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# Siliconated Pyrolytic Graphite

## Part 1 *Preparation and Some Properties*

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Siliconated pyrolytic graphite PG(Si) has been prepared by pyrolysis of a mixture of propane and silicon tetrachloride vapour at 1440 to 2025° C, a total gas pressure of 10 or 50 torr, and a partial pressure of silicon tetrachloride vapour of up to 13 torr. The amounts of silicon in PG(Si) are 0.02 to 4 wt %. The effects of the addition of silicon tetrachloride on the surface characteristics, the microstructure and the density of PG(Si) are examined.

### 1. Introduction

Pyrolytic graphite PG is used as a coating material for nuclear fuel particles and as a material for high-temperature thermal insulators [1-3]. Recent investigations of pyrolytic graphite compounds, prepared by doping foreign atoms or molecules into the graphite matrix, have been made for the purpose of developing new materials. The PG-compounds show specific characteristics which have not appeared in PG [4-6].

Two doping methods are used to prepare these compounds. One is a diffusion technique, the doping element being inserted into the interlayer spaces of the carbon networks in PG. The term "lamellar compound" is generally used for these PG-compounds. The other is by co-deposition, the doping element being added to the graphite matrix by pyrolysis of a hydrocarbon gas mixed with a vapour of the hydride or halide of the doping element. In this article, the latter compound is named "deposited compound", to distinguish it from "lamellar compound". In PG-deposited compounds, the doping element substitutes for carbon in the carbon network, or is introduced into the spaces between the graphite crystallites. PG-boron (boron-doped PG or boronated PG) is an example of a PG-deposited compound. It has been investigated in detail, and has favourable characteristics for use as a high-temperature thermocouple [6].

In this study, silicon was chosen as a doping element since it is somewhat similar to carbon in chemical properties: PG-silicon compound "PG(Si)" was prepared. Some work has been carried out on the preparation of silicon and silicon carbide by gaseous cracking. However, there seem to be no publications on PG(Si). This paper deals with the preparation method and the effects of preparation conditions on silicon content, surface characteristics, microstructure, and density of PG(Si). The structural features of the graphite matrix in PG(Si), its electrical and thermal properties, and its formation mechanism will be described in forthcoming papers.

### 2. Experimental Procedures

PG(Si) was prepared by pyrolysis of a mixture of propane and silicon tetrachloride vapour under the various conditions shown in table I. The apparatus consisted of a water-cooled metal vacuum chamber, a water-cooled copper electrode and a graphite resistance sheet (substrate), as reported elsewhere [7]. The experimental

TABLE I The preparation conditions of siliconated pyrolytic graphite PG(Si).

| | |
|---|---|
| Heating method | Direct heating of substrate |
| Raw gas | Propane gas and $SiCl_4$ vapour |
| Deposition temperature ($T_{dep}$) | 1440 to 2025° C |
| Gas flow rate | 410 $cm^3$/min |
| Deposition time | 20 to 120 min |
| Total gas pressure ($P_{total}$) | 10, 50 torr |
| Vapour pressure of $SiCl_4$ in its constant temperature bath | 0, 60, 80, 200 torr |
| Partial pressure of $SiCl_4$ ($P_{SiCl_4}$) | 0, 2.6, 4, 6, 13 torr |

arrangement is illustrated in fig. 1. The vapour pressure of silicon tetrachloride was regulated by controlling the temperature of a silicon tetrachloride reservoir (− 5 to 20° C). The relation between temperature and vapour pressure of silicon tetrachloride is shown in fig. 2. To compare some properties of PG(Si) with those of PG,

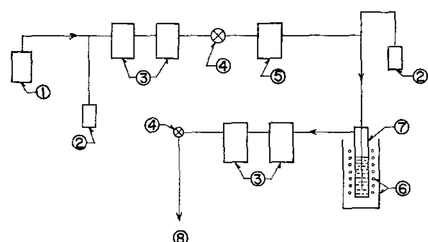

*Figure 1* Schematic diagram of PG(Si) formation apparatus. 1 Propane gas, 2 manometer, 3 $P_2O_5$ and $CaCl_2$, 4 pressure regulator, 5 flow meter, 6 constant temperature bath, 7 $SiCl_4$, 8 furnace.

