Synthesis of Titanium Oxycarbide through Carbothermal Reduction of Titanium Dioxide Nanoparticles and Renewable Biopolymers

J. P. Flach[a,*], P. Figuereido de Lima[a,b*], J. Sparks[a, *], M. Islam[a], and R. Martinez-Duarte[a]

[a] Department of Mechanical Engineering, Clemson University, Clemson, SC 29631, USA
[b] Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil
[*] These authors contributed equally to this work

The goal of this is study is to explore the feasibility of a sustainable method of titanium oxycarbide synthesis through carbothermal reduction of a biopolymer composite. The reaction was studied at different temperatures in vacuum environments and at multiple TiO_2:C ratios in order to determine how these parameters affect the formation of titanium oxycarbide. The results indicate that both the heat treatment and the carbon ratios have a significant impact on the O/C ratio and; therefore, molecular composition and crystal structure of the titanium oxycarbide. The use of renewable biopolymers as a carbon source in the synthesis of oxycarbide can serve as an inexpensive, yet effective alternative to petroleum based sources.

Introduction

Titanium oxycarbide (TiC_xO_{1-x}) is a highly useful engineering material due to its high melting point, high hardness, and excellent thermal conductivity (1). TiC_xO_{1-x} is characterized as a solid solution of titanium carbide (TiC) and titanium oxide (TiO) and is used in the thin film industry, through reactive magnetron sputtering, because of its optical, electrical and structural properties that can be modified with a relatively simple process of tailoring the amounts of carbon and oxygen on the oxycarbide molecule. For example, when the proportion of oxygen increases, the oxycarbide acquires a TiO_2-like behavior, in which it loses DC electrical conductivity and acts like a semi-conducting material. It begins to exhibit insulating properties when oxygen is greater than 60%. There is a positive correlation between better conductivity and lower oxygen content (8). The corrosion resistance of titanium carbide is also associated with the formation of a TiC_xO_{1-x} layer on the carbide surface, indicating a high corrosion resistance of this material (2). Extensive research has shown that TiC_xO_{1-x} is also a highly stable system in nanowire form, resistant to temperatures as high as 1500K (3).
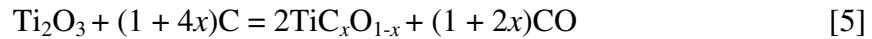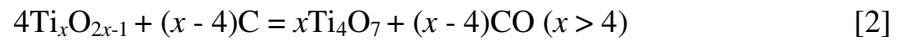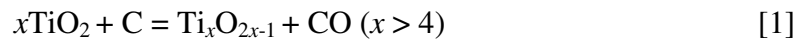
TiC_xO_{1-x} is typically synthesized through carbothermal reduction of titanium dioxide (TiO_2) or sintering of TiC and TiO (1); both of which require a source of carbon. Due to the volatility of the fossil fuel market, the viability of traditional petroleum based carbon sources such as carbon black and graphite is constantly tested by environmental and political strife. This phenomenon was evident in the 1970's and experts predict that the worst is yet to come (4). More recently, oil prices went from $16/barrel in 1998 to $140 in 2008. Consequently, an alternative, equally effective biopolymer carbon source would provide an escape from such drastic market changes. Furthermore, renewable

biopolymers are generally much less expensive than traditional petroleum-based carbon sources. For example, the current prices for a gram of iota-carrageenan, chitin, and activated carbon are $0.62, $0.84, and $5.23 respectively (retrieved from Sigma-Aldrich). According to the International Carbon Black Association (2016), up to 81 metric tons of carbon black is used every year in processes such as carbide and oxycarbide production. The use of biopolymers would provide a much less expensive and more stable method for producing TiC_xO_{1-x} or TiC.

The goal of the work presented here is to assess the feasibility of using renewable biopolymers as carbon sources for the carbothermal reduction of TiO_2 into TiC_xO_{1-x}. The biopolymers used in this study are chitin from shrimp shells and iota-carrageenan from seaweed. Iota-carrageenan serves as a jellifying agent while chitin serves as the primary carbon source. Here, the effects of varying the carbon content of the biopolymer and the heating protocol are studied to determine the most effective and economical method for manufacturing TiC_xO_{1-x}. The objective is to develop an alternative method for carbothermal reduction which provides similar results to traditional methods, but is more sustainable and environmentally friendly.

