

Volume 72 • Issue 2 • October 2015

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

The properties of porous TiO₂ TiC/C and TiC biomorphous materials

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ABSTRACT

Purpose: Purpose of this paper is to present results of the ceramization of biomorphic materials under different conditions. The aim of the study is to characterize the structure and the usefulness of the material resulting in further applications. Possibility of making a porous material made up of different phases and composition depending of high temperature process and the input material has been demonstrated.

Design/methodology/approach: Pyrolisis was done on wood pine samples. Obtained char was subjected to infiltration with solution of titanium alkoxide precursor. After the process of infiltration and drying ceramization subjected in carbon-TiO₂ char in three different conditions. Scanning microscopy investigation and XRD analysis were carried out. Structure and phase composition of various biomorphic materials was determined and compared.

Findings: The result of the processes was to obtain various biomorphic products, for which the phase composition and chemical depending on the atmosphere participating during annealing were investigated.

Research limitations/implications: Biomorphic material is deformed due to loss of integrity during the manufacturing process, which depends on the gaseous atmosphere under annealing processes. Further studies are limited by poor durability and structure easy to pulverize.

Practical implications: reinforcement of composite materials, active filters, precursors to ceramic nanopowders

Originality/value: comparing biomorphic material prepared under different conditions. Comparison of the porous structure of TiC/C biomorphic material with pure TiO₂ after high temperature process and TiC ceramic wood.

Keywords: Biomorphic; Ceramization; Biotemplating; Sol-gel; Ceramics wood; Porous materials; Wood material; Infiltration; Pyrolysis; Carbothermic reaction

Reference to this paper should be given in the following way:

T. Tański, Ł. Krzemiński, M. Wiśniowski, The properties of porous TiO₂ TiC/C and TiC biomorphous materials, Journal of Achievements in Materials and Manufacturing Engineering 72/2 (2015) 75-84.

PROPERTIES

1. Introduction

Among the engineering materials, composite materials represent a strong group of materials. New applications and technologies of engineering materials require to search for new materials. Materials that are combination of at least two or more components are strongly evolving group which allow to obtain new properties. A combination of two or more materials, where one of them is the matrix and the second is reinforcement, allow to combine the best properties each of them. Natural materials are also important for composite engineering materials. Search for a new material structure results in use of natural materials and their typical properties. Application of wood derived materials made it possible to produce biomorphic matrix. It's possible to manufacture composite materials with characteristics plants structure properties: low density due to high porosity and relative tough fiber cell structure [1-3].

Sol-gel method allows to obtain ceramic layers and fibers from liquid precursors solutions by sequence of chemical processes [7]. This method has many advantages over traditional methods of preparing ceramic materials, e.g lower temperature and shorter process time. Proper parameter selection leads to forming of amorphous and crystalline phases able of generating metal oxides in direct contact with the substrates [8, 9].

2. Materials and experimental procedure

Among precursors to produce a biomorphic matrix the necessary is biological material-wood sample in this case. Selection of wood species and the cross-sectional area of the tree trunk from which biological material is downloaded is crucial. Cross-section of wood is represented by ring and layers structure. Sample was selected through choice of material, based on the wood knowledge, porosity research and content of the resin [11-13]. The softwood material exhibits the highest porosity and simple structure with distinction on wood early and late without resin appearance. Hence softwood is lighter and exhibits lower tensile strength than hardwood. Wood is a material that combines biological cells with specific physiological functions. Wood cells have an elongated shape, arranged along the vertical axis of the timber composed of cellulose, hemicellulose and lignin [4-6]. Whole bulk is formed in a porous structure with square similar cross section that allow capillary conduction. Capillary tube represents by whole of the middle part of the capillary cells. Material acquired from softwood and obtained in the form of discs from pine wood on a fixed diameter and thickness from this layer.

Wood samples were drying at 100°C for 3 hours. Diameter, thickness and weight measurement have been performed.

The samples were subjecting pyrolysis in the furnace chamber. The process carried out at final temperature of 800°C and 1500°C with no oxygen in the atmosphere. High temperatures were applied to remove functional groups from the carbon surface and improve the carbothermic reduction reaction of oxides. The heating rate was set at 2°C/min due to prevent damage to the structure during the evaporation of the bound water in the wood. Crucible is connected to the furnace exhaust, allowing the removal of gaseous products of thermal degradation. Cooling of carbonization products (char) was slow-cooling with the furnace to target temperature below 100°C. The samples were measured to define the average percentage of change in dimension and mass.

