

Characterization of the Oxidation of 3D Needled C/C Composite by Synchrotron Radiation X-Ray Micro-Computed Tomography

Yantao Gao (✉ gaoyantao@sues.edu.cn)

Shanghai University of Engineering Science <https://orcid.org/0000-0002-3479-1512>

Sanfa Xin

Shanghai University of Engineering Science - Songjiang Campus: Shanghai University of Engineering Science

Wenfeng Hu

Shanghai University of Engineering Science - Songjiang Campus: Shanghai University of Engineering Science

Hao Yan

Shanghai Institute of Applied Physics Chinese Academy of Sciences

Research Article

Keywords: C/C composite, Oxidation, Characterization, CT

Posted Date: June 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-659962/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

C/C composite has been considering to be used as structural components in the field of nuclear energy. However, the material will be subjected to rapid oxidation in the air. This paper presents the microstructure evolutions of a type of high density C/C composites at 550°C in the air. Synchrotron radiation X-ray micro-computed tomography (SR- μ CT, resolution: 0.65 μ m) was used to characterize the microstructure in different oxidation stages. The results showed that the material was oxidized nearly homogeneous. The large pores play great rule in the oxidation behavior. The pores in the material started to extend quickly in initial stage and the number of pores and porosity were rapidly increased. In addition, it also can be seen that SR- μ CT is a perspective tool for microstructural characterization, especially structure evolutions in the materials.

1. Introduction

C/C composites have been widely used in many fields because of their advantages, such as high specific strength and modulus, high temperature mechanical property, low thermal expansion coefficient, etc ^[1]. Due to their low atomic number and low neutron absorption cross section, C/C composites have also been considered to be used as thermal structural materials in nuclear reactors ^[2-3]. However, oxidation is expected at high temperature in air. As we know, C/C composite is a kind of porous materials. Oxygen can penetrate into the composite and lead to catastrophic degradation of the material under certain conditions. Therefore, a good knowledge of oxidation process is necessary to utilize it ^[4-5].

The oxidation of carbon has been widely studied in the last few decades ^[6-8]. The results showed the mechanism and microstructure of oxidation were highly dependent on the type of carbon and the types of manufacturing processes. Therefore, the quantity and the size of the pores, the fibrous architecture and the nature of fibers are key factors that can have an impact on the oxidation of these materials. Some studies showed oxidation behaviors were strongly temperature-dependent. The 800 °C C/C composite material showed uniform attack, suggesting reaction control of the oxidation process; whereas the 1100 °C sample showed attack at the edges, suggesting diffusion control of the oxidation process. Also, some authors found that surface reaction rates depend on the type of carbon, inducing selective surface attacks as oxidation is preferably carried out along the fiber axis at the fiber/matrix interface ^[9-10]. Therefore, the oxidation is a complex problem. Optical and scanning electron microscopies are common methods to evaluate the impact of oxidation on the microstructure of materials ^[11-12]. However, comparing with them, non-destructive techniques such as tomography have many advantages, such as non-invasiveness, 3D imaging and quantitative analysis ^[13-14]. This technique has been used extensively by few authors to characterize the microstructure of composites during in-situ mechanical tests, different stages of the manufacturing process and after oxidation of the material ^[15-17].

A special C/C composite material for molten salt reactor (MSR) was developed several years ago. The density of the C/C composite material used should be as high as possible to prevent molten salt

penetration. Considering the seriousness of oxidation, it is necessary to study the problem of the special material. As the oxidation mechanism and the resultant microstructure are closely connected, the objective of this paper is to characterize the microstructure during oxidation process. For this purpose, the C/C composite was oxidized repeatedly and characterized at different stages using SR- μ CT. Finally, the microstructure evolution of the C/C composite material is obtained through comparing the 3D results by tomography at different oxidation stages.

2. Material And Methods

2.1 Description of high-density C/C composite

The C/C composite with bulk density of about 1.84g/cm³ is manufactured by hot isostatic pressure process. The 3D needle-punched preform was immersed in pitch, followed by carbonization in a furnace at 1000°C. The immersion and carbonization processes were repeated until the density can't be improved. The fiber used was polyacrylonitrile (PAN)-based fiber named T700 from TORAY, Japan.

2.2 Synchrotron Radiation X-ray computed tomography

X-ray Computed Tomography (CT) is a nondestructive technique which can provide accurate and high-resolution 3D observations of the microstructure. Figure 1 showed a typical setup of SR-CT equipment including an X-ray source, a rotation station stage and an X-ray detector and so on. Usually, a sample rotates ranging from 0° to 180° in an experiment and radiographic images are captured at equal interval angular position; The 2D radiographic images are used to reconstruct a 3D volume image of the specimen by 3D reconstruction.