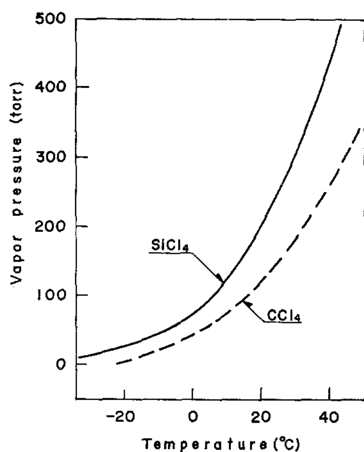


*Figure 2* Vapour pressure of $SiCl_4$ and $CCl_4$.

the latter was also prepared under similar conditions, but without the silicon tetrachloride. In this case, the preparation condition is shown as $P_{SiCl_4} = 0$ torr. The effect of chlorine (produced by the decomposition of silicon tetrachloride) on the properties of PG(Si) was checked by pyrolising a mixture of propane and carbon tetrachloride vapour. The relation between temperature and vapour pressure of carbon tetrachloride is also shown in fig. 2.

The silicon content of PG(Si) was determined by X-ray fluorescence analysis. Surface morphology such as pebble and "plume product" [7] was also examined: the PG(Si) product was mounted in resin, cut perpendicular to the deposition surface and polished by ordinary metallographic techniques. The cross-sections were then examined under polarised light. The density was determined by a displacement technique using toluene [8].

## 3. Experimental Results

### 3.1. Silicon Content of PG(Si)

The amounts of silicon in PG(Si) prepared at the total pressures of the mixed gas ($P_{total}$) of 50 and 10 torr are shown in figs. 3 and 4, respectively.

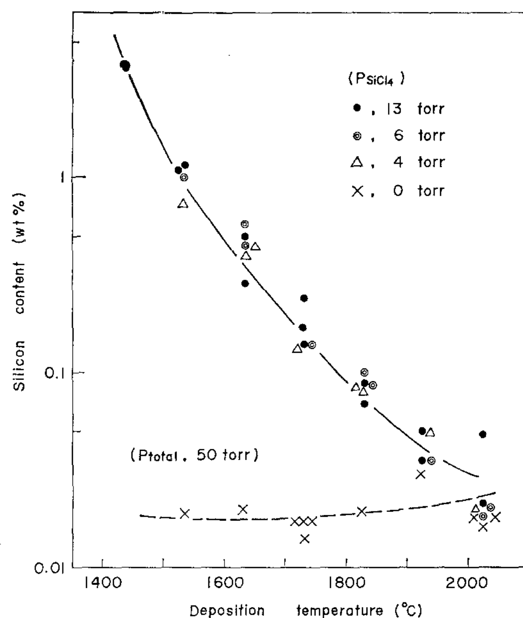


*Figure 3* Silicon content of PG(Si) prepared at a total gas pressure ($P_{total}$) of 50 torr.

The silicon content depends strongly on the deposition temperature and decreases as this temperature is increased. In the low temperature range, 1400 to 1500° C, it is a few wt %, but becomes as little as 0.02 to 0.03 wt % at high temperatures, about 2000° C. That is, the effect of adding silicon tetrachloride to the raw gas is scarcely perceptible at high temperatures. Figs. 3 and 4 show that the silicon content is almost independent of $P_{total}$ and of the partial pressure of silicon tetrachloride ($P_{SiCl_4}$).

