Research Article

Preparation and Microstructure Analysis of TiC-Derived Carbons with Hierarchical Pore Structure

Jin Jia, Aiguo Zhou, Yuanyuan Zhu, Jiang Liu, Shihao Feng, Yufan Tao, Baoling Xing, and Chuanxiang Zhang

School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, China

Correspondence should be addressed to Aiguo Zhou; zhouag@hpu.edu.cn

Received 30 January 2015; Accepted 10 April 2015

Academic Editor: Margarida Amaral

Copyright © 2015 Jin Jia et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Carbide-derived carbons (CDCs) with hierarchical pore structure are prepared from commercial TiC powders by chlorination at temperature range of 600–1100°C. As-synthesized CDCs mainly consist of amorphous carbon and there exists a graphitization trend at chlorinating temperature above 800°C. If chlorinating temperature is below 1000°C, CDC particles maintain the shape of original TiC particles. Above 1000°C, obvious cracks appear in CDC particles and some particles are broken into small parts. The specific surface area (SSA) of CDCs is in the range from 672 m²/g to 1609 m²/g. The highest SSA is 1609 m²/g for CDC chlorinated at 1000°C. Most pores in these CDCs are micropores with the size of 0.7–2 nm. However, some mesopores and macropores also exist.

1. Introduction

Carbide-derived carbons (CDCs) are produced from carbides by removing noncarbon elements in the process of high temperature chlorination. CDCs with tunable pore size have numerous actual and potential applications in the area such as supercapacitors [1, 2], lubrication [3], hydrogen/methane storage [4], and electrode materials [5].

Generally, the pore size of CDCs is continuously distributed in a small range. Recently, it is found that carbons with hierarchical pore (HP) structure have higher performance than general carbons with monosize pore structure in the area of energy storage [6, 7]. These HP carbons have micropores, mesopores, and/or macropores. A hierarchical and highly porous CDC is obtained by chlorination from *mesostructured* SiC/TiC [8, 9] ceramics or preceramic polymer [10]. CDCs with micro-, meso-, and/or even macropores show high gas uptake and excellent performance as electrode materials in supercapacitors [11–14].

Is it possible to make CDCs with hierarchical pore structures (HPCDCs) *directly* from dense monolithic carbide precursor by high temperature chlorination? In this paper,

an attempt is made to synthesize HPCDCs by chlorination from dense TiC.

Titanium carbide (TiC) is one of the most common and widely used carbides to make CDCs [15, 16]. Small and uniform carbon-carbon distance of TiC leads to uniform porosity and narrow pore size distribution of obtained CDCs. Their specific surface area (SSA) and total pore volume increase as chlorination temperature increases from 600°C to 900°C; however, the pore size distributions are almost unchanged [17]. Additionally, the fabrication of HPCDCs by chlorination from mesoporous TiC was studied [8, 18].

In this study, CDCs are prepared from commercial dense titanium carbides by high temperature chlorination. Similar synthesis is reported in previous literature [17]. However, in our opinion, further microstructure study can help us better understand the material and the synthesis process. Although scanning electron microscopy (SEM) cannot be used to observe micropores in CDCs, it can clearly observe the surface morphology of CDC particles. In this paper, CDCs with meso- and macropores are desired. Extensive SEM pictures, combined with the results of X-ray diffraction (XRD) and Raman spectroscopy, are used to study the surface morphology of CDC particles.

FIGURE 1: (a) XRD patterns of TiC and (b) CDC samples synthesized at various temperatures. Complete conversion of TiC to carbon takes place at 600°C and above. Broad peaks show the highly amorphous nature of the carbon produced from TiC.

2. Experimental

2.1. Preparation. CDCs were produced by chlorination from commercial TiC powders (2–4 μm , 99 wt.% pure, Aladdin Industrial Co., China). The TiC powders were placed on a graphite foil and loaded in the effective hot zone of a horizontal quartz tube furnace. The tube was purged with Ar for 30 min (60 cm^3/min) and then heated up to the desired temperature (600–1100°C) at a rate of 20°C/min. Once the desired temperature was reached and stabilized, the flowing Ar was stopped and a chlorinating process for 3 h began in freshly prepared Cl_2 gas. After the chlorinating process completed, the samples were cooled down to room temperature under flowing Ar atmosphere (10–60 cm^3/min) to remove residual metal chlorides and then taken out for further analyses. A description of the chlorination process in detail can be found elsewhere [19].