In this work, imaging was performed at X-ray imaging and biomedical application beamline (BL13W1) at Shanghai Synchrotron Radiation Facility (SSRF, China). The energy of the beam was fixed to 12 KeV and the resolution was 0.65 μ m per voxel within a field of view of 1.3 mm. During the CT scan, the sample was rotated with an angular step of 0.167°. Total 1080 projection images were collected in the experiment. Phase recovery was performed on all projection images to improve the quality of images and then sectional images were reconstructed using a software "PITRE3" developed by researcher in BL13W1. 3D volumetric representations were obtained by stacking 2D images using image processing software FEI Avizo 9.3 (ThermoScientific). The percent porosity was also calculated with the Avizo. In order to evaluate the distribution of the porosity in the 2D sliced images, one sliced image should be binarized into two phases (the black phase corresponding to the porosity and the white phase to the fiber, matrix and interface) through a threshold operation. A suitable threshold value of pixel was selected as cut-off value for binary operation such that the selected pixels covered almost all the area of pores or holes in the 2D images. The volume fraction of porosity was defined as the number of black voxels divided by the total number of voxels within a slice.

2.3 Oxidation experiments

The specimen was machined with the tip of about 1mm diameter. The oxidation experiments were carried out in a chamber as described in Fig. 2. Heating is provided by four 75W Infrared Halogen lamps mounted on the chamber, each with an ellipsoidal reflector aimed at the center of the cell, giving a spherical hot zone of diameter ~ 7 mm. The heating is controllable and the maximum temperature can reach up to 800°C. In this study, the specimen was repeatedly heated six times in air. As the operating temperature in molten salt reactor is under 800°C, the experiments are low temperature oxidation, described as in Table 1. After each oxidation, the specimen was imaged and analyzed.

Table 1
Oxidation process in the experiments

No.	Temperature (°C)
1	5min, 25 to 480; 5min, 480
2	6min, 25 to 540; 4min, 540 to 549
3	2min, 25 to 480; 8min, 480 to 545
4	1min, 25 to 500; 9min, 500 to 552
5	1min, 25 to 500; 9min, 500 to 550
6	1min, 25 to 510; 9min, 510 to 551

3. Results And Discussion

3.1 Characterization of the un-oxidized C/C composite material

Tomography was performed with as a resolution of 0.65 μ m. Figure 3(a) showed 3D tomography of the microstructures in un-oxidized 3D needled C/C composite material. It can be seen that the grey scale difference between pores and material was sufficient to separate and quantity the porosity of the material. The pores were exacted and described as in Fig. 3(b). There were some large pores distributed in the material. The large pores were filled in the spaces between fiber bundles. And the large pores mainly existed in the entangled fiber tows. The reason was that the porosity of the preform was inhomogeneous. When the preform was densified, the large pores can't be fully filled by matrix. Additionally, the small pores also can be found easily and widespread distributed in the material. Therefore, it was a typical porous material, though the density was pretty high.

3.2 Microstructure evolution of oxidized C/C composite

3.2.1 2D characterization

Figure 4(a-d) were cross-sections of C/C composite at different oxidation stages. As circled in these figures, the large pore obviously deteriorated with the increase of oxidation time. It also can be seen that

the number of the observable pores increased a lot. Comparing Fig. 4(d) with Fig. 4(a), many pores appeared in the middle area.

Usually, at low temperatures (below 800°C), the oxidation rate of carbon materials is controlled by the surface reaction of oxygen with the active centers of carbon-defects of crystal structure (vacancies of basic plane, edge atoms, etc.) and macro defects of a sample. As described in Fig. 3, pores in the C/C composite existed in reticular formation. Air can invade the C/C composite through the pores. Therefore, the interior was oxidized similar with the surface and the oxidation of the C/C composite material was homogenous. But the large pore was oxidized more intensive as low-temperature pyrolytic carbon existed.

3.2.2 3D characterization of pores in oxidation process

Figure 5 provided the porous structural changes in oxidation process, No.1, No.3 and No.6. From them, it can be seen that the pores were progressive. However, the large pores extended rapidly and formed serious destruction, which was consistent with Fig. 5. To be interesting, not only did the small pores become more intensively, but some new small pores were detected. The phenomenon could be attributed to several reasons, (1) The origin pore was too small to be detected firstly. It increased as the effect of oxidation; (2) The interface between fiber and matrix were oxidized more intensively and new pores occurred.