### 3.2. Surface of PG(Si)

The surfaces of PG(Si) samples prepared under various conditions are shown in figs. 5 to 10. In

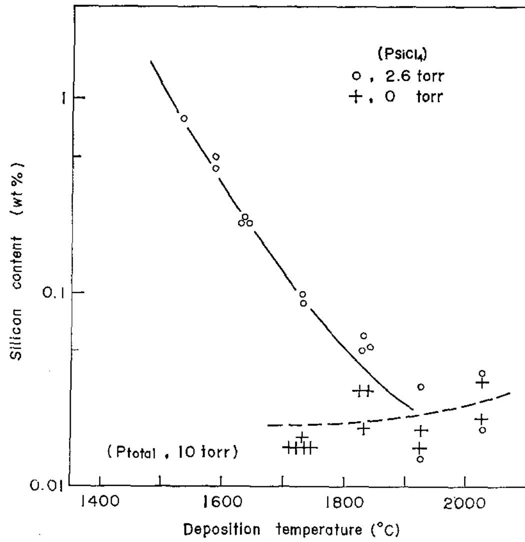


*Figure 4* Silicon content of PG(Si) prepared at a $P_{total}$ of 10 torr.

each figure, upper and lower samples show the surfaces of PG and PG(Si), respectively. Figs. 5 to 7 were obtained at $P_{total} = 50$ torr; and figs. 8 to 10 were obtained at $P_{total} = 10$ torr. These figures show that, at temperatures below 1900° C, the addition of silicon tetrachloride accelerates the rate of formation of PG(Si) as compared with that of PG. The appearance of the plume product formed at higher pressures is more marked in the presence of silicon tetrachloride.

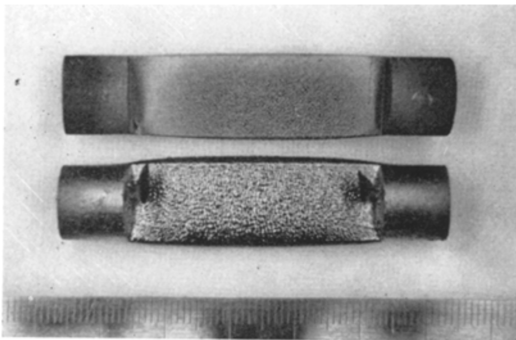

*Figure 5* Surfaces of PG and PG(Si) prepared at a deposition temperature ($T_{dep}$) of 1535° C and $P_{total}$ of 50 torr. Above: $P_{SiCl_4} = 0$ torr; 50 min. Below: $P_{SiCl_4} = 13$ torr; 50 min. 1 division = 1 mm.

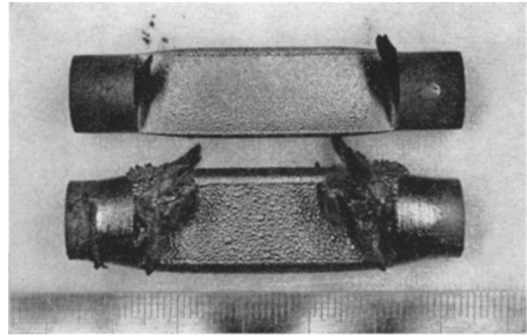

*Figure 6* Surfaces of PG and PG(Si) prepared at a $T_{dep}$ = 1730° C and $P_{total} = 50$ torr. Above: $P_{SiCl_4} = 0$ torr; 50 min. Below: $P_{SiCl_4} = 13$ torr; 50 min. 1 division = 1 mm.

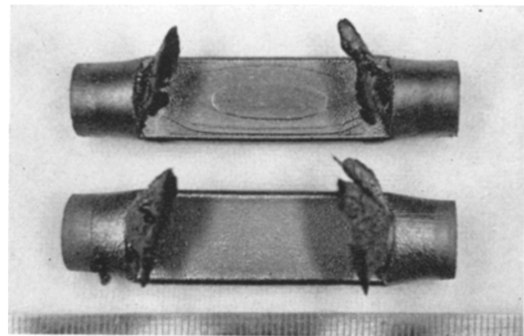

*Figure 7* Surfaces of PG and PG(Si) prepared at a $T_{dep}$ = 2025° C and $P_{total} = 50$ torr. Above: $P_{SiCl_4} = 0$ torr; 60 min. Below: $P_{SiCl_4} = 4$ torr; 60 min. 1 division = 1 mm.