Theoretical Background

The carbothermal reduction of titanium oxide can produce titanium oxycarbide (TiC_xO_{1-x}) as follows.

$$x TiO_2 + C = Ti_xO_{2x-1} + CO \ (x > 4) \tag{1}$$

$$4 Ti_xO_{2x-1} + (x - 4)C = x Ti_4O_7 + (x - 4)CO \ (x > 4) \tag{2}$$

$$3 Ti_4O_7 + C = 4 Ti_3O_5 + CO \tag{3}$$

$$2 Ti_3O_5 + C = 3 Ti_2O_3 + CO \tag{4}$$

$$Ti_2O_3 + (1 + 4x)C = 2 TiC_xO_{1-x} + (1 + 2x)CO \tag{5}$$

Here, x is equal to 4 and was used in order to get an integer molar ratio throughout the stoichiometric calculations. Equation [1] is the generic reaction and equations [2] through [5] are the intermediate steps until the end of the reaction. The reduction begins with equation [2] with the formation of Ti_4O_7 around 900°C (5). As the temperature rises, a number of reactions begin to occur. At 1100°C, some, but not all of the Ti_4O_7 is reduced to Ti_3O_5 as described in equation [3]. At 1200°C, Ti_2O_3 is the predominant form due to the reduction of Ti_4O_7. At 1300°C, TiC_xO_{1-x} is present with Ti_2O_3, while Ti_3O_5 is no longer existent.

Equation [6] is the balanced reaction equation for the synthesis of titanium oxycarbide, which features titanium oxide (TiO_2) and carbon (C) as reactants and titanium oxycarbide (TiC_xO_{1-x}) and carbon monoxide (CO) as products. In order to simplify this test and acknowledge the need for excess carbon in the reaction, the ratio between the precursors of the reaction must follow equation [6]. The temperature region for this reaction is 1300°C - 1900°C (6).

$$xTiO_2 + 3C = TiC_xO_{1-x} + 2CO \ (x = 1) \tag{6}$$
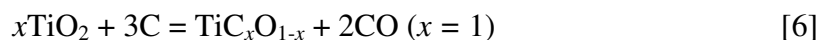
In this equation, x is equal to 1 to cover all the possibilities of oxycarbide formation. The two extreme possibilities for TiC_xO_{1-x} are when $x = 1$ and $x = 0$, *i.e.* when the molecule contains titanium and either only carbon or oxygen. Accordingly, titanium monoxide (TiO) and titanium carbide (TiC) can be analyzed as special cases of the oxycarbide molecule leading the crystalline characteristics of a specific formulation of TiC_xO_{1-x} to lie between the two extremes, allowing for a comparison through x-ray crystallography.

Materials

All materials were purchased from Sigma Aldrich unless otherwise noted. Chitin (CAS 1398-61-4), a product of shrimp shells, was used as the primary carbon source for the carbothermal reduction. Chitin has the chemical formula $C_8H_{13}O_5N$ and is approximately 47.3% carbon. Iota-carrageenan (CAS 9062-07-1) is a product of seaweed and common food thickener and has chemical formula $C_{12}O_{15}H_{16}S_2$. The carbon content of iota-carrageenan is approximately 31%. Here, iota-carrageenan was used as filler to increase the carbon content of the biopolymer mix beyond that of chitin. Titanium dioxide nanoparticles (CAS 13463-67-7, US-Nano) are the source of titanium in this study and have an average diameter of 18 nm. The small size is essential to achieving a homogeneous dispersion in the biopolymer solution. Ultrapure double-distilled water was used as the solvent.