3.2.3 Distribution of pores in the 3D needled C/C composite

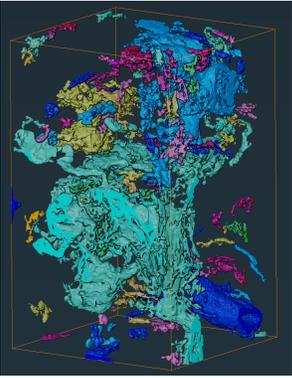
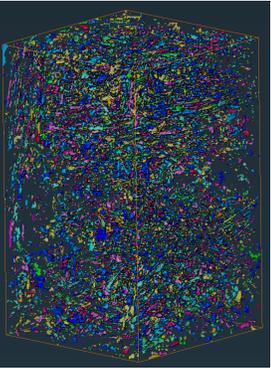
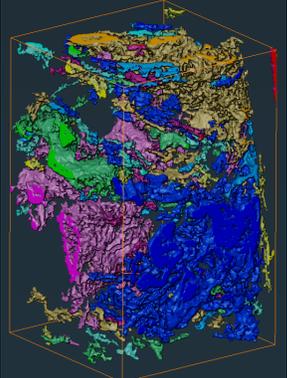
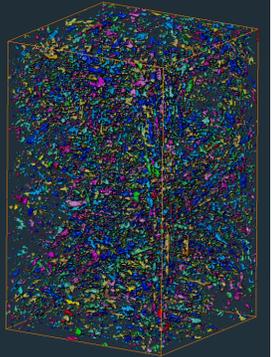
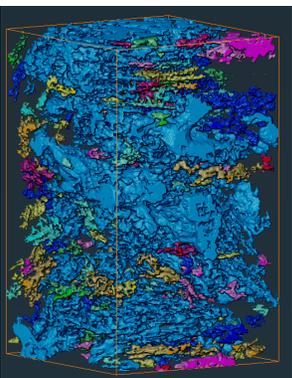
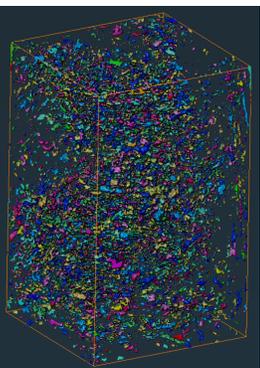
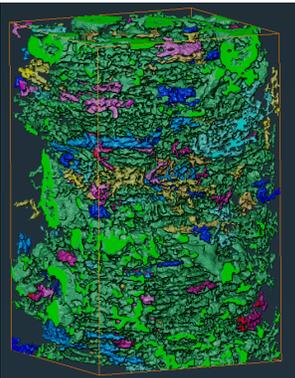
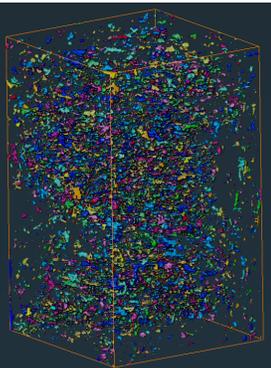
Table 2 showed the pore repartition extracted from pore analysis in the C/C composite at different oxidation stages. The pores were classified in function of their sizes, described through an equivalent volume: More than $8000\mu\text{m}^3$ (macropores) and less than $8000\mu\text{m}^3$ (mesopores) (which corresponds to the majority population by number). Each pore was differently colored if a pore was not connected to neighboring pores. It can be seen that the part of smallest pores (equivalent diameters less than $8000\mu\text{m}^3$) was homogeneous all the time within the composites while the part of biggest pores (with a size greater than $100\mu\text{m}^3$) extended rapidly. Due to the stitch and fiber bundle intertwining in the 3D needled C/C composite, the size of macroscopic pores could be particularly large, which obviously promoted the oxidation rate.

3.3 Analysis of porosity of the oxidized C/C composite

The porosity of the C/C composite in oxidation process was presented in Fig. 6.

It showed that the porosity had a rapid increase in initial stage. Then, it tended to be steady. From Table 2, it can be seen that the size of large pores had spread quickly at initial several stages. After that, the oxidation rate decreased. Therefore, the porosity appeared the trend in Fig. 6.

Table 2 Distribution of pores in the C/C composite material at different oxidation stages

Name	Macropores with an equivalent volume $>8000\mu\text{m}^3$	Mesopores with an equivalent volume $< 8000\mu\text{m}^3$
The un-oxidized 3D needled C/C composite		
The 3D needled C/C composite after the second oxidation		
The 3D needled C/C composite after the fourth oxidation		
The 3D needled C/C composite after the sixth oxidation		

3.4 Discussion

The objective of the analysis was to characterize the oxidation of 3D needled C/C composite by SR- μ CT. Generally, the pores in C/C composites would have striking effect on mechanical properties when the size of them is above micron level. Therefore, it is necessary to study the microstructure of 3D needled C/C composite with high resolution micrography. CT is a non-destructive tool processing 3D imaging capability. Recently, the resolution of SR- μ CT has been up to submicron with the field of view by mm level, which is benefit for observation of microstructure in the C/C composites. It allows the critical defects in the microstructure (e. g. Figure 1) to be observed.

From tomography, some large pores were observed in 3D needled C/C composite. The loose structure in the punched area and intertwining of fiber bundles led to formation of the large pores in the composite. Also, a large number of small pores existed among fibers in the fiber bundles. The small pores limited the diffusion of the air. In low temperature oxidation process, the oxidation was a mixed in-pore diffusion/surface reaction. Oxygen can easily diffuse into the interior through the open pores. Furthermore, there was much pyrolytic carbon in the large pores which possessed many defects. The defects were easy to be attracted. Therefore, the oxidation rate in initial stage was higher. However, crystalline or graphitic carbon was less susceptible to oxidation mode. When the pyrolytic carbon with defects were burned out, the oxidation rate slowed down.

