Micro and mesoporosity of carbon derived from ternary and binary metal carbides

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Abstract

In this work we systematically characterized both the micro- and mesoporosity that develops when Ti3SiC2, Ti3AlC2, Ti2AlC, Ti2AlC0.5N0.5, Ta2AlC, Ta2C, and TaC are chlorinated at different temperatures. The porosity of the carbide-derived carbon varied based on the initial carbide’s structure and chemistry. The carbides with anisotropic structures, such as the layered ternary carbides, result in larger mesopore volumes as compared to more isotropic carbides such as TaC. Furthermore, the carbon pore structure can collapse, resulting in low pore volumes for materials with low molar fractions of carbon, as was the case with Ti2AlC0.5N0.5.

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1. Introduction

Carbide-derived carbon (CDC) is a nanoporous carbon formed by selectively etching metal atoms from metal carbides [1]. The highly tunable porosity of CDC [1–3] has inspired fundamental studies of the effects of pore size, pore volume, and surface area on transport and adsorption of gases, ions and biomolecules [4–8]. The fascinating properties of CDC allowed recent breakthroughs in many demanding applications including H2 storage [4,5], supercapacitors [6], and extracorporeal devices for sepsis treatment [8]. Due to a broad range of pore sizes (0.3–30 nm) and specific surface areas (300–2300 m²/g) of CDCs, the great potential for applications requiring large volumes of either micropores (<2 nm) or mesopores (2–50 nm) has been identified [1].

CDCs can be synthesized through halogenation, thermal and hydrothermal treatments [1,9], a common method being the chlorination of metal carbides at elevated temperatures. Numerous metal carbides have been chlorinated, including binary [10–19] and ternary [2,8,20,21] carbides, the latter, being selected from a group of anisotropic, layered MAX-phase carbides [22], showed particular promise for mesopore size and volume control [8]. This group of ternary carbides have a Mₙ₊₁AXₙ chemistry where M is an early transition element, A is an A-group element, X is carbon and/or nitrogen, and n is either 1, 2, or 3. The unique structure of MAX-phases yields thermal-shock resistant machinable carbides [22–24] and allows control of both the shape of the sample and porosity of the resultant CDC.

CDC has been produced from powders, sintered ceramics, thin films, nanowires, and whiskers [1,15,25]. Based on the initial carbide and synthesis conditions, several carbon structures can form upon chlorination ranging from amorphous carbon and turbostratic graphite, to nanodiamond, and onions to graphitic ribbons, highly ordered graphite, and nanotubes [13,21,26,27]. Changes in CDC structure
and porosity depending on the synthesis temperature and initial carbide chemistry have been documented [1]; however, the reasons for such variations remain unclear.

This work systematically studied the influences of metal carbide chemistry, stoichiometry, and structure on CDC porosity in order to better understand the links between the structure of the initial metal carbide and the resulting CDC and to develop tools to tailor the porosity over a wide range for diverse applications. MAX-phase carbides [22] were used to explore the effect of stoichiometry and metal atom component in the metal carbide. In addition to ternaries, a carbonitride, Ti2AlC0.5N0.5, was investigated to study an extreme low C-concentration case. The binary carbides, Ta2C and TaC, were also studied to determine the influence of chemistry and structure anisotropy on the resulting carbon porosity.

2. Experimental

Powders of Ti3SiC2 (∼325 mesh), and bulk Ti2AlC, Ti2AlC0.5N0.5, and Ta2AlC were obtained from 3-ONE-2, Voorhees, NJ. Powders were created from the bulk machinable carbides by drilling. The particle size distribution was rather broad (0.5−500 μm), the average particle size being in the 5−15 μm range. The Ta2C and TaC powders (Alfa Aesar, Ward Hill, MA) were ∼325 mesh.