2.2. Measurements. XRD patterns were obtained by X-ray diffractometer (XRD, Bruker AXS Co., Germany) based on Cu K_α radiation. Microstructure of CDC particles was observed by scanning electron microscope (SEM, JSM-6390LV, JEOL, Japan). CDC samples were also analyzed by micro-Raman spectroscopy (Renishaw 1000, UK) using an Ar ion laser (wave length: 514.5 nm, spot size: 2 μm) at 500 magnification. Isotherms of CDCs were measured by a N_2 absorption apparatus at 77 K (Autosorb-iQ-MP, Quantachrome, USA). Before N_2 sorption measurements, all samples were dried at 473.15 K for 10 h in vacuum. Brunauer Emmett Teller (BET) SSA was calculated by BET equation from volume of gas adsorbed at relative pressure between 0.05 and 0.3, where the BET isotherm is linear. Pore size distribution (PSD) and SSA of CDCs, assuming slit pores, were evaluated by nonlocal density functional theory (NLDFT).

V-t method was used to obtain the plots of differential micropore area/volume versus synthesis temperature.

3. Results and Discussion

3.1. CDC Structure. Figure 1 shows the XRD patterns of raw material TiC and obtained CDCs. From the figure, all TiC transforms to carbon at temperature above 600°C. The absence of sharp peaks in XRD patterns of CDCs (Figure 1(b)) indicates that as-synthesized CDCs are amorphous. However, it is noticed that there is a weak peak at 26° for samples synthesized at temperature above 900°C. The 26° peak is the characteristic peak of graphite. Therefore, some amorphous carbons transform to graphite at temperature above 900°C.

Figure 2 shows the Raman spectroscopy analysis results of as-synthesized CDCs. For perfectly ordered graphite, only one peak, G band corresponding to in-plane stretching at $\sim 1579\text{ cm}^{-1}$, should be shown in the range studied in Figure 2(a). However, most graphites with disordered carbons generally exhibit a second disorder-induced peak (D band) at $\sim 1349\text{ cm}^{-1}$ as well as two combination bands (2D band at $\sim 2686\text{ cm}^{-1}$ and D + G band at $\sim 2914\text{ cm}^{-1}$) [20]. As shown in Figure 2(a), all samples show two main peaks, D and G bands of graphitic carbon. At chlorinating temperature of 600°C, the carbons are just formed and in amorphous state. The corresponding D band and G band are weak as shown in Figure 2(a). As chlorinating temperature increases, both D band and G band become stronger and sharper obviously. 2D band and D + G band appear at 800°C chlorinated samples and become stronger and sharper as chlorinating temperature increases to 1100°C.

From the analysis of the position of D band and G band, it is found that D band shifts to low angle as temperature

FIGURE 2: (a) Raman spectra of CDC produced by chlorinating TiC for 3 hours at 600–1100°C. (b) Positions of D and G bands of carbon. (c) Ratio of integrated intensities of D and G bands. (d) Full width at half maximum (FWHM) of D and G bands.

increases, as illustrated in Figure 2(b), which should be due to lattice defects and/or sp^2 hybridization of carbons. Figure 2(c) shows the intensity ratio of D band and G band (I_D/I_G , fitting calculation). Below 800°C, it increases with reaction temperature, while, above 800°C, the ratio decreases with temperature. Because G band is from ordered graphite and D band is from disordered graphite, the increase of I_D/I_G below 800°C means more and more carbons in disordered state are formed; the decrease of I_D/I_G above 800°C means more and more carbons transform from disordered state to ordered state. Figure 2(d) shows full width at half maximum of D band (FWHMD) and that of G band (FWHMG) for samples processed at varied temperature. As processing temperature increases, both FWHMs have a trend of decrease. This trend means the sharpening of the two bands, which

indicates that more ordered CDCs are synthesized at higher temperatures.

