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Microhardness of Silicon-containing Pyrolytic Carbon

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The silicon-containing pyrocarbon (PC) deposited from CH_4-$SiCl_4$ gas mixture at 1150 to 1630° C and 50 to 200 torr total gas pressure exhibits great variations in microhardness. Low-Si PC has a very low hardness, slightly higher than pure PC. The hardness of PC with high Si-content is increased and closely related to its microstructure. An increased, uniformly distributed hardness is found in high-Si PC with a homogeneous microstructure, similar to that of pure PC. On the contrary, in the samples with non-uniform microstructure, very large cones growing from lenses were found to exhibit high hardness, which generally decreases along the cone axis from a value corresponding to that of pure SiC in the lens, to relatively low values that may approach that of pure PC. This observation, together with the fact that in the regions adjoining the large cones the hardness is low and approaches that of pure PC, proves that the Si in the form of SiC is concentrated in the large cones. A mechanism of large cone formation is proposed.

1. Introduction

Although there is a steadily growing interest in chemical vapour deposition of a wide variety of materials [1, 2], until very recently there was almost no work on such deposition of silicon-containing pyrolytic carbon. Recently, Emyashev and Lavrova, working at 2100° C, have deposited pyrolytic carbon (PC) with up to 0.3 wt % Si [3], while in the work of Yajima and Hirai [4-7] the deposition was effected in a rather broad temperature range (1440 to 2025° C) and the resulting PC contained up to 4 wt % Si in the form of β-SiC. In both cases, a homogeneous distribution of Si in the product was found.

In our previous work concerning chemical vapour co-deposition of carbon and silicon [8], the CH_4-$SiCl_4$ gas mixture was decomposed at 1340 to 1630° C and 50 to 200 torr total gas pressure. The results indicated that the PC could admit up to 0.2 wt % Si into substitutional solid solution, higher Si content being present as a separate phase, β-SiC. However, the microstructure of the product with higher Si-content (up to about 15 wt %) is greatly changed as compared to that of pure PC: in addition to the narrow growth-cones, characteristic of a low-Si product, very large cones appear which grow from lens-shaped inclusions (see fig. 1a). Electron probe microanalysis has proved that the large cones contain an increased Si concentration, which is a maximum in the lens and decreases as the cone grows up. Microhardness tests have shown that the large cones are characterised by higher hardness. However, the values found, in particular those for low hardness regions, were rather subject to errors. The present work was undertaken with the aim of investigating in more detail the PC with different Si-content, using an improved method of microhardness measurements, in order to get more information concerning the SiC distribution. The microhardness is in this respect a favourable property, SiC being among the hardest crystals known. Since Si content and deposition temperatures are factors of utmost importance in determining properties of the product, the results will be considered in connection with these parameters.

2. Experimental

The details of the experimental procedure used for the preparation of Si-containing PC are given in [8]. The preparation conditions used were: deposition temperature 1150 to 1630° C; gas mixture CH_4-$SiCl_4$; total gas pressure 50 to 200 torr; 2 to 75 vol % $SiCl_4$ in the gas mixture. A number of PC samples that were examined contained various Si concentrations in the range 0.0 to 13 wt %.

The polished cross-sectional surface of the Si-bearing PC was coated with a thin aluminium film (about 200 Å thick) using standard vacuum evaporation technique. This procedure was found very useful in making the indentations more visible [9].

Microhardness measurements were performed by the Vickers method using the Reichert reflection optical microscope with an attachment for microhardness measurements. The diagonals of the indentations, produced by means of a diamond pyramid, were measured to an accuracy ± 0.08 μm. All measurements were done with 93 and 56 g loads, the loading time being 30 sec. For a given load and sample region, a mean hardness value from 8 to 15 indentations was taken as representative of the region.

In order to assess the systematic error introduced by coating the sample surface with aluminium, the hardness of two reference materials, silicon carbide and fused silica, was measured using the same procedure of sample preparation and measurements. The influence of the aluminium coating on experimentally determined hardness can be seen from the values found for SiC and SiO$_2$, which are 2500 kp mm^{-2} and 678 kp mm^{-2} without coating, and 1500 kp mm^{-2} and 578 kp mm^{-2} with coating, respectively.

Since the measured microhardness values depend, in general, on the loading used, in order to check this influence two series of measurements with various loadings in the range 9.3 to 93 g were effected with pure PC (manufactured by Societé Le Carbone Lorraine, Paris), and with our sample containing 4.2 wt % Si homogeneously distributed. From the fact that the Meyer plot [10] had in both cases a slope 2.03 (i.e. very close to 2), it follows that the loading does not influence the measured hardness values.