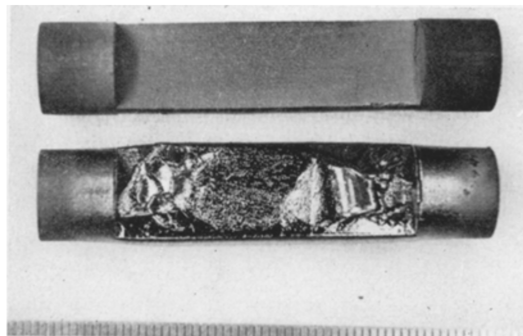

*Figure 8* Surfaces of PG and PG(Si) prepared at a $T_{dep}$ = 1535° C and $P_{total} = 10$ torr. Above: $P_{SiCl_4} = 0$ torr; 120 min. Below: $P_{SiCl_4} = 2.6$ torr; 100 min. 1 division = 1 mm.

One of the characteristics of PG(Si) is the noticeable brightness of its surface. As shown in figs. 5 to 10, the brightness increases markedly as the temperature is lowered, and the surface is mirror-like at 1400 to 1500° C. The surfaces of PG and PG(Si) at high magnification are

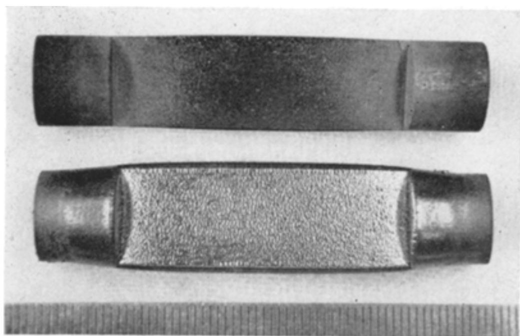

*Figure 9* Surfaces of PG and PG(Si) prepared at a $T_{dep}$ = 1635° C and $P_{total}$ = 10 torr. Above: $P_{SiCl_4}$ = 0 torr; 120 min. Below: $P_{SiCl_4}$ = 2.6 torr; 100 min. 1 division = 1 mm.

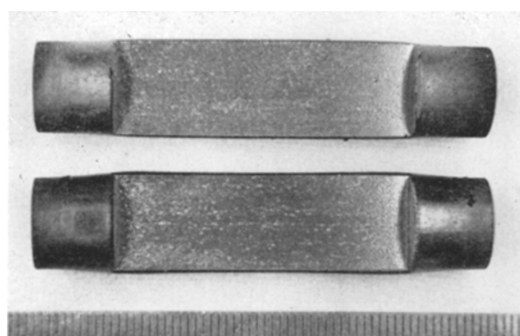

*Figure 10* Surfaces of PG and PG(Si) prepared at a $T_{dep}$ = 1925° C and $P_{total}$ = 10 torr. Above: $P_{SiCl_4}$ = 0 torr; 50 min. Below: $P_{SiCl_4}$ = 2.6 torr; 50 min. 1 division = 1 mm.

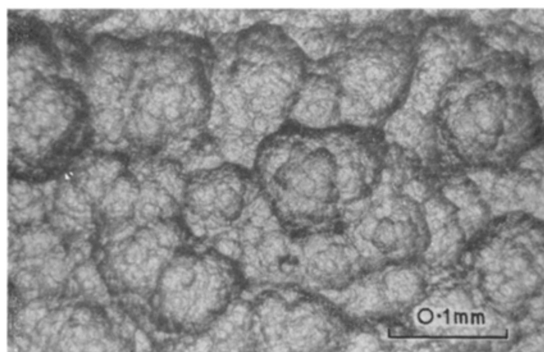


*Figure 11* Pebble structure of PG. $T_{dep}$ = 2025° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 0 torr.

illustrated in figs. 11 and 12 and figs. 13 to 15, respectively. That shown in fig. 11 was prepared at 2025° C and that in fig. 12 at 1440° C. The surface of PG shows the pebble-like pattern which gives the top of the growth cones. The

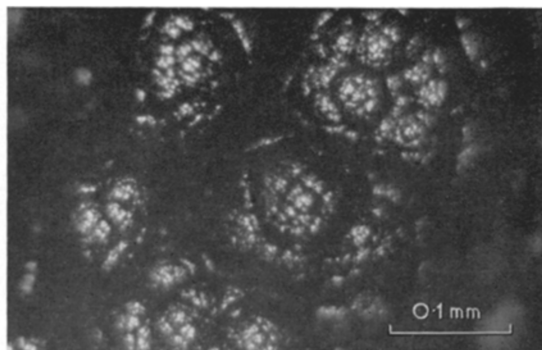


*Figure 12* Pebble structure of PG. $T_{dep}$ = 1440° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 0 torr.