Figure 3 shows the SEM images of TiC powders and synthesized CDC powders. Figure 3(a) is the SEM image of TiC particles. Figure 3(b) is that of CDC particles processed at 600°C. The surfaces of that CDC are rough; however, they exhibit no obvious pores or cracks. Compared with TiC particles (Figure 3(a)), CDC particles obtained at 600°C have similar particle shape (Figures 3(a) and 3(b)). For samples obtained at 700°C, similar results are obtained. However, for samples made at 800°C, some cracks appear on the surface of CDCs (Figure 3(c)). Moreover, more obvious cracks appear in the CDCs made at higher temperatures (Figures 3(d) and 3(g)). Thus, the chlorinating process can result in the formation of intragranular cracks on the surface

FIGURE 3: SEM images of (a) TiC powders before chlorination; (b) CDC chlorinated at 600°C; (c) CDC chlorinated at 800°C; ((d) and (e)) CDC chlorinated at 900°C; (f) CDC chlorinated at 1000°C; and (g) CDC chlorinated at 1100°C.

of CDC particles, particularly in the CDCs produced at higher temperatures. The macroscopic shapes of obtained CDC particles are similar to that of TiC preformed during the chlorination below 1000°C. However, above 1000°C

(Figures 3(f) and 3(g)), the particles are broken into several small parts.

As the authors know, this is the first time to observe and report this phenomenon. There are two reasons for

FIGURE 4: (a) N_2 adsorption isotherms of CDCs. (b) Differential BET SSA, NLDFT SSA, and total pore volume versus the synthesis temperature plots. (c) Micropore area and micropore volume of CDCs.

the formation of these cracks. The first one is a chemical reason. At high temperature, Ti element in TiC particles is carried off by chlorination very fast, which results in the collapse of the just formed CDC structure, and in turn causes the formation of these cracks. The second one is a physical reason. Thermal stress generated during heating up and cooling down results in the cracks. The thickness of the cracks is up to $\sim 1 \mu\text{m}$. These cracks are actually macropores that can act as molecule-buffer reservoirs and gas-channels in the energy storage application of CDCs.

As shown in Figure 3(d), at 900°C, there are some clear traces of graphitic layers in the surface of CDCs. Combining with XRD results (Figure 1) and Raman results (Figure 2), we drew the conclusion that the CDC changes from amorphous carbon to graphitic structure with increasing chlorination

temperatures. Additionally, some pits are formed on the surface of CDCs made at 900°C (inset of Figure 3(e)). The formation of these pits should be related to the remotion of some carbons on the particle surface.

3.2. Specific Surface Areas and Pore Size Distributions. Isotherms of CDC samples are shown in Figure 4(a). A steep increase was observed at low relative pressure, followed by a moderate slope at intermediate pressure. Isotherms of all CDC samples, especially that of samples obtained at 700°C, are linear (type I), which is the characteristic of isotherms of microporous materials (pore size less than 2 nm). However, there exists small hysteresis, particularly in the isotherm of 1100°C sample, which is usually associated with mesopore structures (type H4); moreover, there are minor upwarps at

FIGURE 5: Pore size distributions of CDC samples.

the end of the isotherms of CDCs chlorinated at temperature above 800°C, which are associated with macropores in the samples [21]. Therefore, CDCs prepared at 700°C have only micropores. However, as chlorinating temperature increased, small amount of mesopores and macropores appeared in CDCs. The isotherms of CDCs obtained at 800–1100°C exhibit the combined effects of the micropores, mesopores, and macropores in the CDCs. In combination with SEM images (Figure 3), the N_2 isotherms of CDCs clearly support the evolving development of a multiscale pore structure from typical monosized microporous CDCs.

Figure 4(b) shows the SSA and pore volume of CDCs chlorinated at various temperature. BET SSA increases from 672 m^2/g to 1609 m^2/g with processing temperature if the temperature < 1000°C. However, the value of BET SSA decreases if the temperature > 1000°C. The largest BET SSA is 1609 m^2/g at 1000°C. The NLDFT SSA shows similar trend. And, total pore volume of CDCs increases with temperature at the range of 600–1000°C (Figure 4(b)); for 1100°C samples, the volume value decreases slightly. Figure 4(c) shows the different micropore area and micropore volume of CDCs chlorinated at varied temperature. Similar to the trends shown in Figure 4(b), both micropore area and volume increase and then decrease with temperature. The maximum values are obtained for 1000°C samples.