Experimental Procedure

Following the stoichiometric calculations, a ratio of 1g of titanium dioxide to 0.95g of chitin is the minimum to have a complete reaction, *i.e.,* equivalent to 1:3 molar ratio of TiO_2 to C. The biopolymer composite was obtained after mixing dry powders of chitin, iota-carrageenan, and the TiO_2 nanoparticles using a vortex mixer for 20 minutes. Ultrapure water at 70°C was then added. The water and powder were mixed manually using a spatula until the gel appeared homogeneous. Four different molar ratios of TiO_2 to C, 1:3, 1:6, 1:9 and 1:12, were explored in this work to determine the impact on the composition of TiC_xO_{1-x}. Since carbon is a reducing agent, excess carbon is expected to lead to greater reduction of TiO_2 (7). The biopolymer composite was then loaded into a plastic syringe and manually extruded into different shapes.

These shapes were then heat treated in a tube furnace (Across International TF1700) under a high vacuum. Two different heating protocols were implemented as shown in Table I. The columns denote dwells in the process at specific temperatures and for the given amount of time. For example, Protocol 2 features a dwell time of 30 min at 300°C and a dwell time of 12 hours at 1450°C. The rationale behind implementing intermediate stops was to stabilize at specific temperatures to facilitate the intermediate reactions detailed above. Hence, the heating holds at 1300°C for 2 hours, 1400°C for 2 hours and 1550°C for 12 hours. Protocol 2 was implemented to define the impact of the final temperature. The intermediate stops were not implemented to serve as a reference to

compare the effect of the intermediate stops on Protocol 1. All protocols featured a heating rate of 5°C/min and a cooling rate of 4°C/min.

TABLE I. Heating protocols used in this work.

Protocol	300°C	900°C	1300°C	1400°C	1450°C	1500°C	1550°C
1	30 min	-	2 hours	2 hours	-	-	12 hours
2	30 min	-	-	-	12 hours	-	-

The heat-treated samples were then characterized using x-ray diffraction (XRD). In the case of XRD, studies were conducted using a Rigaku Ultima IV diffractometer. Each sample was characterized at a maximum velocity of 2.5°/min and with Cu radiation at 40kV and 40mA from a range of 15° to 70°.

Results and Discussion

Titanium oxycarbide was obtained in both processes. Figure 1 presents the XRD results for the 1:9 titania:carbon molar ratio sample of Protocol 2, which was treated at 1450°C for 12 hours.
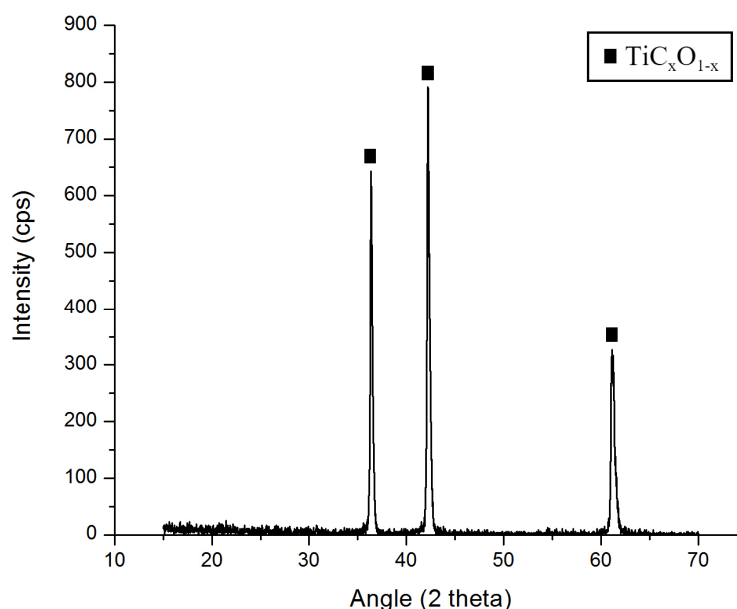

Figure 1. X-ray diffraction plot of sample with 1:9 titania:carbon molar ratio heat treated at a maximum temperature of 1450°C for 12 hours (Protocol 2).