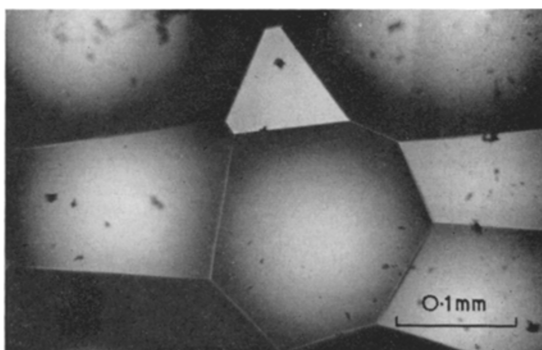


*Figure 13* Pebble structure of glossy PG(Si). $T_{dep}$ = 1535° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 5 torr.

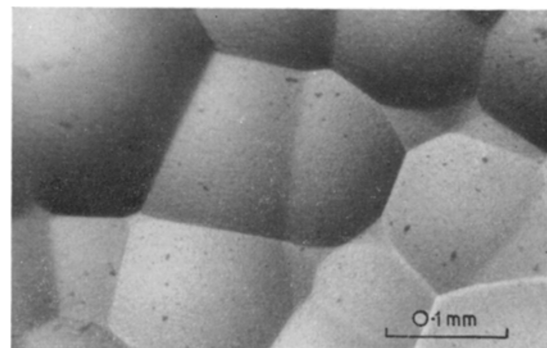


*Figure 14* Pebble structure of very glossy PG(Si). $T_{dep}$ = 1440° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 13 torr.

large pebbles (primary cones) are composed of the small pebbles (secondary cones). The pebble-like pattern of PG is not much changed with temperature. The patterns of PG(Si) prepared at the medium and high temperatures, 1700 to 2000° C, are similar to those of PG shown in fig. 11. However, when PG(Si) is prepared at low

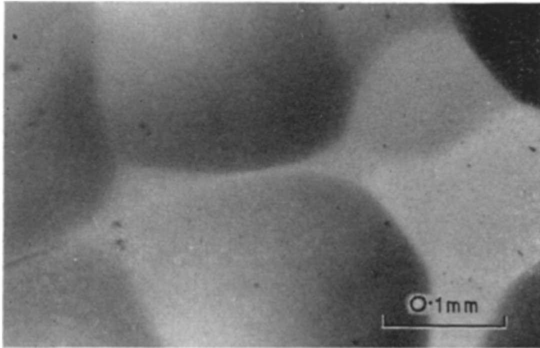


*Figure 15* Pebble structure of mirror-like PG(Si). $T_{dep}$ = 1440° C; $P_{total}$ = 10 torr; $P_{SiCl_4}$ = 4 torr.

temperatures (1400 to 1500° C), the secondary cones disappear and only the primary cone boundaries are found (figs. 13 to 15). Furthermore, the boundary lines of the primary cones cross at an angle of about 120 degrees. In the mirror-like surface of PG(Si) shown in fig. 15, the boundary lines lack the clarity of those in figs. 13 and 14.

### 3.3. Microstructure of PG(Si)

As with PG [8], the (transverse) microstructures of PG(Si) prepared under various conditions can be divided into four types, shown in figs. 16 to 19. The relation of the microstructure to $P_{SiCl_4}$ is shown in figs. 20 and 21, which were obtained at $P_{total}$ = 50 and 10 torr, respectively. The microstructure of PG(Si) is still the "fine regenerative structure" at fairly low temperatures. The microstructure "C*" of PG(Si) prepared at low $P_{total}$ and low temperature is different from the microstructure "C" of PG prepared at the same $P_{total}$ and temperature. It is observed in PG(Si)

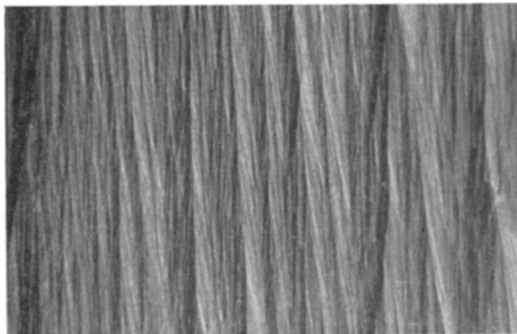

*Figure 16* Fine regenerative structure "F" (× 90). $T_{dep}$ = 2025° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 4 torr.