Figure 5 shows pore size distribution of CDC samples. The pore size of all CDC samples is mainly distributed in the range of 0.7–2 nm. These are micropores that contribute maximized space sites for molecule storage or gas storage in the application of energy storage. However, there are some mesopores (2.0–4.5 nm) in CDCs as shown in Figure 5, and the amounts of mesopores increase with processing temperature. The distribution curves of CDC samples made at 700–900°C are not continuous and a gap exists in the range of 2.1–2.3 nm. Therefore, these CDCs have hierarchical pore structure. The mesopores are greatly significant for providing

channels with lower gas-transport resistance and shorter diffusion routes.

In addition, as processing temperature increases, cumulative pore volume increases; however, the ratio of micropore/mesopore decreases and CDCs processed at higher temperatures contain more mesopores. The volume of micropores increases with temperature below 1000°C and decreases above 1000°C. 1000°C is the best chlorinating temperature to acquire CDCs with the highest SSA (Figure 4(b)) and the largest micropore volume (Figure 4(c)).

In previous work [17], SSA and total pore volume increase as chlorination temperatures increase from 600°C to 900°C. Here we report a maximum value at 1000°C. Above 1000°C, both SSA and pore volume decrease with temperature. This is because the increase of mesopore volume causes the decrease of micropore volume, and cracks appearing in the CDC (Figure 3) decrease the micropore volume further more. This is first report on the optimal chlorinating temperature, which is important for the production of CDCs with high SSA and large micropore volume.

Compared with previous method making HP CDCs from TiC with mesoporous structure [18], this is a simple and cheap method to produce HP CDCs directly from commercial TiC powders.

4. Conclusions

Hierarchically porous TiC-CDCs were successfully synthesized from commercially available titanium carbides via high temperature chlorination process and their microstructure, specific surface area, and pore size were analyzed. In the chlorinating process, CDCs with different microstructure were acquired by controlling the reaction temperature. The CDCs obtained in this experiment mainly consisted of amorphous carbon and maintained the shape of TiC particles. At 800°C, the CDCs started transforming from amorphous carbon to graphite. As reaction temperature increased, the BET SSA increased from 672 m^2/g to 1609 m^2/g . Furthermore, the chlorinating process can induce the formation of intragranular cracks (macropores) and pits on the surface of CDCs, particularly in the CDCs produced at higher temperatures such as 800°C and 1100°C. As the authors know, it is the first time to observe and report this phenomenon.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors appreciate Professor Ruijun Zhang and Mr. Peng Chen for the help in building chlorinating equipment. This work is supported by Nature Science Foundation of China (51472075), Plan for Scientific Innovation Talent of Henan Province (134100510008), and Program for Innovative Research Team of Henan Polytechnic University (T2013-4).