The Ti3AlC2 powders were obtained by first reactively hot pressing TiC, Ti, Al, and Sn powders (Alfa Aesar, Ward Hill, MA) in a 2:1:1:0.2 molar ratio, respectively. The powders were mixed, placed in graphite dies and hot pressed in a vacuum hot press for 1 h at 1300 °C; the applied load corresponded to a stress of 30 MPa.

The powders were chlorinated using high purity Cl2 (99.5%) followed by an Ar (99.998%) anneal. Both gases were obtained from Airgas, Radnor, PA.

The chlorination was carried out as a function of temperature in the 400−1200 °C temperature range. The chlorination setup is described elsewhere [1]. Samples were always heated and cooled in the inert Ar atmosphere. In an attempt to remove residual species, including chlorine, within the carbon pore network, selected CDCs were annealed in H2 in the 400−1000 °C temperature range for 5 h. If the chlorination and H2 annealing temperatures were the same, Ar was still purged for 30 min to remove residual Cl2 gas and prevent the uncontrolled exothermic formation of HCl in the system.

The CDC structures produced after chlorination were characterized using X-ray diffraction, XRD (Rigaku, Tokyo, Japan) with CuKα radiation, Raman microspectroscopy (Renishaw 1000, Gloucestershire, UK) with Ar-ion laser (514.5 nm) and 50X objective, scanning electron microscopy (SEM) using an XL-30 (FEI, Eindhoven, Netherlands) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK), and transmission electron microscopy, TEM, (2010F, JEOL, Tokyo, Japan, operated at 200 kV) using copper grids coated with lacey carbon as sample holders.

The elemental composition of CDC was evaluated by EDS (Oxford, UK) and coefficients of elemental sensitivity were used in all calculations. While absolute values of elemental composition can be determined with limited accuracy, for this work it was important to obtain comparative values that show the effect of the processing on the composition of CDC.

Porosity was characterized from adsorption and desorption isotherms using Ar and N2 sorption at 77 K, using an Autosorb-1 or a Quadrasorb (Quantachrome Instruments, Boynton Beach, US). Prior to sorption analysis, the samples were outgassed at 300 °C overnight to remove moisture and surface contaminants. Pores up to 7 nm were measured via Ar-sorption and pores up to 35 nm were measured via N2 sorption. Pore size distributions were determined from the sorption isotherms using a non-local density functional theory (NLDFT) assuming pores are slit shaped [28]. Ar data were used to calculate pore volume of micropores (below 2 nm) and nitrogen data were used for mesoporosity analysis (2−35 nm). Hysteresis in isotherms is indicative of mesoporosity and is linked to capillary condensation phenomenon.

Calculations of theoretical pore volumes were performed assuming the transformation from carbide to carbon is conformal. The theoretical pore volumes (v_{pore}) per gram of CDC were calculated assuming

$$v_{pore} = \frac{1}{\rho_{CDC}} - \frac{1}{\rho_{C}}$$

where

- $\rho_{C}$ is the density of graphitic carbon, assumed to be 2.24 g/cm3.
- The density of CDC, $\rho_{CDC}$ is assumed to be given by

$$\rho_{CDC} = \frac{n(M_C)}{M_{MC}} \rho_{MC}$$

where $n$ is the number of moles of carbon in a formula unit of carbide, $M_C$ is the molecular weight of carbon, $M_{MC}$ is the molecular weight of the metal carbide, $M_{n+1}AX_n$, and $\rho_{C}$ is the density of the binary or ternary metal carbide.

3. Results and discussion

Energy dispersive spectroscopy, EDS, analysis, Table 1, was performed on all chlorinated powders to ensure complete removal of metal atoms, thereby, complete conversion to carbon.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Average chemistry composition of CDC based on EDS after 3 h of chlorination at 800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial carbide</td>
<td>M (at.%)</td>
</tr>
<tr>
<td>Ti3SiC2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ti2AlC3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ti2AlC</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ta2AlC</td>
<td>1</td>
</tr>
<tr>
<td>Ta2C</td>
<td>1</td>
</tr>
<tr>
<td>TaC</td>
<td>1</td>
</tr>
<tr>
<td>Ti2AlC0.5N0.5</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
When comparing the maximum pore volumes obtained from Ar-sorption for each CDC, the pore volume was found to increase with increasing initial carbide density (Fig. 1). The latter is proportional to the size and correspondingly mass of the metal or metalloid within the initial carbide.