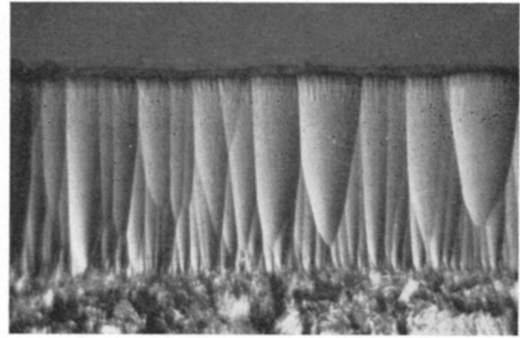

*Figure 17* Coarse structure "C" (× 90). $T_{dep}$ = 1535° C; $P_{total}$ = 10 torr; $P_{SiCl_4}$ = 0 torr.

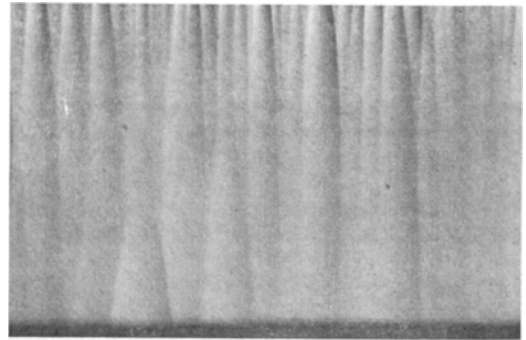

*Figure 18* Coarse structure "C*" (× 90). $T_{dep}$ = 1535° C; $P_{total}$ = 10 torr; $P_{SiCl_4}$ = 2.6 torr.

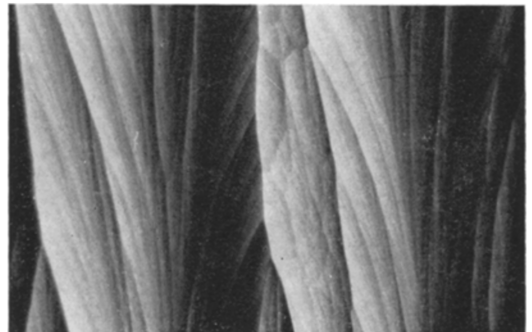

*Figure 19* String structure "S" (× 90). $T_{dep}$ = 1635° C; $P_{total}$ = 50 torr; $P_{SiCl_4}$ = 4 torr.

with the very glossy surface (figs. 14, 15). Here, the primary cone boundaries lack clearness, and the secondary cone boundaries are barely detectable.

### 3.4. Density of PG(Si)

The addition of silicon tetrachloride markedly affects the density of the product. The results

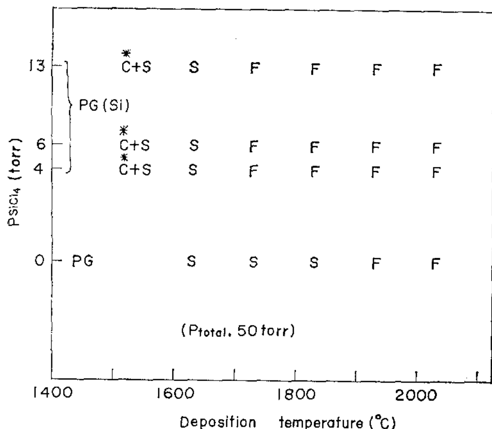


*Figure 20* Effect of preparation conditions on the microstructure of PG and PG(Si) prepared at a $P_{total}$ of 50 torr. F fine regenerative structure (fig. 16), S string structure (fig. 19), C* coarse structure (fig. 18).