Obtained char was subjected to infiltration with solution of titanium alkoxide precursor. The aim of the infiltration by solution is to produce thin film coatings of inorganic oxide materials. For preparation sols were used four components: Titanium Isopropoxide (TTiP, Ti[OCH(CH3)2]4, purity \geq 97%), Hydrochloric Acid (HCl, 40%), Ethanol (anhydrous CH3CH2OH, purity 99.8%) and distilled water. TTiP is metal alkoxide, with the general formula M(OR)n (M - metal, OR-alkyl group). Titanium precursor was mixed with 40ml Ethanol with 1ml Acetic Acid and a minor amount of distilled water. During addition solution was being stirred using a magnetic strirrer for at least 30 min. Liquid was being hold at temperature of 5°C to slow down condensation reactions in time of 1 day.

Carbon char was infiltrated by Ti-sol in cycle process repeating to obtain weight gain. After infiltration each sample was subjected to drying in a manner which prevents clogging of pores and to allow further filtration cycles. The chemical reaction inside char mainly based on hydrolysis (1) and condensation (2,3) of metal alkoxides. In the presence of water alkoxides of titanium had hydrolyzed. During reaction the alkoxy group (OR) were replaced either by hydroxo ligands (OH) within the meaning of reaction:

$$Ti-(OR)_{Z}+H_{2}O \rightarrow Ti-(OH)(OR)_{Z-1}+ROH$$
(1)

The results are strongly determined by the kinetics of hydrolysis and condensation of the alkoxide precursor [17].

$$Ti-(OR)_{Z} + (OH)-Ti \rightarrow Ti - O - Ti + ROH$$
(2)

$$Ti-(OH) + (OH)-Ti \rightarrow Ti - O - Ti + H_2O$$
(3)

Polycondensation of alkoxide leads to formation of oxide extended network. After the process of infiltration and drying at 110° C during 2h, carbon char with TiO₂-gel subjected to an annealing process at three different conditions (Fig. 1):

- 1. Calcination in air atmosphere;
- 2. Calcination in inert atmosphere;

3. Calcination in inert atmosphere and next in air atmosphere.



Fig. 1. Flow chart of manufacturing biomorphic Ti ceramics

Samples after drying were being subjected ceramization at 1500°C for 2 h and slow cooling with the furnace in any case.

Infiltration was made in Struers CitoVac vacuum impregnation apparatus at 0.2 bar. Uninfiltrated and infiltrated chars were analized by Axio Observer light microscopy and Supra 35 Carl Zeiss scanning electron microscope. The researches were carried out with the accelerating voltage of 20kV. The analysis of phase composition was carried out using the X-ray diffraction method on the X'Pert Pro apparatus of Panalytical Company, in the Bragg-Brentano system, applying the filtered radiation of cobalt tube with the step of 0.05°. Quantitative phase analysis was made using Rietveld Method.

3. Results and discussions

As a product of pyrolysis process received pure carbon chars of weight 0.44g exhibiting porous structure which can be seen on SEM images. Structures are characterized by two distinct layer of early wood (pore diameter 20-35 μ m) and more density late wood (pore diameter 2-5 μ m). Wall thickness of this layer is 2- late wood is more dense, with pore diameter of about $5\mu m$ and wall two times thicker than in early wood. Entire pore system is a structure of hollow square tubes arranged parallel (Figs. 2, 3).



Fig. 2. Jars arrangement of pine wood, layers of early and late wood, SEM



Fig. 3. Front view of cell system, cells walls with section pits, SEM

XRD analysis show two peaks in the high angle region: a broad high intensity peak at 23° , 50° and a further peak at 96° (Fig. 4). The presence of these peaks may indicate the presence of phases like graphite. Increase carbonization temperature may contribute to the long range order structure and result in wide angle region of XRD [15]. Carbon char annealed at higher temperature showed higher and more narrow peaks.



Fig. 4. XRD patterns of carbon char (pine wood), pyrolysed at 800°C and 1500°C

As a result of repeated infiltration, carbon char obtained weight gain and the final value was 1.58g. Infiltrated char mostly exhibited of non-clogging pores.

The product of ceramization under oxidizing atmosphere is yellow-white sample with many cracks arranged by late wood and early wood ring structure. Weight reduced to 0,91g. Parallel cracks formed as a result of removed carbon from the late wood structure which exhibiting high content of carbon.

As a result of oxidation of carbon in the lower temperature there was no carbothermic reduction reaction. During temperature increasing transformation from TiO_2 -gels into ceramics phases of dioxide appear. Biomorphic structure damaged during heating at temperature near melting point in time of 1 hour. The porosity of which showed a sample before ceramziation disappeared as a result of high temperatures impact and semi metling (Figs. 6-8). Due the sintering in air atmosphere there have been obtained large particles of pure TiO_2 with large pores (Fig. 8). However partial biomorphic structure preserved in the form of fibrous structure (Fig. 9) and separation of late wood (Fig. 7).

