MONTANA STATE UNIVERSITY

Silicon carbide synthesis using high-sulphur petroleum fluid coke and Montana silica
by Raymond Clayton Suiter

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
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Abstract:
This thesis is based on a study of the technical feasibility of synthesizing silicon carbide from high-sulfur petroleum fluid coke and Montana silica. A laboratory pilot-plant carbon resistance furnace was designed and constructed for this purpose.

Several possible reactions which might occur were studied thermodynamically to determine the theoretical feasibility of the completion at about 2100° C and any pressure. It was also found that losses in yield, due to the formation of silicon sulfides, were unlikely. The formation of the sulfides did not appear to be thermodynamically feasible, based on estimated thermodynamic data of fair reliability. Should these thermodynamic conclusions be in error, however, any sulfides formed would merely dissociate at temperatures above 1000&deg,C.

Both the high-temperature (alpha) and low temperature (beta) species of silicon carbide were synthesized from these materials, as substantiated by x-ray diffraction powder analysis. The maximum size crystals produced were about 0,2 millimeters on a side.

It was found that silicon carbide could best be produced when the resistance furnace was operated at a 1950-2100 watt power input at an optically observed temperature of about 1700°C and a current input not exceeding 440-450 amperes. This operation yielded a true temperature of about 2100°C in the reaction zone. Nitrogen purging was used to reduce the reaction zone oxygen content.

A maximum concentration of 55.7 per cent of an alpha-beta mixture of silicon carbide was obtained in the reacted mass, using the fluid coke as a carbon source and operating at optimum furnace conditions. The concentrations were compared with those obtainable by using pure graphite as a carbon source. Yields obtained using fluid coke appear to be about 90 per cent of those obtained by using graphite.

In a fixed reaction volume, the bulk volume per cent of the raw material ingredients affects the total yield. An increase in the bulk volume per cent of silica in the charge results in an increased yield of silicon carbide. It was found that the volume per cent of silica in the reaction charge could be varied from 40 to 55 per cent and this resulted in a silicon carbide concentration increase of about 20 per cent in the reacted mass.

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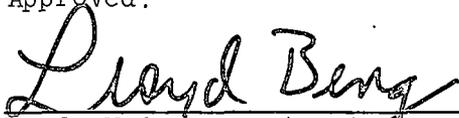fulfillment of the requirements for the degree

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iii

ACKNOWLEDGMENT

iv

TABLE OF CONTENTS

v

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (continued)

ABSTRACT

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INTRODUCTION

What is Silicon Carbide?

Silicon carbide (SiC) is a crystalline substance varying in color from pale green or yellow to black depending primarily on the amount and type of impurities present. The compound exists in two crystallographic species and several sub-forms (2).

A low temperature species, or beta silicon carbide, was discovered in 1926 and has a cubic structure. For many years, this material was considered amorphous due to the lack of such methods as x-ray diffraction crystal exmination. It is still considered microcrystalline and attempts to obtain quantities of very large crystals have been largely unsuccessful and the maximum size crystal is usually about 0.5 mm (2). Even crystals of this size rarely exhibit any developed crystal faces. Beta silicon carbide was formed at temperatures as low as 525°C by Baumann from silicon and carbon; however, in commercial furnaces it is believed that the material begins to form somewhere in the range of 1300° - 1400°C. It is known to be stable up to approximately 2000°C, at which point there is a transition from the cubic to other forms (2, 15).

By and large, the major constituent of commercial processing is the high temperature species, alpha silicon carbide. This material occurs in at least ten different crystalline sub-forms, or modifications, which are very closely related. A discussion of these modifi-

cations is not related to this project and will not be presented.
In general, alpha silicon carbide can merely be referred to as the
commercial or hexagonal variety, although it occurs in both the
hexagonal and rhombohedral classes. Alpha silicon carbide results
from the beta transition and is then stable to about 2700°C. Figure
1 shows a plot taken from Baumann (2) showing time-temperature re-
lationship of beta silicon carbide to alpha silicon carbide.

