

# Carbon with an onion-like structure obtained by chlorinating titanium carbide

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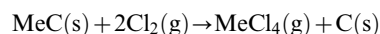
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Nanoporous carbon prepared by chlorination of TiC powder has been characterized by high-resolution transmission electron microscopy (HRTEM) and showed a disordered amorphous structure of graphite planes with areas of an onion-like structure, where the graphite planes are ordered with concentric spherical graphitic shells (15–35 nm) interpenetrating and overlapping each other.

In the last twenty years fullerenes<sup>1</sup> and carbon nanotubes<sup>2</sup> have received great attention due to their special atomic configurations and potential applications.<sup>3,4</sup> Onion-like graphite<sup>5</sup> structures represent another new allotropic nanophase of carbon, which is different from the former structure groups. Since Iijima<sup>6</sup> first found the onion-like structures in vacuum deposited carbon films, other techniques, such as electron irradiation and carbon ion implantation, have been reported to result in similar structures.<sup>7–9</sup> With increased radiation energy input, which in some respects resembles a very high-temperature regime, there is a gradual reorganization of the starting carbon material into particles structurally composed of concentric graphitic shells.<sup>9</sup> Metal-carbon soot particles prepared by other high-energy techniques, like an electric arc, have also been studied by HRTEM and it was found that nanocrystals of gold or cobalt could be encapsulated by carbon onions.<sup>10,11</sup>

One obvious feature of all these preparation methods is that they are high energy demanding techniques using small laboratory scale instrumentation. In contrast, the method of chlorinating metal carbides allows large quantities to be prepared at lower energy costs. Gordeev and Vartanova predicted the observed large specific pore volume of decomposed metal carbides, when the metal was removed.<sup>12</sup> Carbon obtained from SiC has been successfully tested as carbon electrodes for super-capacitors.<sup>13</sup> We report in this communication a preparation method for larger quantities of high surface area carbons with a new type of amorphous as well as onion-like structure.

In a typical preparation route 5 g TiC (H.C. Starck, grade C.A.) or 5 g SiC (Norton, grade F1200) powder was used as the starting material. For TiC the reaction with Cl<sub>2</sub> took place in a silica tube furnace at a temperature of 900 °C. As a comparison, SiC powder was used as the starting material at a higher reaction temperature of 1000 °C to ensure gaseous SiCl<sub>4</sub> was removed. Thus, the metal atoms in the carbides were etched and removed as gaseous metal chlorides to leave porous carbon powders as the products. Argon gas was used to flush the tube furnace before chlorination to remove air and after chlorination to remove the used Cl<sub>2</sub> gas and any residual metal chloride from the carbon. A summary of the preparation results and process parameters is listed in Table 1. The general reaction equation is given below:



A general feature of the process is that the overall powder morphologies of the precursor and the carbon product are very similar, which was found by SEM observation, see Fig. 1. This suggests that no long distance diffusion of carbon atoms took place during the chlorinating reaction at these moderate temperatures. The carbon structure is assumed to form by “local re-bonding” of each carbon atom in the carbide with a close neighboring carbon when metal atoms are removed from their structure sites by chlorine. Migration of metal or metal chloride within the graphitic domains might take place with a similar mechanism as discussed for metal encapsulated onions previously.<sup>10,11</sup> A detailed discussion of this mechanism, however, and the influence of different precursor carbide crystal structures and sp<sup>2</sup> versus sp<sup>3</sup> bonds will be published elsewhere.<sup>14</sup>

Carbon powders were ground and characterized by high-resolution transmission electron microscope (HRTEM). The HRTEM images of carbon fragments from TiC revealed that the major part of the carbon structure consisted of three-dimensionally disordered graphite planes. However, the formation of areas of an “onion-like” structure was easily seen at the fragment edges, cf. Fig. 2(a). The latter structure is represented by concentric spherical graphitic shells, interpenetrated and overlapped by each other. The outer diameter size of spherical graphitic shell structures is between 15 and 35 nm. The distance between two graphitic planes in the shells is 0.34 nm, similar to the interplanar distance in the well-ordered graphite structure itself. Incomplete spheroidal shells could be found also in the amorphous structure that formed the larger particles (Fig. 2(b)). In general, the onion-like structure obtained from chlorinating TiC at 900 °C is not as well ordered as those onion-like structures reported to form in small amounts by Ugarte, for instance.<sup>9</sup>