XRD graph show only rutile TiO_2 without the participation of other titanium carbide and residual of carbon (Fig. 5). The effect of oxygen occurence in the reaction is removal of carbon from char and transformation into rutile TiO_2 .

As a result of ceramization with the absence of oxygen, the reaction produces the TiC. Product of this process is a carbon char (Fig. 10) coated with TiC (Figs. 11, 12) in the form of spheroidal crystals with diameter about 0.5- 4μ m adhering to the walls of the carbon (Figs. 13-15). Weight of the obtained TiC/C is 0.68g. Spherical particles not completely cover base material leaving uncovered carbon walls.



Fig. 5. XRD patterns of rutile TiO_2 sample, ceramized at 1500°C in air atmosphere



Fig. 6. Photography of TiO_2 sample after ceramization at 1500°C in air



Fig. 7. TiO₂ sample after ceramization at 1500°C in air, early wood layers, 25x



Fig. 8. TiO₂ sample after ceramization at 1500°C in air, front view, 50x



Fig. 9. Cross section TiO_2 sample after ceramization at 1500°C in air, fibrous structure, 25x



Fig. 10. Photograph of TiC/C biomorphic ceramics sample after ceramization at 1500° C



Fig. 11. Cellular C/TiC structure after ceramization at 1500°C, optical micrographs 500x



Fig. 12. Cellular C/TiC structure after ceramization at 1500°C, SEM 500x



Fig. 13. Cellular C/TiC structure after ceramization at 1500°C, SEM 3000x



Fig. 14. Cellular C/TiC structure after ceramization at 1500°C, SEM 7000x

In the sample there is an excess of carbon relative to the ceramic phase TiO_2 during ceramization process. Due to this not all carbon reacted to generate the phase of TiC. Unreacted carbon remains as a scaffolding covered with crystals of TiC. Spherical form of carbides and dioxides may be explained by melting indirect phases of TiO before becoming carbothermic reduction reaction and the creation of titanium carbides. Dioxide phase may be melting and forming a spherical shape. Above temperature of 1500°C the reaction between spherical TiO and carbon occur [19].

There is also the residue small amount of TiO_2 phase (11,8%) and majority participation of TiC as show in XRD Rietveld graph (Fig. 16). The reason for this may be

difficulty in diffusion of carbon over long distances through crystallites and the newly formed ceramic phase of TiC. The spherical form of the oxides may also indicate that the reaction was incomplete.

Third sample, which has been subjected to ceramization in two steps, have partial biomorphic structure. After first ceramization without access to oxygen structure was adequate to second sample (Fig. 12). Next annealing process taken in air atmosphere made excess of carbon removed and weight decreased to 0.66 g. The remaining phase of TiC was partially melted and created reproduction of biomorphic structure (Figs. 17-20).



Fig. 15. Cellular C/TiC structure after ceramization at 1500°C, SEM 20000x



Fig. 16. Rietveld method quantitative phase analysis XRD graph of C/TiC/TiO₂ biomorphic ceramics after ceramization at 1500°C under non-oxygen atmosphere

On SEM image pore system derived from the cellular structure of the pine wood can be seen. Open pores exhibit deformation. The reason may be loss of stiffness during the heating at high temperature, as a result the partial melting of TiC. The reason may be also an incomplete coating the inner wall by TiC ceramic phase, which led to a deformation of the structure. The cross view of biomorphic structure shows arrangement of pipes, consisting of holes in the walls, due to the incomplete coating carbon wall by TiC before second ceramization. The most probable way to complete reproduction of biomorphic structure is method of coating a carbon char inner walls with TiO-sol in a greater extent. This ensures denser cover carbon wall by ceramic particles. This prevents the deformation biomorphic porous structure during removing carbon in the next ceramization process.



Fig. 17. Photograph of TiC/C biomorphic ceramics sample after ceramization at 1500°C



Fig. 18. Cellular C/TiC structure after ceramization at 1500°C, optical 500x



Fig. 19. Cellular C/TiC structure after ceramization at 1500°C, SEM 500x



Fig. 20. Cellular C/TiC structure after ceramization at 1500°C, SEM 3000x

XRD studies indicate the presence of TiC ceramic phase (Fig. 21). The residual carbon content in the form of carbon structure has been completely removed leaving only the TiC ceramic phase.