Comparing with the small pores, the large pores had an important influence on the oxidation behavior in low temperature oxidation. Due to large pores in 3D needled C/C composite, it deteriorates rapidly in the oxidation process. Firstly, there were plenty of pyrolytic carbon in the large pores. Secondly, more air can be penetrated into the large pores. Last but not least, the large pores were open pores which connected to outside. So, it is necessary to control the formation of large pore in the composite.

Conclusions

The oxidation of 3D needled C/C composite was characterized by SR- μ CT. It can be concluded that SR- μ CT can be successfully used to study the oxidation of the C/C composite by observing the microstructure morphologies. 3D visualizations of the pores provided insights into oxidation properties of the composite. The large pores, especially in the punched area, had great influence on the material degradation. The oxidation around the small pores was relatively mild as a result of oxygen limitation. The oxidation behavior would be primarily controlled by the large pores in low temperature oxidation.

Declarations

Acknowledgments

This work was supported by the National Nature Science Foundation of China under grant No.11802317. The authors would like to thank faculties of BL13W1 Beamline at Shanghai Synchrotron Radiation

Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, for their invaluable help in the experiments.

Data Availability Statements

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

1. T. Windhorst, G. Blount. Carbon-Carbon composites: a summary of recent developments and applications, 1997,18(1): 11-15
2. Y. T. Gao, Y. X. Guan, K. Li, etc. Failure behaviors of C/C composite tube under lateral compression loading, Nuclear Engineering and Technology, 2019, 51:1822-1827
3. T. D. Burchell. Carbon Materials for Advanced Technologies, Pergamon Press, New York,1999.
4. P. Crocker, B. Mcenaney. Oxidation and fracture of a woven 2D Carbon-Carbon composite. Carbon, 1991, 29(7): 881-885
5. T. Li, Y. L. Zhang, Y. Q. Fu, etc. High strength retention and improved oxidation resistance of C/C composites by utilizing a layered SiC ceramic coating, Ceramics International, 2021, 47: 13500-13509
6. J. R. Mirasol, P. A. Thrower, L. R. Radovic. On the oxidation resistance of carbon-carbon composites: importance of fiber structure for composite reactivity. Carbon, 1995, 33(4): 545-554
7. V. Z. Shemet, A. P. Pomytkin, V. S. Neshpor. High-temperature oxidation behavior of carbon materials in air, Carbon, 1993, 31(1):1-6
8. D. W. Mckee. Oxidation and behavior and protection of Carbon/Carbon composites, Carbon, 1987, 25(4): 551-557
9. N. S. Jacobson, D. M. Curry. Oxidation microstructure studies of reinforced carbon/carbon, Carbon, 2006, 44 :1142–1150
10. F. Lamouroux, X. Bourrat, R. Nasalain. Structure/oxidation behavior relationship in the carbonaceous constituents of 2D-C/PyC/SiC composites. Carbon, 1993, 31(8):1273-1288
11. K. Li, Y. T. Gao, H. P. Zhang, etc. Efficient three-dimensional characterization of C/C composite reinforced with densely distributed fibers via X-ray phase-contrast microtomography. Chinese Optics Letters, 2021, 19(7): 073401
12. V. Z. Shemet, A. P. Pomytkin, V. S. Neshpor. High-temperature oxidation behavior of carbon materials in air, Carbon, 1993, 31(1):1-6
13. J. P. Goulmy, O. Caty, F. Rebillat. Characterization of the oxidation of C/C/SiC composites by Xray micro-Tomography, Journal of the European Ceramic Society, 2020, 40: 5120–5131
14. F. Wan, T. J. Pirzada, R. J. Liu, etc. Microstructure Characterization by X-Ray Computed Tomography of C/C-SiC Ceramic Composites Fabricated with Different Carbon Fiber Architectures. Applied

Composite Materials,2019, 26:1247-1260

15. Y. T. Gao, Y. D. Wang, X.M. Yang, etc. Synchrotron X-ray tomographic characterization of CVI engineered 2D-woven and 3D-braided SiC f /SiC composites, Ceramics International, 2016, 42: 17137-17147
16. H. A. Bale, A. Haboub, A. A. MacDowell, etc. Real-time quantitative imaging of failure events in materials under load at temperatures above 1600°C, Natural Materials, 2013, 12:40-46