The first variable of interest was the carbon content in the matrix. Protocol 1 was used for heat treatment of all samples. The titania:carbon molar ratios explored were 1:3, 1:6, 1:9, and 1:12. The XRD results are shown in Figure 2a, where the angles of the strongest intensity peaks obtained from the samples are plotted as dark circles, while the lines denote the characteristic angles of TiC and TiO intensity peaks. A peak shift between TiC and TiO can clearly be observed depending on the titania:carbon ratio. As expected, there is a clear shift towards a TiC-like material as the carbon content increases.

The excess of carbon not only determines the oxygen/carbon (O/C) ratio in the oxycarbide formed, but also changes the reaction yield, or the amount of product obtained from the reaction. Although the sample with no carbon excess did not react completely, the oxycarbide formed in that sample had a diffraction pattern that is close to that of TiO diffraction. This behavior demonstrates that the O/C ratio of the oxycarbide molecule is directly related to the amount of excess carbon of the reaction. As the carbon excess increases, the x value on TiC_xO_{1-x} increases.
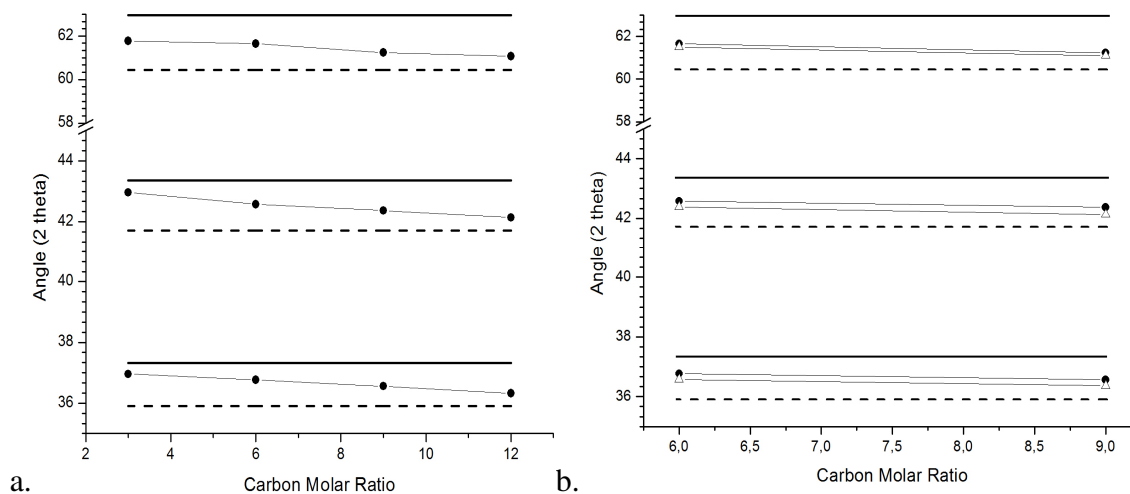

Figure 2a. Oxycarbide peaks (solid circles) plotted with respect to TiO (solid lines) and TiC (dashed lines) as the carbon:titania ratio increases. Protocol 1 was implemented. Figure 2b. Oxycarbide peaks (triangles) plotted with respect to TiO (solid lines) and TiC (dashed lines) as the carbon:titania ratio increases. Protocol 2 was implemented.

The second parameter of interest was the final heating temperature. In order to further study this parameter, Protocol 2 was implemented in which the dwell time at the final temperature remains constant at 12 hours, but the final temperature decreases to 1450°C. Only titania:carbon ratios of 1:6 and 1:9 were characterized. These results are depicted in Figure 2b where solid circles represent the case when using Protocol 1 and triangles denote data points obtained using Protocol 2. The dashed and solid regular lines again indicate the characteristic angles for TiC and TiO respectively. Figure 2a shows samples of 1:3, 1:6, 1:9, and 1:12 titania:carbon ratios that were treated at 1550°C for 12 hours and Figure 2b shows samples of 1:6 and 1:9 titania:carbon ratios that were treated at 1450°C for 12 hours. Figure 2b shows that samples that were treated to 1450°C had an overall greater amount of carbon in the oxycarbide molecule than the respective ones that were heated to 1550°C.