Silicon carbide is best known for its extreme hardness, being
the first material to enter the range of hardness between corundum
(Al_2O_3) and diamond or between 9 and 10 on Moh's hardness scale (25).
The discovery of boron carbide necessitated a better scale of hard-
ness between corundum and diamond. Knoop and his co-workers devised
a diamond indentation method of measurement, whereby fused alumina
measured 1635; silicon carbide 2000; boron carbide 2230; and diamond
8000-8500 (18). More accurate methods for measuring relative hard-
ness values have also been developed and include abrasion tests and
impact abrasion tests.

Silicon carbide, in addition to its extreme hardness, is very
stable chemically. Very few chemicals attack it; however, air will
oxidize it at high temperatures and it will dissociate completely at
about 2700°C. The compound is thus a very desirable fabricating
material in many systems and its high thermal conductivity (90 BTU/hr/
ft.^{2}/in./°F) deems it desirable for a multitude of refractory uses.

Uses of Silicon Carbide

Although best known for its abrasive and cutting qualities, silicon carbide has tremendous versatility. Table III shows a list of the major uses of silicon carbide as compiled by Butler (4). It is noted that the uses are broken down into six major divisions. There is every indication that this outstanding material will become even more diversified in the future. Many new applications are expected as methods for obtaining large quantities of ultra-pure material are developed.

History of Silicon Carbide

In our highly sophisticated and specialized era of space age science, it is hard to imagine a discovery, invention, and industry as being the net product of a single individual. However, this is precisely what happened in the development of silicon carbide.

Edward G. Acheson, the discoverer of silicon carbide was born in Washington, Pennsylvania in 1856. Mr. Acheson was among a school of "practical scientists" which evolved as a result of the era of American mechanization (24). After several years of practical and academic training (including study at Thomas Edison's famed Menlo Park Laboratory) in electricity and other areas, Mr. Acheson began to emerge as a skilled scientist, able administrator, and financial wizard. Finally, in the summer of 1891, after an already impressive period of accomplishments, Acheson made his famous discovery of silicon

carbide (25). In a small iron bowl, Acheson sent an electric current
from a carbon electrode through a mixture of clay and powdered coke to
the iron container. It is interesting that he was attempting to form
diamonds by dissolving carbon in molten clay (hoping the carbon molecules
would rearrange to the crystalline form of diamond). The paradigms of
the electrochemical field of Acheson's day, led him to believe that the
attainment of diamonds was quite possible (19).

When Acheson first examined the results of his experiment, he
saw little of interest. However, closer inspection of the carbon rod
revealed small blue crystals which had formed on the end of the electrode.
Very delighted, he felt that the crystals could only be a mixture of
carbon and corundum, since they were obviously not diamonds. Thus,
he named the new product "Carborundum", a trade name which exists
today (25).

Acheson immediately recognized the possibilities of these hard
crystals and, after enlarging his small furnace, he made enough product
to take to the lapidaries in New York for examination. He sold his
supply immediately and used the proceeds to buy his first good micro-
scope with which to study his new product. After a few months of study,
Acheson suspected that his crystals were actually silicon carbide. He
further substantiated his suspicions by qualitative and crystallographic
observations. On this basis, the reaction which had taken place was
hypothesized as: $SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$
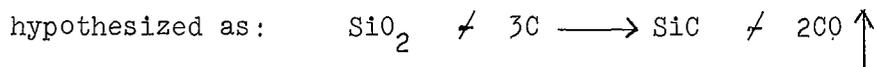
We now know that this reaction actually takes place in two steps, the second reaction being almost instantaneous, and the reactions beginning somewhere in the range of $1400° - 1500°C$ (27, 31).

$$(1) \quad SiO_2 + 2C \rightleftharpoons Si + 2\ CO\uparrow$$
$$(2) \quad Si + C \rightleftharpoons SiC$$
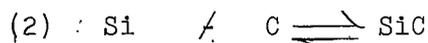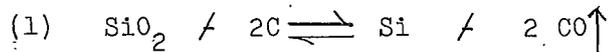
When Acheson discovered he had actually synthesized silicon carbide, he had the vision to organize the Carborundum Company. This firm, first started on September 21, 1891, is a leader in the electrochemical field today. The first manufacturing plant was built in Monongahela City, Pennsylvania and here Acheson started manufacturing grinding wheels. Silicon carbide thus began to replace the most popular current abrasive, ferro-silicon. The silicon carbide industry has been one of steady growth through expanded uses.