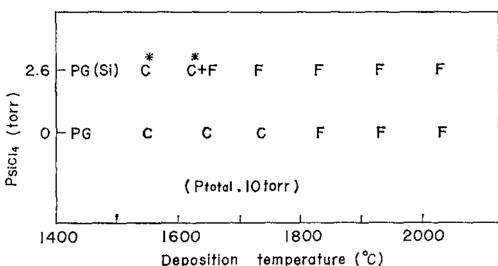


*Figure 21* Effect of preparation conditions on the microstructure of PG and PG(Si) prepared at a $P_{total}$ of 10 torr. C coarse structure (fig. 17).

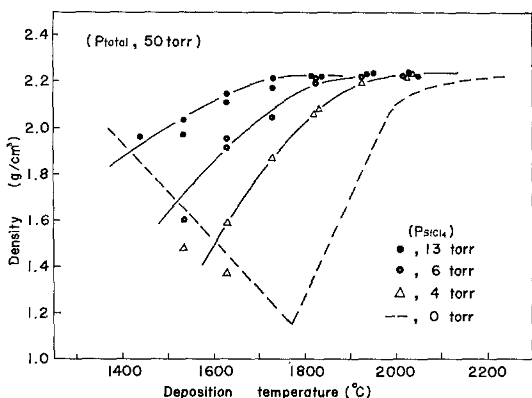


*Figure 22* Effect of preparation conditions on the density of PG(Si) prepared at a $P_{total}$ of 50 torr.

obtained at $P_{total} = 50$ and 10 torr are shown in figs. 22 and 23, respectively. At medium temperatures (1600 to 1700° C), the density of PG(Si) is

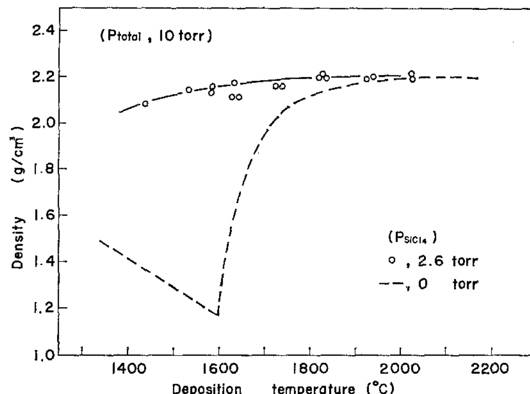


*Figure 23* Effect of preparation conditions on the density of PG(Si) prepared at a $P_{total}$ of 10 torr.

up to 70 to 80% greater than that of PG. The effect increases with increasing $P_{SiCl_4}$. It seems that the presence of silicon tetrachloride shifts the density minimum, observed for PG, to a lower temperature.

## 4. Discussion

As shown in fig. 24, carbon and silicon are mutually insoluble in the solid state [9]. In this system, silicon carbide is the only intermediate

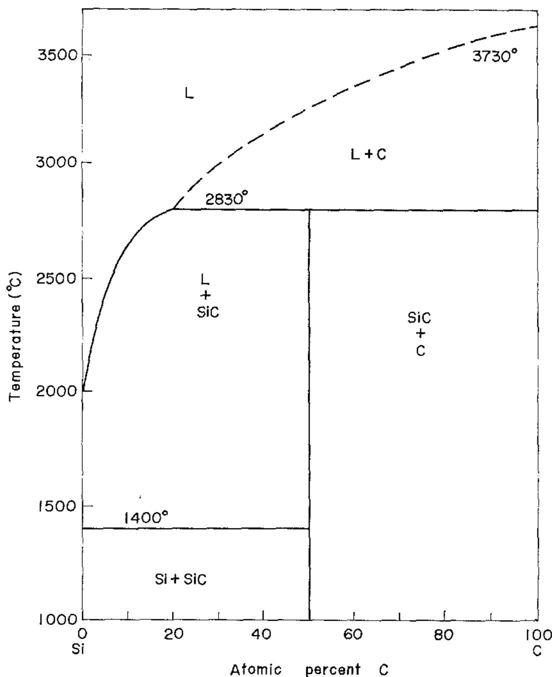


*Figure 24* Phase diagram of the binary system Si–C [10].