Figures

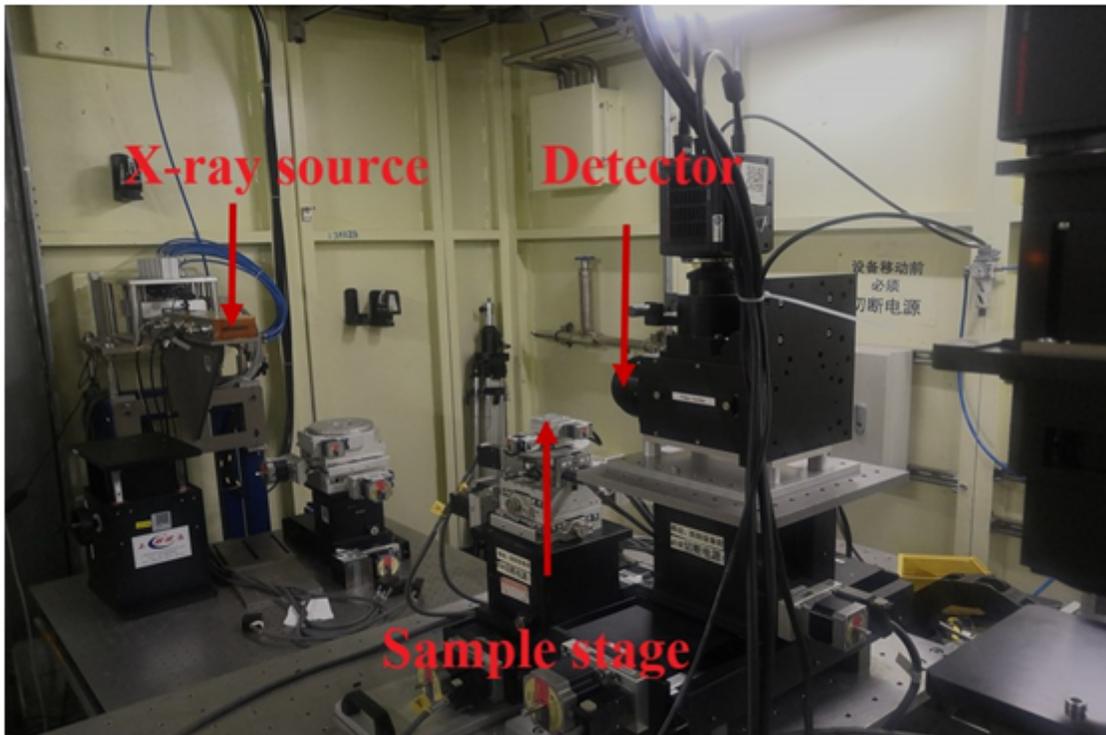


Figure 1

Experimental setup of SR- μ CT equipment

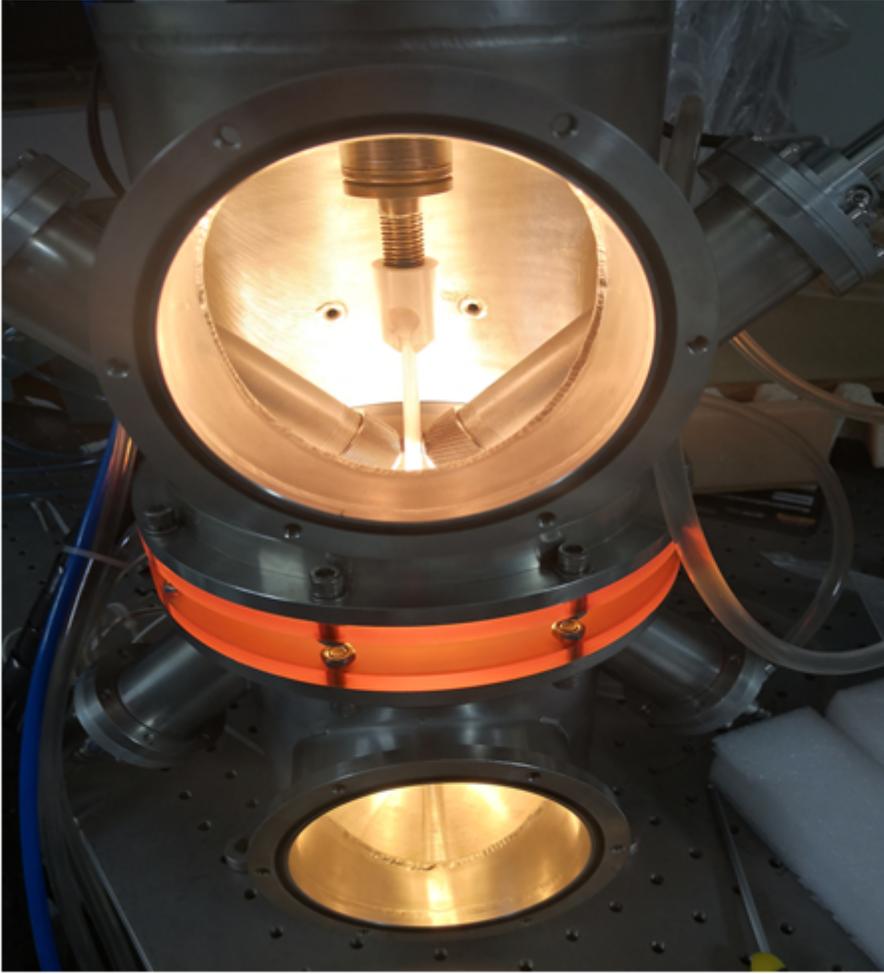


Figure 2

Chamber for heating samples