Unlike most minerals, silicon carbide was found in nature only after synthesis. In 1905, Henri Moisson (23) found that material in meteorites of the Canon Diablo area in Arizona was identical to electric furnace silicon carbide. Two other natural occurrences are reported in the literature. In 1958, beta silicon carbide was identified in Green River, Wyoming soda ash mines (26). Recently, a deposit of the hexagonal form was again reported in Bohemian volcanic outcroppings (1). In both cases, the deposits were not extensive. On this basis, the SiC manufacturing industry has had little competition from other sources.

Current Silicon Carbide Industry

The art of manufacturing silicon carbide has not departed radically from Acheson's method (21). The furnaces are larger and easier to load and unload; however, the principle of heating through an electrical resistance from within is still used (19, 28). The furnace consists of a trough built with removable side sections of refractory material and end structures through which large carbon electrodes enter the furnace (25). These electrodes are connected through the use of a granular core of carbon which acts as the power producing resistance. A high voltage is applied to the electrodes and current is passed through the carbon core, thus producing the necessary heat to carry out the reaction. The temperature of the central core increases as the reaction proceeds and the power requirements change, going from 1900°C after about an hour to a maximum of over 2400°C after about eighteen hours. From this point until the end of the total thirty-six hour run, the temperature drops off and stabilizes at about 2040°C (25). The power requirements increase due to the formation of semi-conducting silicon carbide. Figure 2. (27) represents R. R. Ridgway's discussion of how the temperature in various furnace zones changes throughout the run (19). These zones may be depicted as follows:

(A.) Before Run   (B.) Completed Run
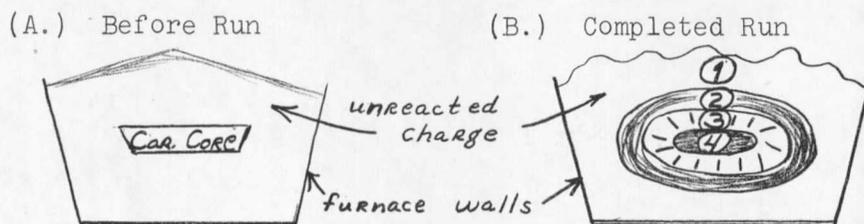
An explanation of these zones is as follows:

(A.) Zone (1) contains unreacted material which did not reach synthesis temperatures.

(B.) Zone (2) contains partially reacted material, or "firesand" (a low temperature form of silicon carbide) which must be recharged to the furnace.

(C.) Zone (3) contains silicon carbide which is processed into sized material.

(D.) Zone (4) contains graphite which has either formed as a result of graphitizing the granular carbon core or has resulted when silicon carbide formed, became too hot, and then dissociated leaving graphite. This material is used for the core material in future runs.

The raw materials of course are mainly sand (SiO_2) and carbon, in the weight ratio of 60% : 40% respectively. Sawdust is also added to promote porosity in the bed, allowing for the circulation of reacting vapors. Salt (NaCl) is also added to remove metal impurities as volatile chlorides.

Recent changes in core composition and geometry had improved the overall efficiency of the furnaces. (21). In addition, the physical and chemical properties of the product have been improved by varying the mix composition and furnace operating conditions. However, as yet, no methods of controlling the purity and crystal size and shape have been

reported. The material is still made in a batch-type operation, although several attempts have been made to devise a continuously operating furnace.

The U. S. Bureau of Mines reports (25) that, since 1946, the annual tonnage of silicon carbide produced in the U. S. and Canada has increased from approximately 60,00 short tons to a 1960 production rate of over 130,000 short tons. The amount and value of this production, in general, reflects business conditions, due to the large number of industries using the product. The industry has not overexpanded and there appears to be room for both incremental increases in production as well as for new limited capital investments.