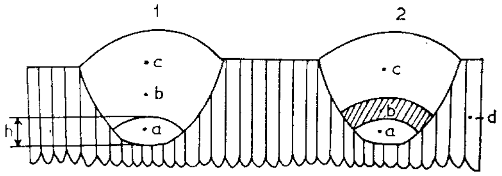
Precision of the measurements in terms of the coefficient of variation was found to be 2% for the interval of hardness encountered.

3. Results and Discussion

Results obtained from a number of Si-bearing PC samples are summarised in table I. These results show that the hardness of the SiC and of the fused quartz, used as reference materials, is 1500 kp mm^{-2} and 580 kp mm^{-2}, respectively.

The hardness of the pure PC prepared in this laboratory is about 90 kp mm^{-2} (fig. 1b, c). This value is higher than the corresponding value for the PC Carbone Lorraine (70 kp mm^{-2}), which is presumably a consequence of better structural properties of the latter.

TABLE I Microhardness of pyrocarbon with incorporated silicon



Sample	Si-content (wt %)	Deposition temperature (° C)	Microhardness (kp mm^{-2})			
SiC					1500	
Fused quartz					580	
PC	0.0	up to 1600			90	
PC + Si	⩽ 0.2	up to 1500			90–100	
PC + Si with lenses	1.5–13	1300–1400	a	b	c	d
	type 1 (see sketch)		1500	→600 →200	→decreases to ⩽ 200 →200	90–100 90–100
	type 2 (see sketch)		1500	→500	→⩽ 200	90–100
PC + Si without lenses	1.5–6	1300			~ 200	