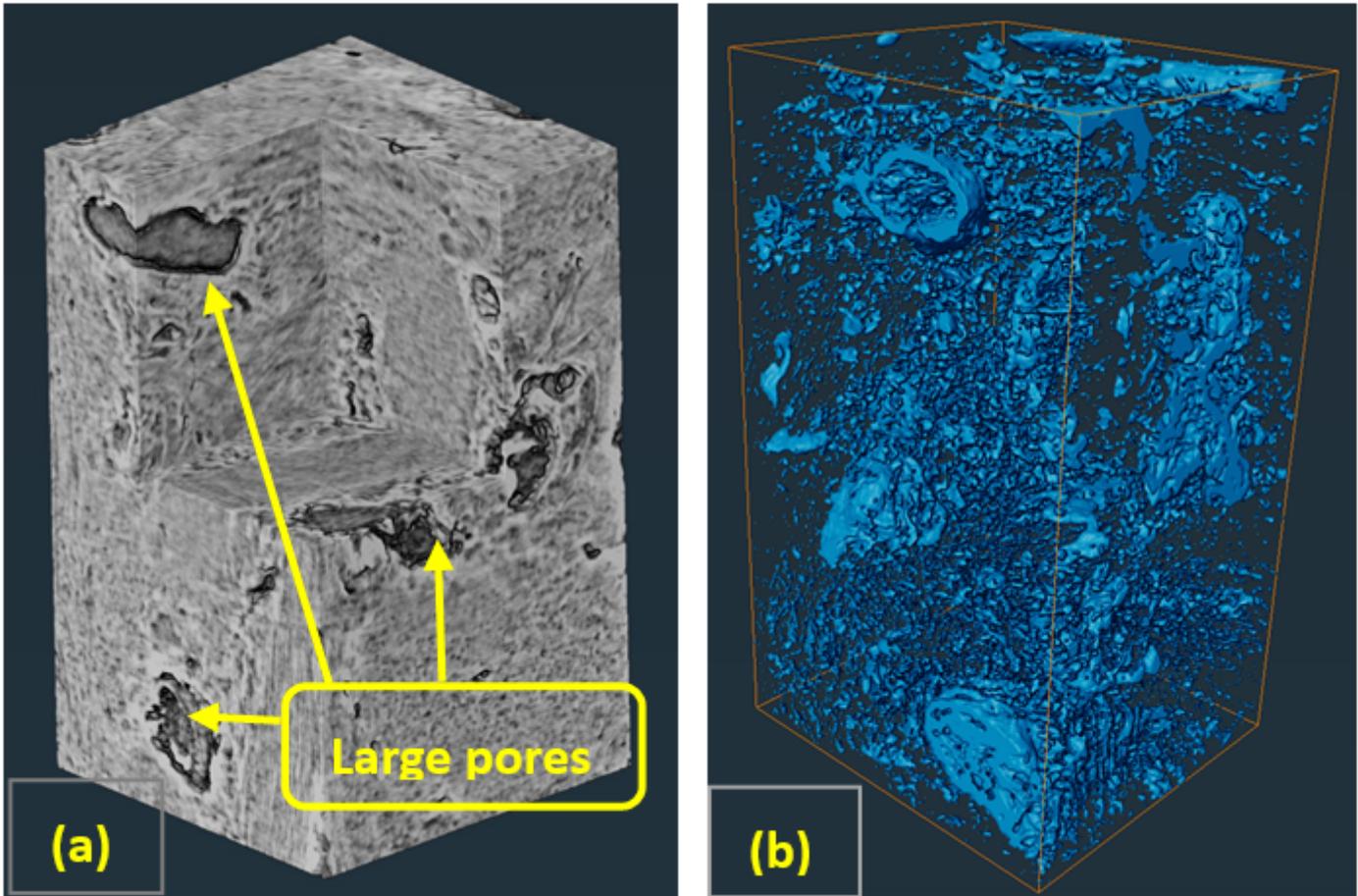


Figure 3

3D tomography of the un-oxidized C/C composite. (a) 3D volume visualization of the un-oxidized C/C composite; (b) Pore distribution in the un-oxidized C/C composite.