Purpose of this Study

Montana's economy has traditionally depended on the agricultural conditions in the state and the nation. The cattle and farming industry ranks first in Montana, with tourism and recreation expanding steadily. This situation prevails mainly because of Montana's geographical location, which restricts local industry with necessarily high plant-to-market freight costs. Based on the decline in the employment which has been taking place in the agriculture in Montana for many years, concerned Montanans have been trying to build tourism as well as supplement the state's economy with the development of industry. Among these is the manufacturing of specialized, high value per unit cost, products. Silicon carbide falls into this category. The

market price of grained silicon carbide varies from about $0.20 to $0.80 per pound, depending on size, purity, package, etc. This would, more than likely, make freight costs to reach markets a significant but not a major cost. These factors, along with the known availability of carbon and silicon dioxide in Montana, provided the necessary incentive for undertaking this study to investigate silicon carbide production from Montana raw materials.

Carbon exists as a by-product of petroleum refining at the Humble Oil and Refining Company plant east of Billings. A fluid coking operation at the refinery to obtain additional gasoline was installed in 1955. Since that time, attempts to find market outlets for the by-product fluid coke have been only partially successful. A significant amount of the material is currently being sold for metallurgical purposes, however it appears that a further upgrading of the product would be desirable and also that a 7-8 year stockpile remains for disposal. A silicon carbide plant in the area would dispose of a small amount of the coke, in addition to upgrading it to a significantly higher valued product.

In addition to a large supply of carbon, southern Montana also contains extensive deposits of high-purity silica. The availability of this material further enhances the idea of a local manufacturing plant. Selling either of these materials outside of the state provides only a marginal incentive. Upgrading both would certainly be desirable.

Finally, one of the major costs in the manufacture of silicon carbide is electrical power. Current construction of Yellowtail Dam near Hardin, Montana, which is 60 miles southeast of Billings, has indicated that an abundant supply of competitive electrical power will be available in the near future.

In summary, a silicon carbide plant in Montana could significantly stimulate the area's economy, provide jobs, and provide an investment opportunity. The overall incentive exists due to the availability of an abundant supply of carbon, high-purity silicon dioxide sand, and electrical power.

RESEARCH OBJECTIVES

The primary objectives of this project were as follows:

A. Predict the thermodynamic feasibility of producing silicon
   carbide from high-sulfur, petroleum fluid coke available
   in Montana and Montana silica by studying the thermodynamics
   of reactions which might possibly be involved.

B. Determine whether or not silicon carbide could be synthesized
   from the materials in question on a laboratory scale.

C. Optimize the operating conditions necessary for producing the
   silicon carbide in a small laboratory pilot furnace.

D. Determine the relationship between yields of silicon carbide
   obtainable using the fluid coke and using conventional
   high-purity carbon, such as graphite. Determine any other
   apparent differences between the two products.

E. Determine whether or not a relationship exists between the
   particle size and/or bulk density of these raw materials
   and the yields obtainable.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Materials

Petroleum Fluid Coke

Table IV. lists the typical properties of Humble petroleum fluid coke (33). Also included in this table are inspections made on the material by the author. It will be noted that the sulfur content of the material runs approximately 6 per cent, accounting for much of the market limitation.

Graphite

For those runs in which graphite was used as a raw material instead of fluid coke, National Carbon Company, grade CS, graphite was ground to the desired particle size. This material consists of graphitized petroleum coke and a graphitized pitch binder. Ash content runs less than 0.5 per cent.

Silica

The silica used in this study consisted of a fine quartz sand obtained in the Pryor-Dryhead area of southern Montana. The Montana Bureau of Mines and Geology examined the material with the following conclusions: (20)

"The material is fine white quartz grains with no other minerals present. The material is not radio-active. The material may be used for silica refractory brick for lining furnaces providing the deposit is large enough and the

material is of high purity."

The author has analyzed this material quantitatively and found it to run in the range of 99.0-99.8 per cent SiO_2. Table V.

Equipment

Economic considerations dictated the type of experimental equipment which was used in this study. Very sophisticated graphite-tube furnaces are available commercially, similar to those described by Gartland (10) and with even more sophisticated design features. It was felt that these type of furnaces were financially out-of-reach for this study. In addition, a limited power supply was available which in turn placed a restriction on the type and size of resistor which could be used. A DC motor-generator was available as a power source with a maximum output of 500 amperes at 6 volts.