The pore volume of CDC determined from Ar-sorption (Table 2) was typically found to be less than the theoretical pore volume calculated from Eq. (1). The following factors can account for the difference:

(i) Closed pores or pores blocked by metal chlorides, chlorine, or residual metals.
(ii) Collapse of structure forming cracks too large for the adsorbate to condense into.
(iii) Formation of mesopores >7 nm undetectable by Ar at 77 K.

Note, in the case of TaC, the measured pore volume is larger than the calculated pore volume. This discrepancy could be due to partial etching of carbon by chlorine or oxygen residues remaining in the system.

3.1. Blocked pores

H₂ annealing of CDC led to a reduction in the amounts of residual Cl₂ as measured by EDS (Table 3) and to opening the blocked pores. For example, by 5 h H₂ annealing of a Ti₃SiC₂-CDC powder chlorinated at 400 °C, the pore volume increased from 0.42 to 0.64 cc/g (Fig. 2). Note that while H₂ annealing opened blocked pores, especially those <1 nm (see Fig. 2), the theoretical pore volume remained greater than the measured one. Removal of hydrophobic chlorine termination from CDC likely resulted in the formation of hydrophilic functional groups upon exposure of samples to air and possibly led to a higher moisture uptake, as observed by higher oxygen content in the annealed samples.

3.2. Collapse of structure

According to Eq. (1), the theoretical pore volumes for Ti₂AlC₀.₅N₀.₅, Ti₂AlC and Ti₃AlC₂ should decrease from 5.11 to 2.33 and to 1.47 cc/g, respectively. Somewhat surprisingly, the respective measured pore volumes (Fig. 3), 0.25, 0.99 and 1.16 cc/g were in the reverse order. The exact reason for this state of affairs is not entirely clear. However, the simplest explanation is that the C-content in the Ti₂AlC₀.₅N₀.₅ CDC was too small to sustain a fine-pore structure. In other words, large cracks formed within the sample, as visible in the SEM micrograph (Fig. 4a). Interestingly, and despite the collapse of structure on a micro- and mesoscale, the overall macroscopic shape of the sample did not shrink as a result of the chlorination process. This implies that the pores were replaced by large cracks into which the Ar and N₂ do not measurably condense. Even in Ti₃SiC₂-CDC (Fig. 4b) where the difference between theoretical and Ar-sorption pore volumes was not as dramatic as for the case of Ti₂AlC₀.₅N₀.₅ (Fig. 4a), several inter- and intragranular cracks are visible (inset Fig. 4b). Due to the anisotropic structure of MAX-phases, a preferred direction of shrinkage [21] results in the formation of large cracks, which can be considered a source of pore volume. Here again the formed cracks are larger than 35 nm and are thus not detected by either Ar or N₂ sorption measurements.

3.3. Mesopores

The N₂ sorption isotherms recorded at 77 K for Ti₂AlC-CDC and Ti₃AlC₂-CDC chlorinated at 600, 800, and 1200 °C for 3 h, are shown in Fig. 5. For both Ti₂AlC-CDC and Ti₃AlC₂-CDC, the isotherms for CDCs chlorinated at 800 °C have the largest hysteresis loops, suggestive of large mesopore volumes. Interestingly, samples chlorinated at the slightly lower temperature of 600 °C show little hysteresis and thus should be almost entirely microporous. Fig. 6 summarizes the data on measured pore volumes in

![Diagram](image)

**Fig. 1.** Influence of precursor carbide density on pore volume of resulting CDC. Inset, MAX-phase carbide unit cell structures for 211, 312, and 413 stoichiometries from left to right.