Very small amounts of nanotube-like structures were formed at the edge of the fragments, as shown in Fig. 2(c). These structures have multiple walls with 4–6 nm inner diameter and 8–12 nm outer diameter. In addition, some tube-like thin walled structures might be seen to form at the surface. It cannot be excluded that the latter phenomenon is a secondary process involving some growth from the gas phase, where a small amount of CCl<sub>4</sub> might be present.

The HRTEM image of the carbon from SiC indicated that no onion-like graphitic shells existed in the structure, and none were observed by investigating a large number of particle fragments. After chlorination of SiC the carbon atoms formed a disordered amorphous nanoporous structure of graphite planes, see Fig. 3. This indicates that the technique of chlorinating a metal carbide does not necessarily result in the formation of structure elements like the onion-like carbon

**Table 1** Parameters and results of chlorination process

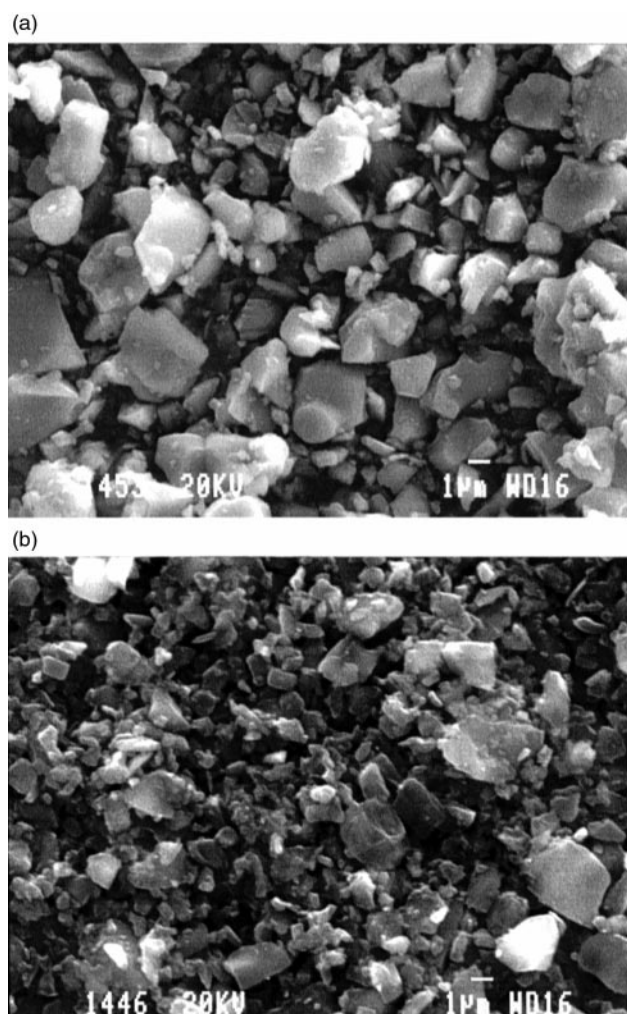
Parameters			C product	
Raw material	Temperature/°C	Time/h	BET/m <sup>2</sup> g <sup>-1</sup>	C yield (wt.%)
TiC	900	1	1400	> 99
SiC	1000	1	1200	> 99

structures. The obtained structure is related to the atomic configuration of the carbide precursor, *e.g.* atomic arrangement, C–C bond angle and bond length and the metal:C atomic ratio, as will be described elsewhere.<sup>14</sup>