On this basis, a simple carbon-rod resistance furnace was constructed as shown by the schematic diagram in Figure 3 and an actual picture of the apparatus in Figure 4. The critical point in the design of this apparatus was the sizing of the resistor. As reported by National Carbon Company (14), carbon-rod resistors less than two inches in diameter are limited by surface evaporation. Depending on the temperature of the surroundings, those rods with diameters larger than two inches are limited either by surface evaporation or by interior temperature considerations which would cause the resistor to explode because

of rapid sublimation of the graphite. The power supply available and the desired temperature set the size of the carbon resistor used.

If the correlation between limiting current density and diameter of carbon resistors in Figure 5 is observed (14), it will be seen that for a given furnace temperature the limiting current density in the rod is set. Above this current density, and at the given temperature, the surface evaporation of the rod becomes considerable, due to the rod surface temperature exceeding 2200°C. Therefore, if the desired furnace temperature is taken as 2050°C, or at the line-out temperature of the core in a commercial furnace (25), the following limiting current densities and limiting currents prevail for different size rods (see Figure 5):

Rod Size	Crossectional Area	Limiting Current Density	Limiting Current
1/2 inch	0.1963 in^2	2300 amp/in^2	452
9/16 "	0.2485 "	2160 "	537
5/8 "	0.3068 "	2120 "	652
3/4 "	0.4418 "	1875 "	830

It may be seen from these values that a 1/2 inch diameter rod is the maximum size which can be used with the given power supply. Although it is not desirable to exceed the maximum current density, it is desirable to approach it as closely as possible to obtain maximum temperatures. Any rod larger than 1/2 inch in diameter, required more current than was available with the power source available.

It was found that the size of the rod was the most important consideration. Two grades of rods were used:

(A.) "National grade AUC graphite

(B.) Ultra Carbon Corporation, UF-4-S graphite.

The UF-4-S rods were found to be denser than the AUC rods and theoretically should have oxidized slower at the same temperature. This may have been true in a few cases; however, inconsistencies in the UF-4-S rods overshadowed any advantages due to the higher densities. As a result, it was concluded that the two grades of resistors were essentially equal for use in this furnace.

The carbon resistor was imbedded in two cylindrical copper blocks, two inches in diameter. The holes in these blocks were machined 1/64 of an inch oversize and the rod was then imbedded in the hole and bonded with acid-core solder. The rods had to be replaced quite frequently and the jig arrangement shown in Figure 6 was used for this operation. This resistor-electrode arrangement was then bolted to 1/4 x 2 inch copper bus-bar leads, which in turn were connected to the DC motor-generator.

The resistor was then inclosed in the furnace wall structure made of Transite.[1] Any openings adjacent to the rod were sealed during the runs to prevent oxidation of the resistor. In addition, the furnace

1. Trade name, Johns-Manville Corporation.

was provided with nitrogen purging connections, as shown in Figure 3.
The copper blocks, or electrodes, were provided with water cooling-
coils, for holding the temperature of the copper within reasonable
limits.

The amperage was measured by the use of a shunt arrangement and
a DC ammeter. Power measurements could then be made by including a
DC voltmeter in the circuit. A circuit diagram of the apparatus is
shown in Figure 7.

Optical temperature measurements were made by providing the
furnace with a carbon observation sight-tube. This tube was con-
structed of National Carbon Company, 3/4 inch I.D., schedule B, carbon
pipe. The outer opening of the tube was fitted with a clear fused
quartz window.[1] The tube fittings were sealed with carbon paste[2]
and the tube was purged during the runs with nitrogen. Temperature
measurements were made with a "Pyro" optical pyrometer, model 84,
made by The Pyrometer Instrument Company. The pyrometer was provided
with a neutral filter allowing for temperature measurements in the
two ranges, 1000° - 1800°C and 1800° - 3250°C.

Immediately beneath the carbon rod, a removable reaction chember
was constructed. This chamber consisted of a graphite semi-cylindrical

1. Manufactured by Thermal American Fused Quartz Co., Montville, N.J.
2. Cement Grade C-9, National Carbon Company