<table>
<thead>
<tr>
<th>Initial carbide</th>
<th>Ar-pore volume (cc/g)</th>
<th>Theoretical pore volume (cc/g)</th>
<th>DFT Ar-surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₃SiC₂</td>
<td>0.79</td>
<td>1.37</td>
<td>1380</td>
</tr>
<tr>
<td>Ti₃AlC₂</td>
<td>0.57</td>
<td>1.47</td>
<td>920</td>
</tr>
<tr>
<td>Ti₂AlC</td>
<td>0.60</td>
<td>2.33</td>
<td>810</td>
</tr>
<tr>
<td>Ti₂AlC₀.₅N₀.₅</td>
<td>0.25</td>
<td>5.11</td>
<td>390</td>
</tr>
<tr>
<td>Ta₂AlC</td>
<td>1.14</td>
<td>2.41</td>
<td>1000</td>
</tr>
<tr>
<td>TaC</td>
<td>1.27</td>
<td>1.63</td>
<td>1950</td>
</tr>
<tr>
<td>TaC</td>
<td>0.88</td>
<td>0.71</td>
<td>1955</td>
</tr>
</tbody>
</table>

Values for DFT specific surface area are provided for a reference.

* Values for Ti₂AlC₀.₅N₀.₅ are for CDC chlorinated at 600 °C.
two ranges (<2 nm and 2–35 nm) calculated from Ar and N₂ sorption isotherms, respectively. Independently of the chlorination temperature and carbide stoichiometry, the micropore volume calculated was in the 0.4–0.7 cc/g range. The obtained porosity values are supported by trends revealed by other techniques. For example, adsorption of proteins on the CDC produced from the same initial carbides, Ti₂AlC and Ti₃AlC₂ at the identical synthesis conditions, showed the maximum proteins’ uptake in CDCs produced at 800 °C [8]. Since there was little correlation between the total surface area and the sorption of large (5–10 nm) protein molecules and a good correlation between the meso-pore volume and protein absorption we take that to be indirect evidence for the formation of mesopores in the 800 °C CDC. This temperature was thus used to explore the effect of chemistry and stoichiometry on mesopore formation.

![Fig. 2. Influence of H₂ annealing at 1000 °C for 5 h on pore size distribution of Ti₃SiC₂-CDC chlorinated at 400 °C. Sharp drops in pore size distribution are artifacts of the DFT analysis. The dotted curve depicts an estimation of a more realistic pore size distribution.](image)

![Fig. 3. Comparison of pore size distributions from Ar-sorption at 77 K of Ti₂AlC₂-CDC, Ti₃AlC-CDC, and Ti₃AlC₀.5N₀.5-CDC chlorinated at 600 °C. Sharp drops in pore size distribution are artifacts of the DFT analysis. The dotted curve depicts an estimation of a more realistic pore size distribution.](image)

Fig. 2 shows N₂ sorption isotherms of the CDC derived from Ti₂AlC, Ti₃AlC₂, Ti₃SiC₂, Ta₂C and TaC. CDC produced from ternary Ti₂AlC and Ti₃AlC₂ carbides showed the highest uptake of N₂ with over 1750 and 1250 cc/g, respectively. Both CDCs have large hysteresis loops indicating a large volume of mesopores. Changing the carbide chemistry to Ta₂AlC resulted in a weaker hysteresis with a maximum uptake of only ~750 cc/g. CDC produced from binary TaC and Ta₂C, resulted in isotherms with minimal hysteresis, indicative of the near absence of mesoporosity.

With two exceptions, the sum of meso- and microporosity volumes was still smaller than the theoretical pore volume (Fig. 8). The larger measured pore volume (Ti₂AlC and TaC, Fig. 8) could be explained by the partial reaction of carbon atoms during synthesis with traces of oxygen in the reaction gas or the formation of carbon chlorides; in other words, the etching of C atoms.