The process seems to require a need for excess carbon in order to complete the reaction and it appears that the maximum temperature of the heat treatment is also indispensable for the reaction to occur. Implementing consecutive dwells at intermediate temperatures where the titanium dioxide reduction takes place does not seem to be relevant since the direct ramp up to the maximum temperature (even a lower temperature) resulted on the same yield. Hence, a shorter heating protocol can be implemented. Further studies are required to characterize the size of the grain in both cases.

The oxycarbide properties are directly related to its crystal structure. Although the exact crystal structure of TiC_xO_{1-x} with high amounts of carbon is still under active and extensive study (8), its electrical conductivity increases as the carbon content increases, acquiring a TiC-like behavior. On the other hand, when the oxygen content increases, its crystal structure becomes more like the TiO structure, leading to an oxide behavior similar to TiO_2. This decreases its electrical conductivity and the material adopts a semiconductor behavior (8). As discussed before, high oxygen titanium oxycarbide can be manufactured using low to no excess of carbon at temperatures around 1550°C or higher, resulting in a semiconductor or insulator material. High carbon titanium oxycarbide can be manufactured using high excess of carbon at temperatures around 1450°C or lower, resulting in a conductor material.

Conclusion

This experiment successfully produced titanium oxycarbide through carbothermal reduction of TiO_2 using renewable polymers as carbon source. This process is significantly less expensive than implementing traditional carbon sources and can provide a sustainable method for the fabrication of oxycarbide materials. The determinant parameters of this reaction were also analyzed, revealing that there is a dependency on the excess of carbon to the success of the carbothermal reduction process. This excess is a determinant for the yield of reaction. Furthermore, the final temperature of the reaction changes the ratio between carbon and oxygen on the oxycarbide molecule. In other words, the O/C ratio increases as the temperature increases. The effects of the carbon ratio and temperature can be used to produce a titanium oxycarbide that is tailored to a specific electrical conductivity capacity with high resistance to corrosion and stability, which is also resistant to high temperatures.

The work that is ongoing explores the next step of the carbothermal reduction of titania in order to optimize carbide output. This is done in order to analyze the mechanical properties of titanium oxycarbide and titanium carbide when infused in metallic matrices.

Acknowledgements

References

1. B. Jiang, K. Huang, Z. Cao, and H. Zhu., *Thermodynamic Study of Titanium Oxycarbide*. The Minerals, Metals, & Materials Society and ASM International. (2012).

2. C.Oshima, S.Otani, M.Aono,S.Zaima,Y.Shibata. *Titanium oxycarbide on TiC (100) surface*. Japanese journal of applied physics. V 22, n 6 1983, 930-933

3. Enyashin, A. N. & Ivanovskii, A. L. *Structural, cohesive and electronic properties of titanium oxycarbide nanowires and nanotubes: DFT modelling*. Chem. Phys. 362, 58-64

4. D. Uren. *Worst oil crisis could lies just ahead,* The Australian. March 05,2012

5. T.Tsumura,Y.Hattori, K. Kaneko, T.Hirose, M.Inagaki, M.Toyoda, *Formation of the Ti_4O_7 phase through interaction between coated carbon and TiO_2*, Desalination, 2004, vol.169, p 269-275

6. Y. Hashimoto: J. Jpn. Inst. Met., 1989, vol. 53 (12), pp. 1229–35

7. Jiwoong Kim*a and Shinhoo Kangb, *Stable phase domains of the TiO2–Ti3O5–Ti2O3–TiO–Ti(CxOy)–TiC system examined experimentally and via first principles calculations,* Journal of materials chemistry A, J. Mater. Chem. A, 2014, 2, 2641

8. J.M. Chappé , A.C. Fernandes , C. Moura , E. Alves , N.P. Barradas , N. Martin , J.P. Espinós , F. Vaz. *Analysis of multifunctional titanium oxycarbide films as a function of oxygen addition,* Surface and coatings technology 206. 2012, 2525-2534.