During the annealing of titanium oxide in the presence of carbon at high temperature the carbothermic reduction reaction of titanium oxides occurs. This process takes place under temperature higher than 1073K in the presence of oxides and carbon forming Ti-O-C bonding [20]. Form of the final product is dependent on the stoichiometric ratio of the titanium oxide and carbon.

Form of the obtained product depends also on the nature of contact between titanium oxide, carbon and presumably TiO form of grains and their distribution on the carbon surface. Due non stoichiometric reaction of carbide difficulties of ceramics phase formation process occur. This results of a certain amount of the excess of one of the components [20, 21]. As shown in SEM image (Figs. 13-15) grains of the resulting TiC cover excess amount of carbon in the form of biomorphic walls. The ideal solution is the absence of carbon phase and existence of only TiC biomorphic structure after ceramization process. Aim of achieving the stoichiometric ratio of reactants is proper carrying of infiltration process and merge carbon char and TiO-gel substrates.



Fig. 21. XRD patterns of rutile sample, ceramized at 1500°C in air atmosphere

It's required to fill in the carbon char of a sufficient amount of the organometallic sol precursor in order to achieve a sufficient amount of TiO_2 involved in convertion

Table 1.

Selected analytical amount of substrate and products in producing reaction of biomorphic TiC phase using sol gel technology

Infil. char weight [g]	Reacted C weight [g]	Vol. of C rest [g]	Reacted C weight [cm ³]	Reacted C vol. [cm ³]	Gel mass [g]	Gel volume [cm ³]	TiO ₂ mass [g]	TiO ₂ volume [cm ³]	TiC volume [cm ³]	TiC volume [g]	Products volume [cm ³]	Products mass [g]
1.65	0.44	0.00	0.00	0.22	1.21	0.58	0.98	0.23	0.15	0.73	0.15	0.73
1.48	0.38	0.06	0.03	0.19	1.04	0.50	0.84	0.20	0.13	0.63	0.16	0.69
1.06	0.23	0.21	0.11	0.11	0.62	0.30	0.50	0.12	0.08	0.38	0.18	0.59
0.65	0.08	0.36	0.18	0.04	0.21	0.10	0.17	0.04	0.03	0.13	0.21	0.49
0.44	0.00	0.44	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.44

to TiC phase. Due a series of processes there is a need to determine the mass of the TiO-sol and TiO-gel required to obtain the stoichiometric reaction.

On the basis of published analytical discussion [21] defined quantities and volumes of the components involved in the whole process of biomorphic TiC phase manufacture. The input parameters are the number of infiltration, gel mass, char mass and its porosity allows to fill by TiO-sol. For carbon chars used in this thesis with the mas of 0.44 g analytically determine participation of initial amount of substrate and other products of the reaction (Table 1) for a few selected amount of gel. The maximum impregnation occured by infiltration should be adjusted to amount of carbon participating in the carbothermic reduction process. Further increase of the fulfillment of TiO-gel over 1.65 g weight of whole char cause a complete conversion of carbon with the remains of unreacted TiO2. TiC phase content increases in inverse proportion to amount of unreacted carbon and is entire product with TiO-gel infiltration level near 1.20 g in a carbon char of 0.44 g (Fig. 22).



Fig. 22. TiC phase content in the function of TiO-gel weight

4. Summary

Biomorphic material can be produced using porous natural plant materials and metal alkoxides. Preform was obtaining from sapwood of pine wood. Samples were pyrolysed in 1500°C and weighed. XRD analysis showed appearance of ordered structure similar graphite [15]. The degree of arrangement depends on the time and temperature of carbonization [16]. Pine char infiltrated with TTIP sol and dried in few cycles. Weight increased about 150% through oxides coating deposition in porous structure of char.

Ceramization process carried out in three different conditions. The result of the processes was to obtain various products, for which the phase composition and chemical depending on the atmosphere participating during annealing. Samples subjected to ceramization under air atmosphere reacted into pure dioxide ceramics, with no residual of carbon. Samples subjected ceramization without oxygen access condition and temperature allowing to occur reaction carbothermic reduction reacted into biomorphic TiC/C template. Further ceramization under air atmosphere led to removing carbon and leaved only porous TiC constitutes biomorphic template. In oxygen conditions carbon phases not formed, probably due to oxidation of the carbon at the lower temperature. Preventing oxygen to the sample resulted in the reaction of carbothermic reduction TiO₂ and forming TiC phase. Degree of biotemplating is dependent on chemical and phase composition and the way in which was formed. Manufacturing process contain carbotheramal reduction reaction of dioxide phase is more to templating biomorphic structure without able deformation. The ratio of manufacturing phase of the final product, ie. unreacting carbon and TiC depends on the amount of the sol infiltrated into the porous char. Stoichiometric content of substrates prevents occurrence of unreacted phase as the product of carbothermic reduction.