phase: it forms at temperatures above about 1410° C. Popper and Mohyuddin [10] prepared pyrolytic silicon carbide by pyrolysis of methyltrichlorosilane at 1400° C and examined the product by optical and electron microscopy. They reported that the deposit showed silicon carbide with layers of PG. Kawashima *et al* [11] pyrolysed silicon tetrachloride with toluene and obtained metal-free $\beta$-silicon carbide at 1400 to 1450° C. In the present experiments, optical microscopy did not reveal either silicon or silicon carbide in the cone boundaries (figs. 13 to 16, 18, 19). However, as we report in a following paper, X-ray diffractometry showed that silicon carbide and graphite co-existed in PG(Si). It seems likely that the silicon in PG(Si) is dispersed in the form of silicon carbide.

Chlorine must be formed when the propane + silicon tetrachloride mixture is decomposed. It is therefore important to investigate the effect of chlorine on the formation of PG(Si). Higgs *et al* [12] prepared PG by the pyrolysis of a gaseous mixture of methane (5%), algon (95%) and chlorine (0.179%) at 1350 to 2000° C. From their results, the addition of chlorine lowers the temperature at which the minimum density occurs from 1900 to 1550° C, and increases this density from about 1.25 g/cm³ to about 1.40 g/cm³. The effect of chlorine gas seems to be different from that of chlorine produced by the decomposition of a chloride such as silicon tetrachloride. Carbon tetrachloride vapour was therefore mixed with propane and the mixed gas was pyrolised at $P_{total} = 50$ torr and $P_{CCl_4} = 6.5$ torr. Fig. 25 shows that the addition of carbon tetrachloride did not affect the density of PG. From these results it may be supposed that some intermediate products of the Si—H—Cl—C system play a more important role than chlorine gas in the formation process and properties of PG(Si). Moreover, the fact that the pebble boundaries intersect at about 120 degrees (fig. 13) suggests that PG(Si) may be formed from a liquid intermediate.

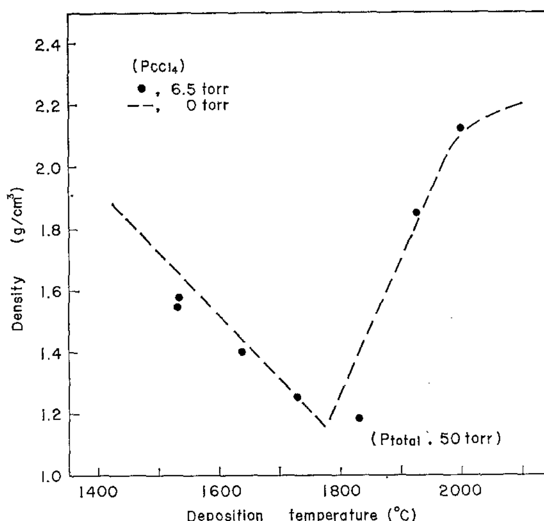


*Figure 25* **Effect of $CCl_4$ pyrolysis on the density of PG.**

## 5. Summary

Siliconated pyrolytic graphite PG(Si) was prepared by the pyrolysis of a mixture of propane and silicon tetrachloride vapour under various conditions. The product has the following characteristics as compared with PG:

1. The amount of silicon in PG(Si) increases with the decreasing temperature, being about 4 wt % in PG(Si) prepared at about 1440° C and 0.02 to 0.03 wt % in PG(Si) at about 2000° C.
2. The rate of formation of PG(Si) and of the plume product is accelerated.
3. The surface of PG(Si) prepared at low temperature, 1400 to 1500° C, shows a mirror-like brightness.
4. The microstructure is still the fine regenerative structure at fairly low temperatures.
5. The density at the low and medium temperatures (1400 to 1800° C) is 70 to 80% greater than that of PG. A minimum density in PG(Si) was not observed in this temperature range.
6. At low temperatures, PG(Si) seems to be formed from a liquid intermediate product of the Si—H—Cl—C system.

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