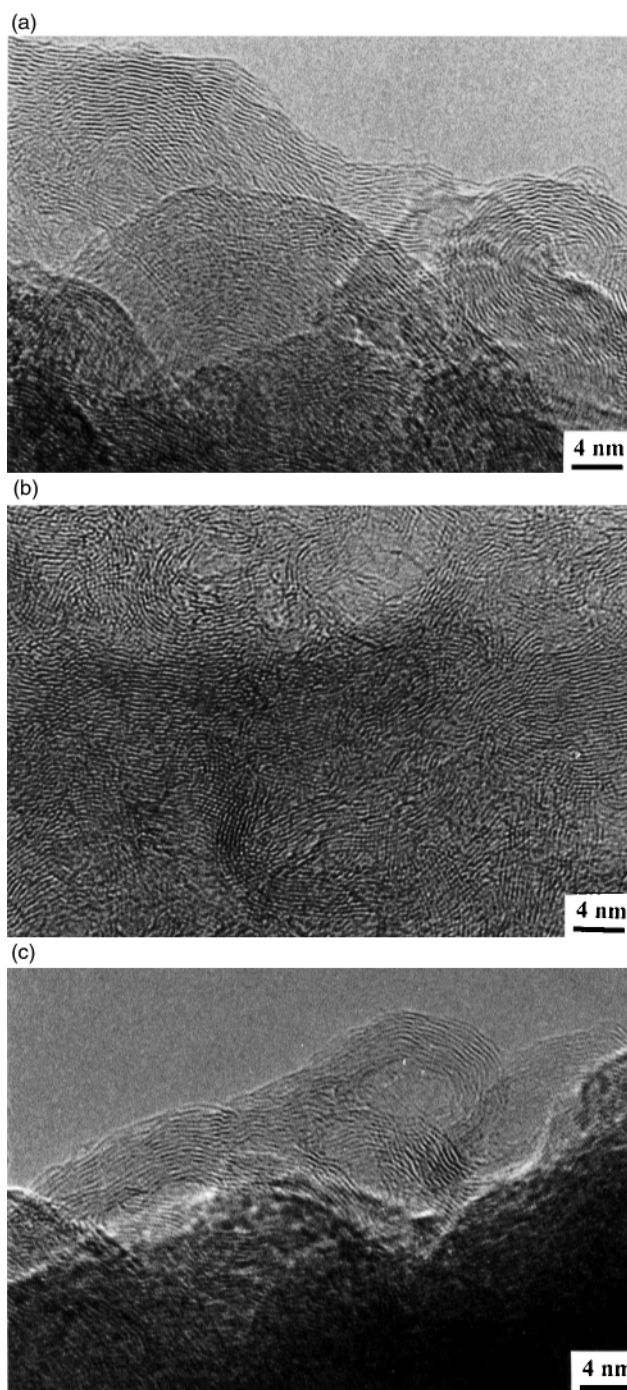
The structure of carbon from TiC may also be looked upon as macroscopically very disordered. However, the formation of many incomplete spheroidal shells and/or disordered intergrowth of the onion-like structure indicated that the process might need to be optimized to achieve a higher fraction of the onion-like structure. This type of structure is believed to be formed by “local re-bonding”, in a more ordered way, of carbon atoms during chlorination. Thus, the carbons initially found ordered in the carbide structure will bond with neighboring carbons when the Ti atoms are removed. This preparation technique may be used to produce highly porous carbons with the new structures in larger quantities. The study of the influence of different process parameters such as temperature is in progress.