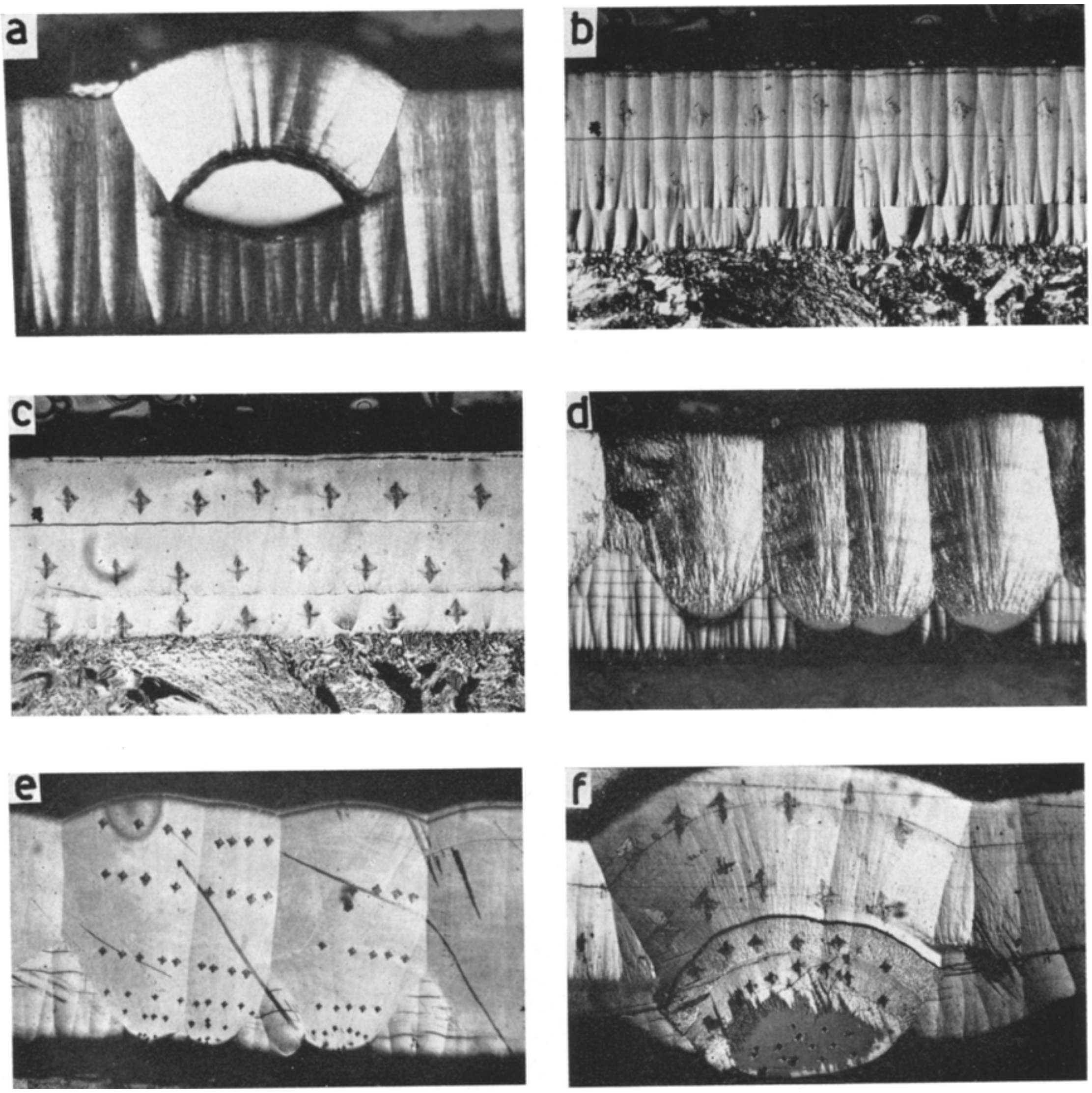


Figure 1 (a) Typical microstructure of pyrocarbon with high Si-content (> 1.5%) deposited at 1300 to 1400° C (× 260); (b, c) pure pyrocarbon (× 105); (d, e, f) pyrocarbon with high Si-content deposited at 1300 to 1400° C; (d, e) sample with large cones of type 1 (see table I) (× 52); (f) sample with a large cone of type 2 (see table I) (× 105). All photographs were taken with polarised light. The photographs (b, c) and (d, e) respectively, show the same sample region, the conditions being adjusted to show microstructure (b, d) or indentations (c, e).

The PC which contains a small amount of Si (up to 0.2 wt %) shows a slight increase in microhardness, the values being 90 to 100 kp mm^{-2}. The microstructure of these samples is also similar to that of the pure PC, showing the narrow growth cones.

Products with higher Si contents (1.5 to 13 wt %) deposited at temperatures above 1300° C show substantial differences both in microstructure and hardness. Characteristic for these samples is the presence of small lens-shaped inclusions from which very large cones grow up. Regarding the distribution of hardness values along the large cones, two classes can be distinguished:

(i) Only one, very steep drop of hardness occurs at the boundary between the lens and the remaining part of the large cone (fig. 1d, e and table I, PC+Si with lenses, type 1).

(ii) Two transitions may be distinguished along the large cone: first, a marked drop of hardness occurs again at the boundary between the lens and a relatively narrow zone immediately behind it; the other, less distinct drop occurs at the boundary between this zone and the rest of the large cone (fig. 1f and table I, PC+Si with lenses, type 2). These hardness zones correspond to the microstructural zones: (a) the lens is seen under the microscope as a smooth surface. Its height, measured along the cone axis (*h* in the sketch, table I), varies from 20 to 80 μm; (b) the zone behind the lens has a spongy appearance; (c) the remaining, relatively large part of the cone has a structure more or less similar to that of the pure PC.

The lens is characterised in almost all cases by high microhardness values, being of the same order as that corresponding to pure SiC (1500 kp mm^{-2}), although values as low as 1200 kp mm^{-2} and as high as 1600 kp mm^{-2} are also found. Behind the lens, hardness decreases more or less steeply (according to the class to which the cone belongs) to fall finally to a value in the range 90 to 200 kp mm^{-2}.

Large cones without lenses, but still having zones of increased hardness, were sometimes found in some samples. The lens (if this exists at all) being too small to be visible under the microscope, the situation is otherwise analogous to that in the class 2 cones.

In spite of a high average Si-content of these samples, those parts which are composed of narrow cones (*d* in the sketch, table I) were found to have low hardness (90 to 100 kp mm^{-2}), which corresponds to the values obtained for PC with low Si-content.

Products prepared at lowest deposition temperatures (below 1300° C) and having relatively high Si-content (1.5 to 6 wt %) do not exhibit the presence of lens-shaped inclusions, but are built of homogeneous narrow cones. With respect to the hardness, these samples are uniform and the values are higher than that of the pure PC – 180 to 200 kp mm^{-2}.

In order to check the presumption that the hardness should be related to the presence of SiC, the change of hardness along the large cones was compared to the curves representing variation of Si-content in the same samples as measured by an electron microprobe. Fig. 2 shows the concordance of curves I and II (hardness and Si-content respectively) for both classes of large cones.