References

- P. Greil, T. Lifka, A. Kaindl, Biomorphic cellular silicon carbide ceramics from wood: I. Precessing and Microstructure, Journal of the European Ceramic Society 18 (1998) 1961-1973.
- [2] M. Mituzani, H. Takase, N. Adachi, T. Ota, K. Daimon, Y. Hikichi, Porous ceramics prepared by mimicking silicified wood, Science and Technology of Advanced Materials 6 (2005) 76-83.
- [3] H. Sieber, Biomimetic synthesis of cermics and ceramic composites, Material Science and Engineering A412 (2005) 43-47.

- [4] X. Li, T. Fan, Z. Liu, J. Ding, Q. Guo, D. Zhang, Synthesis and hierarchical pore structure of biomorphic manganese oxide derived from woods, Journal of the European Ceramic Society 26 (2006) 3657-3664.
- [5] C.E. Byrne, D.C. Nagle, Carbonization of wood for advanced materials applications, Carbon 35/2 (1997) 259-266.
- [6] P. Greil, Biomorphous ceramics from lignocellulosic, Journal of the European Ceramic Society 21 (2001) 105-118.
- [7] D. Sangeeta, Inorganic materials chemistry desk reference, CRC Press, New York, 1997.
- [8] Y. Kurokawa, H. Ota, T. Sato, Preparation of carbide fibres by thermal decomposition of cellulose-metal (Ti, Zr) alkoxide gel fibres, Journal of Materials Science Letters 13 (1994) 516-518.
- [9] R. Subramanian, J.H. Schneibel, FeAl-TiC cermetsmelt infiltration processing and mechanical properties, Materials Science and Engineering A 239/1-2 (1997) 633-639.
- [10] M. Mahmoodi, L. Ghazanfari, Fundamentals of biomedical applications of biomorphic SiC, Properties and Applications of Silicon Carbide, Ed. R. Gerhardt, InTech, Open Access Publisher, 2011.
- [11] N. Grioui1, K. Halouani, A. Zoulalian, F. Halouani, Experimental study of thermal effect on olive wood porous structure during carbonization, Maderas. Ciencia y tecnologia 9/1 (2007) 15-28.
- [12] P.R. Blankenhorn, D.P. Barnes, D.E. Kline, W.K Murphey, Porosity and pore size distribution of black cherry carbonized in an inert atmosphere, Wood Science 11/1 23-29.
- [13] O. Keech, C. Carcaillet, M.C. Nilsson, Adsorption of allelopathic compounds by wood-derived charcoal: the role of wood porosity, Plant and Soil 272/1-2 (2005) 291-300.
- [14] O. Paris, C. Zollfrank, G.A. Zickler, Decomposition and carbonisation of wood biopolymers a microstructural study of softwood pyrolysis, Carbon 43 (2005) 53-66.
- [15] Z. Yang, Y. Xia, R. Mokaya, Periodic mesoporous organosilica mesophases are versatile precursors for the direct preparation of mesoporous silica/carbon composites, carbon and silicon carbide materials, Journal of Materials Chemistry 16 (2006) 3417-3425.
- [16] M. Krzesińska, J. Majewska: Biomorphous carbon and carbon/polymer materials, Scientific Publishing Śląsk, Katowice, 2011, ISBN 978-83-7164-678-2 (in Polish).
- [17] M.E. Simonsen, E.G. Søgaar, Sol-gel reactions of titanium alkoxides and water: influence of pH and

alkoxy group on cluster formation and properties of the resulting products, Journal of Sol-Gel Science and Technology 53/3 (2010) 485-497.

- [18] A.C. Pierre Introduction to sol-gel processing, Kluwer Academic Publishers, ISBN 978-0-7923-8121-1, Boston, 1998.
- [19] S. Wei, X. Bao-qiang, Y. Bin, S. Hong-yan, S. Jian-Xun, W. He-li, D. Yong-nian, Preparation of TiC powders by carbothermal reduction method in

vacuum, Transactions of Nonferrous Metals Society of China 21 (2011) 185-190.

- [20] M. Wysiecki, A. Biedunkiewicz, Preparation of nanometric titanium carbide and nitride by sol gelmethod, Material Engineering 6 (2003) 421-423.
- [21] C.R. Rambo, J. Cao, O. Rusina, H. Sieber, Manufacturing of biomorphic (Si, Ti, Zr)-carbide ceramics by sol-gel processing, Carbon 43 (2005) 1174-1183.