References

- [1] P. Huang, M. Heon, D. Pech et al., "Micro-supercapacitors from carbide derived carbon (CDC) films on silicon chips," *Journal of Power Sources*, vol. 225, pp. 240–244, 2013.
- [2] J. W. Campos, M. Beidaghi, K. B. Hatzell et al., "Investigation of carbon materials for use as a flowable electrode in electrochemical flow capacitors," *Electrochimica Acta*, vol. 98, pp. 123–130, 2013.
- [3] J.-H. Jeong, H.-T. Bae, and D.-S. Lim, "The effect of iron catalysts on the microstructure and tribological properties of carbide-derived carbon," *Carbon*, vol. 48, no. 12, pp. 3628–3634, 2010.
- [4] S.-H. Yeon, I. Knoke, Y. Gogotsi, and J. E. Fischer, "Enhanced volumetric hydrogen and methane storage capacity of monolithic carbide-derived carbon," *Microporous and Mesoporous Materials*, vol. 131, no. 1–3, pp. 423–428, 2010.
- [5] T. M. Arruda, M. Heon, V. Presser et al., "In situ tracking of the nanoscale expansion of porous carbon electrodes," *Energy & Environmental Science*, vol. 6, no. 1, pp. 225–231, 2013.
- [6] D.-W. Wang, F. Li, M. Liu, G.-Q. Lu, and H.-M. Cheng, "3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage," *Angewandte Chemie International Edition*, vol. 47, no. 2, pp. 373–376, 2008.
- [7] S. J. Yang, T. Kim, J. H. Im et al., "MOF-derived hierarchically porous carbon with exceptional porosity and hydrogen storage capacity," *Chemistry of Materials*, vol. 24, no. 3, pp. 464–470, 2012.
- [8] H.-J. Liu, J. Wang, C.-X. Wang, and Y.-Y. Xia, "Ordered hierarchical mesoporous/microporous carbon derived from mesoporous titanium-carbide/carbon composites and its electrochemical performance in supercapacitor," *Advanced Energy Materials*, vol. 1, no. 6, pp. 1101–1108, 2011.
- [9] Y. Korenblit, M. Rose, E. Kockrick et al., "High-rate electrochemical capacitors based on ordered mesoporous silicon carbide-derived carbon," *ACS Nano*, vol. 4, no. 3, pp. 1337–1344, 2010.
- [10] M. Oschatz, L. Borchardt, K. Pinkert et al., "Hierarchical carbide-derived carbon foams with advanced mesostructure as a versatile electrochemical energy-storage material," *Advanced Energy Materials*, vol. 4, no. 2, 2014.
- [11] M. Oschatz, E. Kockrick, M. Rose et al., "A cubic ordered, mesoporous carbide-derived carbon for gas and energy storage applications," *Carbon*, vol. 48, no. 14, pp. 3987–3992, 2010.
- [12] E. Kockrick, C. Schrage, L. Borchardt et al., "Ordered mesoporous carbide derived carbons for high pressure gas storage," *Carbon*, vol. 48, no. 6, pp. 1707–1717, 2010.
- [13] S.-H. Yeon, P. Reddington, Y. Gogotsi, J. E. Fischer, C. Vakifahmetoglu, and P. Colombo, "Carbide-derived-carbons with hierarchical porosity from a preceramic polymer," *Carbon*, vol. 48, no. 1, pp. 201–210, 2010.
- [14] M. Oschatz, L. Borchardt, M. Thommes et al., "Carbide-derived carbon monoliths with hierarchical pore architectures," *Angewandte Chemie International Edition*, vol. 51, no. 30, pp. 7577–7580, 2012.
- [15] Y. Gogotsi, A. Nikitin, H. Ye et al., "Nanoporous carbide-derived carbon with tunable pore size," *Nature Materials*, vol. 2, no. 9, pp. 591–594, 2003.
- [16] V. Presser, L. Zhang, J. J. Niu et al., "Flexible nano-felts of carbide-derived carbon with ultra-high power handling capability," *Advanced Energy Materials*, vol. 1, no. 3, pp. 423–430, 2011.
- [17] R. Dash, J. Chmiola, G. Yushin et al., "Titanium carbide derived nanoporous carbon for energy-related applications," *Carbon*, vol. 44, no. 12, pp. 2489–2497, 2006.
- [18] G. Cheng, D.-H. Long, X.-J. Liu, and L.-C. Ling, "Fabrication of hierarchical porous carbide-derived carbons by chlorination of mesoporous titanium carbides," *New Carbon Materials*, vol. 24, no. 3, pp. 243–250, 2009.
- [19] J. Xu, R. Zhang, S. Ge, J. Wang, Y. Liu, and P. Chen, "Effect of iron catalyst on the microstructure and electrochemical properties of vanadium carbide-derived carbons," *Materials Chemistry and Physics*, vol. 141, no. 1, pp. 540–548, 2013.
- [20] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, pp. 14095–14107, 2000.
- [21] K. S. Sing, "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984)," *Pure and Applied Chemistry*, vol. 57, no. 4, pp. 603–619, 1985.