Another feature of the process is that the produced carbon powder has a very high specific pore volume and surface area and a statistically very narrow pore size distribution. The

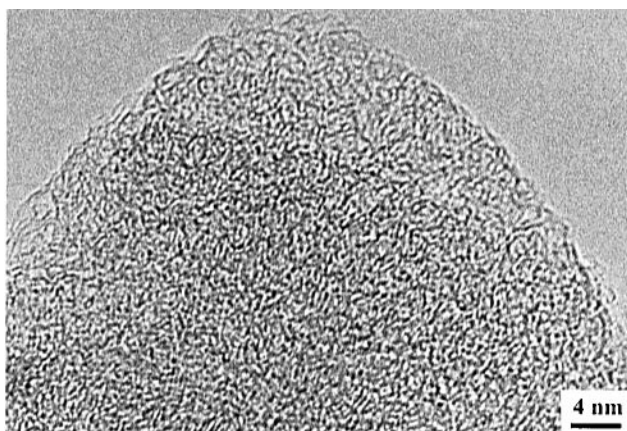
surface areas (BET) of the porous carbons from TiC and SiC are 1400 m<sup>2</sup> g<sup>-1</sup> and 1200 m<sup>2</sup> g<sup>-1</sup>, respectively. The pore sizes of two carbon products from TiC and SiC fall around 0.7–2 nm with a maximum below 1 nm. This was determined by gas-porosimetry, and the pore size distributions assuming slit-like porosity are illustrated in Fig. 4. This means that the pore size



**Fig. 1** SEM images of (a) TiC powders before chlorination, (b) carbon powders obtained after chlorination.



**Fig. 2** High-resolution TEM images of carbon from TiC powder showing (a) onion-like structures in the carbon fragment, (b) incomplete spheroidal shells in the structure, and (c) nanotube structures.

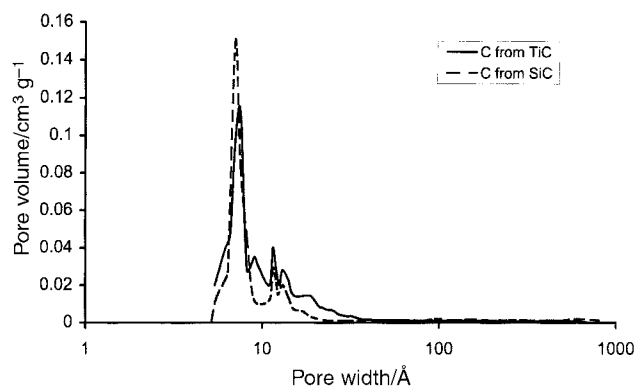


**Fig. 3** High-resolution TEM image showing the amorphous structure in a carbon fragment produced from SiC powder.

of the resulting carbon is more related to the atomic configuration of the carbon skeleton in the structures than the different radii of metal ions that are removed. By proper choice of metal carbide precursors, porous carbon with different pore volumes or pore sizes may be produced, as predicted by Gordeev and Vartanova.<sup>12</sup>

Carbon materials have excellent chemical stability and good conductivity in general, combined with the special features mentioned above for these nanoporous carbons. Therefore, the latter materials become excellent candidates for many applications, such as for gas storage, adsorbents or electrodes for super-capacitors and batteries. Capacitance tests of carbon electrodes made from TiC show excellent capacitance up to  $320 \text{ F g}^{-1}$  and  $140 \text{ F g}^{-1}$  in water and organic electrolyte capacitors with cell voltages of 1 V and 3 V, respectively. Furthermore, preliminary  $\text{H}_2$  storage measurements of carbon from TiC show that 2 wt.% of hydrogen can be stored at 77 K and a pressure of 0.5 MPa. This corresponds to a H/C atomic ratio of 0.24.<sup>15</sup> Therefore, the process may provide a new route for production of large quantities of nanoporous carbons with new structures for these applications.

It should also be mentioned that carbon onions formed by electron irradiation in HRTEM seem to be able to transform their cores to diamond if simultaneously heated to  $700^\circ\text{C}$ .<sup>16</sup> Under these conditions the graphite plane spacing (0.3 nm) decreases to 0.22 nm, indicating considerable compression towards the particle centers. Further studies are needed to determine whether this is a true transformation of graphite into diamond, and so far similar structural transformations have not been seen during the chlorination of metal carbides.



**Fig. 4** Pore size distribution of carbon powder made from TiC and SiC, measured by gas-porosimetry.

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