addition of boron and carbon elements to SiC powder assists in the densification of SiC during pressureless sintering. Carbon is added to remove surface oxygen present as a film of SiO₂ on the SiC particles. Boron, on the other hand, is added to prevent grain growth at lower temperatures before reaching the sintering point. A density of 97% of the theoretical density can be reached depending on the temperature and characteristics of the SiC powder. Other sintering aids include oxides, such as alumina, zirconia and yttria. In this system, the oxide phase melts at relatively low temperatures enhancing SiC particle flow, resulting in shrinkage and densification. However, due to the presence of the liquid phase, there are limits to the high temperature applications of the densified parts.

For the fabrication of SiC/SiC composites, a preform is first prepared from continuous SiC fibers with 20-30% loading by volume. A SiC matrix can be applied via the CVI process, or slurry processing, to make SiC/SiC composite. The SiC matrix can also be produced by impregnating the SiC preform with liquid carbon precursor, such as a resin, followed by pyrolysis and silicon infiltration to form reaction-bonded SiC/SiC composite. The SiC fiber preforms can also be impregnated with silicon powder in the form of slurry, followed by nitridation to form SiC-fiber reinforced Si₃N₄ matrix composites. SiC-fiber reinforced ceramic composites are used in high-temperature structural applications due to their high strength and fracture toughness.

The processes discussed above produce SiC materials that contain high levels of impurities associated with the processing steps. Impurities, such as metal-based sintering additives, are not acceptable in the semiconductor industry. Conventional purification by high-temperature chlorination results in the depletion of silicon from the SiC and carbon enrichment. In addition, the presence of impurities in SiC may become an issue in high-temperature applications depending on the type and level of these impurities.

1.5 POCO Process

A proprietary process developed by POCO takes advantage of the ease of graphite machining. POCO’s process starts with graphite that has already been processed, pre-machined into the desired part, and purified, followed by the chemical conversion to SiC, without altering the shape or purity of the part. This approach yields a SiC product that has superior chemical properties.
and very high purity as compared to traditionally produced SiC products.

The conversion of the graphite parts to SiC takes place when they are exposed to silicon-carrying species, such as silicon monoxide (SiO) gas, at high temperatures. Figure 1.3 is a flowchart showing, in sequence, all the steps involved in POCO’s SiC conversion process. The SiO gas is generated in-situ using a proprietary mixture of high-purity silica and carbon powders in inert atmosphere. The following is a typical reaction for the generation of SiO gas:

\[
\text{SiO}_2 + C \rightleftharpoons \text{SiO} + \text{CO}
\]  

(1.1)

It is essential that the graphite material have a reasonable open porosity for the SiO gas diffusion. POCO’s specially-developed graphite grade, with the tailored porosity and particle size distribution properties, meets the requirements of the conversion process. The generated SiO is transported from the generation zone to the conversion zone, which contains the graphite parts to be converted to SiC. POCO has engineered the process so that SiO gas is transported efficiently from the generation zone to the conversion zone and distributed evenly to ensure uniform conversion. In the conversion zone, the reaction between the SiO and graphite takes place according to the following reaction:

\[
\text{SiO} + 2 \text{C} \rightleftharpoons \text{SiC} + \text{CO}
\]  

(1.2)

Following the chemical conversion of the net-shape graphite part to SiC, the parts are usually grit blasted using high purity SiC to remove any surface debris, followed by ultrasonic cleaning to remove any dust and loose particles. The as-converted SiC material is POCO’s basic grade of SiC, denoted as “SUPERSiC-1”.

Some SiC products cannot be fabricated as a contiguous part due to part complexities. One example in the semiconductor industry is the vertical wafer carrier, in which the individual components (rails and plates) are fabricated as described above and then assembled using a specially developed joining material. POCO has developed a joining material that is currently being used in the assembly process. The constituents and composition of the joining material, as well as the application procedure, is considered proprietary information. However, the joining material is applied as a paste at room temperature and, after processing, the material converts to high purity, high strength SiC material. The types and characteristics of the raw materials constituting the paste were selected to exhibit minimum shrinkage and cracking during processing for maximum strength.

SUPERSiC-1 is subjected to additional post processes for the purpose of sealing the surface by eliminating surface porosity. Two approaches being used for this purpose are described below:

**CVD SiC Coating:** POCO has developed the capability to apply a thick, dense SiC coating on its basic SUPERSiC-1 grade using chemical vapor deposition (CVD) technology. CVD-SiC coating has very high density and purity and excellent uniformity. In addition, POCO’s process is very flexible and controllable to meet desired properties, such as the coating thickness and microstructure. A coated SUPERSiC-1 grade is denoted as “SUPERSiC-2” and is available as a standard product.

**PG Infiltration/Conversion/SiC Coating:** To increase the efficiency of the CVD SiC coating mentioned above, the porous SiC part, or SUPERSiC-1, is first infiltrated/coated with pyrolytic carbon using a proprietary process developed by POCO, followed by conversion to SiC as described above. This treatment provides a new layer of SiC that is partially impeded in the porous substrate. The converted SiC layer is much less porous and the pore size is much smaller than that of the SUPERSiC-1 substrate. The part will still be coated with a CVD SiC layer as described above, as this will improve the adhesion of the CVD SiC coating and sealing efficiency. The new grade is denoted as SUPERSiC-4.