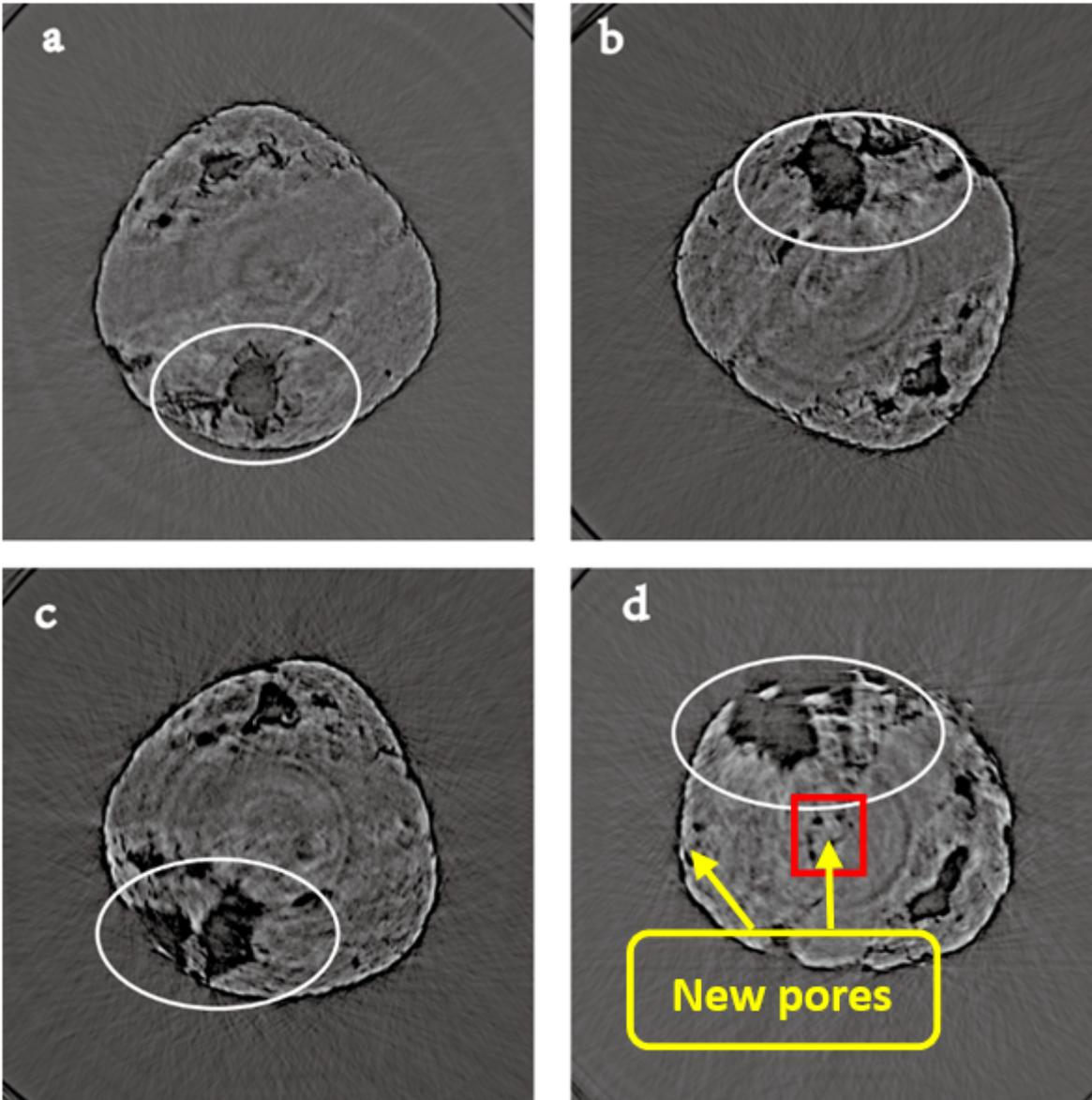


Figure 4

Microstructure evolution of C/C composite material in two dimensions a) b) c) d)