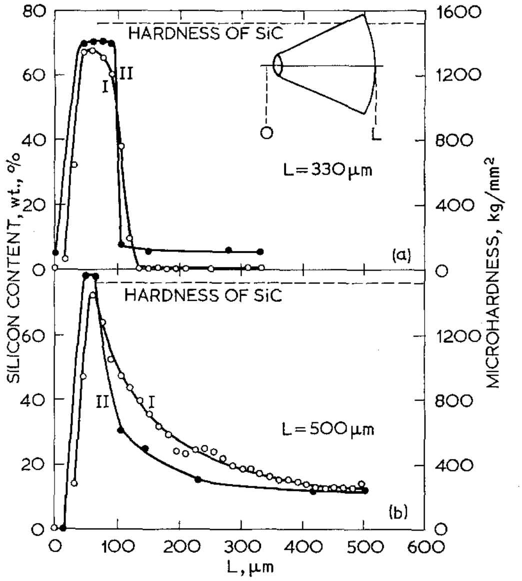


Figure 2 Curves showing distribution of Si concentration (I) and microhardness (II) along the axis of large cones with lenses: (a) type 1; (b) type 2 (see table I).

The experimental results here presented indicate the possibility that the lens-shaped inclusions are formed by carbidisation of microdrops of pure Si which, in turn, might be formed by hydrogen reduction of $SiCl_4$ (hydrogen being evolved by CH_4-decomposition). This supposition could explain:

(i) The abrupt drop of hardness and of Si-concentration at the boundary between the lens and the remaining part of large cones. This would be a consequence of simultaneous deposition of both SiC and PC at the lens-shaped pure SiC inclusions, serving as nuclei. On the other hand, the increased hardness of the large cones with respect to the narrow ones shows that SiC is preferentially deposited on the SiC nuclei, while carbon is deposited on both the SiC and carbon nuclei.

(ii) Absence of the lenses (and of large cones growing from these) in the samples deposited at lowest temperatures. Too low a temperature would prevent melting of Si and, consequently, formation of the lenses. The homogeneous distribution of SiC in these samples could be a consequence of an increased nucleation rate and relatively low rate of growth at these temperatures.

According to this assumption, the $SiCl_4$ is reduced by hydrogen (evolved by CH_4-decomposition) to the elementary Si. The process for hydrogen reduction of $SiCl_4$ has already been used for the deposition of pure Si at as low a temperature as 1000° C [1]. However, since the only source of hydrogen here is the CH_4, which is very slowly decomposed at low temperatures in the absence of $SiCl_4$, while in our co-deposition experiments the deposition rate was found to increase by a factor 4 to 5 [8], it seems possible that another mechanism of deposition might take place at low temperatures.

4. Conclusion

(i) The microhardness of the cross-section of the Si-containing PC depends on Si-content and deposition temperature, and is related to the microstructure, which also depends on these conditions of deposition.

(ii) Pure PC samples having microstructure with narrow growth cones are characterised by low hardness values (90 kp mm^{-2}). Low Si-concentration (up to 0.2 %) leads to insignificant change of microstructure and hardness (90 to 100 kp mm^{-2}).

(iii) Pyrocarbon with high Si-content (1.5 to 13 %) prepared at deposition temperatures above 1300° C is characterised by the presence of large cones, in addition to the narrow cones characteristic of the low-Si product. The large cones grow from lenticular inclusions, the hardness of which corresponds to that of pure SiC. At the boundary between the lens and the remaining part of the large cone, the hardness drops steeply and then further decreases to reach, at the end of the cone, a value which is almost equal to, or slightly above, the hardness of pure PC.

(iv) Pyrocarbon with high Si-content (up to 6 %) but prepared at temperatures below 1300° C is characterised by a microstructure similar to that of pure PC (absence of large cones) and by uniform hardness values, lying above that of pure PC, throughout the sample volume.

(v) There is complete similarity in behaviour of microhardness and of Si-concentration (as measured by the electron microprobe) along the axes of the large cones.

(vi) A possible mechanism of the large cone formation might involve the following steps: (a) reduction of $SiCl_4$ by hydrogen evolved by CH_4-decomposition, and formation of droplets of molten elementary Si; (b) carbidisation of Si droplets and formation of SiC nuclei; (c) growth by co-deposition of SiC (which is preferentially deposited on SiC nuclei) and of PC.

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