### Table 3
EDS results from Ti₃SiC₂-CDC chlorinated at 400 and 800 °C and annealed for 5 h in H₂

<table>
<thead>
<tr>
<th>Synthesis temperature (°C)</th>
<th>Annealing temperature (°C)</th>
<th>Cl (at.%)</th>
<th>Ti (at.%)</th>
<th>Si (at.%)</th>
<th>C (at.%)</th>
<th>O (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>None</td>
<td>2.9</td>
<td>0.1</td>
<td>0.2</td>
<td>88.9</td>
<td>7.8</td>
</tr>
<tr>
<td>400</td>
<td>400</td>
<td>1.7</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>88.4</td>
<td>9.5</td>
</tr>
<tr>
<td>400</td>
<td>1000</td>
<td>0.0</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>89.5</td>
<td>10.3</td>
</tr>
<tr>
<td>800</td>
<td>None</td>
<td>1.8</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>90.0</td>
<td>7.9</td>
</tr>
<tr>
<td>800</td>
<td>400</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>91.5</td>
<td>8.2</td>
</tr>
<tr>
<td>800</td>
<td>1000</td>
<td>0.0</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>89.8</td>
<td>10.0</td>
</tr>
</tbody>
</table>
The smaller measured pore volumes (Ti$_3$SiC$_2$, Ti$_2$AlC, Ta$_2$AlC, and TaC, Fig. 8) may be linked to closed pores or, more probably, the formation of pores >35 nm (such as macropores and the large cracks shown in
Ti₃AlC₂, Ti₃SiC₂, Ta₂AlC, Ta₂C, and TaC. Values for microporosity were determined from Ar-sorption results, while mesoporosity was determined from N₂ sorption results. Calculated theoretical porosity is denoted by dotted line.

Fig. 4), undetectable by sorption measurements. The binary CDCs produced from carbides with uniform distribution of carbon atoms in the lattice, TaC in particular, showed the largest micro- to mesoporosity ratio. In contrast, the layered nature of the ternary carbides in general promotes formation of mesopores (Ti₃AlC₂, Ti₃SiC₂, Ta₂AlC, Ta₂C, Fig. 8), suggestive of a strong effect of the anisotropy in the initial carbide unit cell on the mesopore formation. Substantial variations in the micro-to-mesoporosity ratio observed within CDC from MAX-phase carbide family (compare Ti₃AlC₂ to Ti₃SiC₂ or Ti₂AlC to Ta₂AlC, Fig. 8) reveal a strong effect of carbide M and A elements on CDC pore size distribution. For example, the larger size of M atoms and/or their chlorides, appear to favor the formation of larger micropore volumes, and inhibit the formation of mesopores (compare Ti₃AlC₂ to Ti₂AlC, Fig. 8, or TaC, Fig. 8, to TiC [29]). Unlike microporosity, the initial carbide density does not appear to be influence mesopore formation.

4. Conclusions

Both micro and mesopore formation are influenced by chlorination temperature. Micropore formation is strongly influenced by initial carbide density. Mesopore formation is influenced by carbide structure and chemistry, but not carbide density. Mesopores tend to form in larger quantities from the layered MAX-phase carbides as compared to the isotropic binary carbides. It is not possible to increase the pore volume indefinitely. If the initial carbon concentration in the carbide is too low, chlorination leads to a collapse of structure in such a way as to form macropores and/or large cracks, thereby resulting in substantially reduced pore volume as compared to theory.

Fig. 8. Comparison of sum of measured micro and mesoporosity to calculated theoretical porosity in CDC produced at 800 °C from Ti₃AlC₂, Ti₃SiC₂, Ta₂AlC, Ta₂C, and TaC. Values for microporosity were determined from Ar-sorption results, while mesoporosity was determined from N₂ sorption results. Calculated theoretical porosity is denoted by dotted line.

Acknowledgments

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