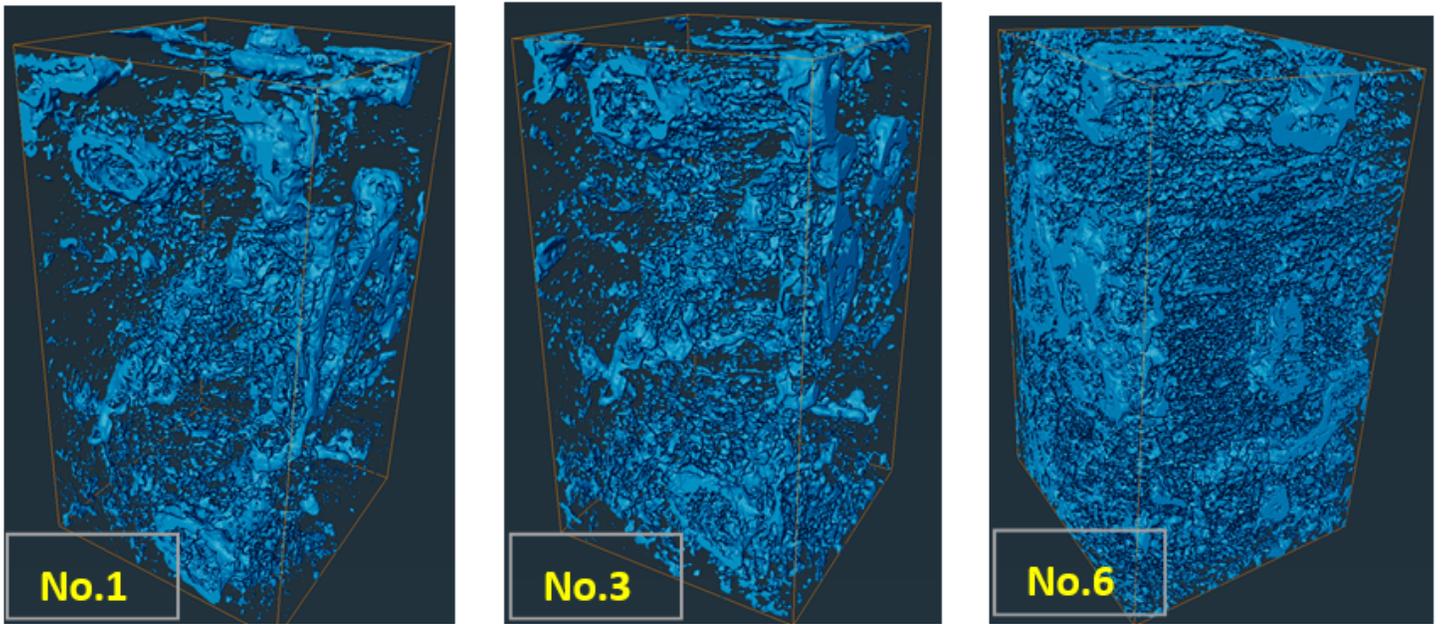


Figure 5

3D evolution of pores in oxidized C/C composite

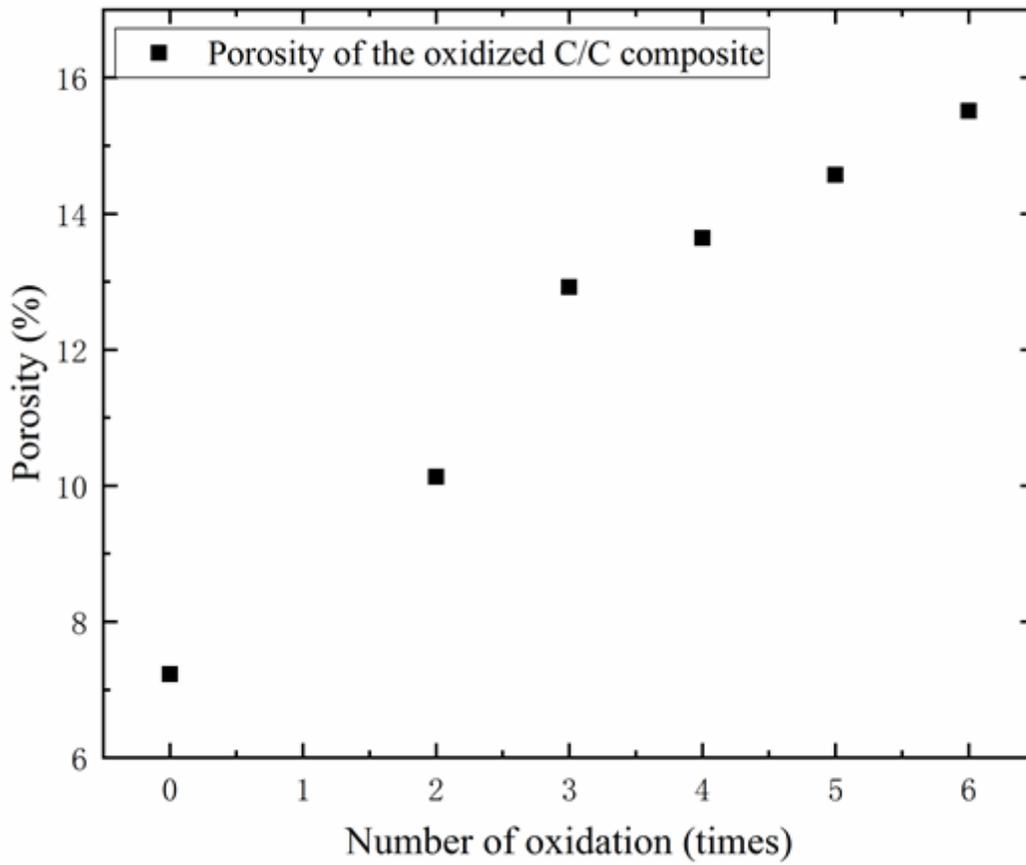


Figure 6

Porosity of the oxidized C/C composite as a function of the oxidation process