

## STUDY ON CORROSION PROPERTIES OF CARBON-CARBON COMPOSITES

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The corrosion resistance of carbon-carbon composite materials (C–C composites) was studied in a corrosive media of coolant NaF+ZrF<sub>4</sub> salt (a model heat-transfer) at 700 °C in the air flow. It has been shown that C–C composite material is resistant to the model heat-transfer even under conditions of critical temperature accident. The main mechanism that leads to the C–C composite corrosion is a mechanism of composite material oxidation due to the contact with the air. The study has evidenced that the C–C composite burn-up rate well correlates with the pyrocarbon matrix content in the composite, the matrix content increase by 25...30% results in the composite corrosion resistance increase by a factor of 2–4. So, by developing corrosion-resistant carbon-carbon composites one has a problem of finding an optimum fiber-matrix ratio in the composite. It has been confirmed experimentally that by silication of C–C composites with the use of the methods which were developed in NSC KIPT it is possible to increase the service life of products under simulated accident conditions by a factor of 7–7.5.

### INTRODUCTION

At GJF forum held in 2002 a program of main priority was a problem of developing a new generation of nuclear energy systems. The development of IV generation reactors requires also new approaches to the reactor core material development. Such materials should withstand high temperatures and have a high mechanical resistance, radiation and corrosion resistance in order to maintain the serviceable condition of systems over a period of time necessary, at the minimum, for the accident elimination. One of promising materials satisfying these requirements is carbon-carbon composite material (C–C composite).

A carbon-carbon composite is a wide class of composite materials consisting of a reinforced frame (preform) which is composed of carbon fibers and pyrocarbon or graphite matrix that fills the gaps between the fibers and thus forms a solid composite.

The NSC KIPT has developed original thermogradient gas-phase methods of forming the C–C composite by densification of porous carbon media with resistive heating [1]. Subsequently, these methods were advanced that resulted in the development of a gas-phase densification using a radially moving pyrolysis zone [2].

Paper [3] presents a brief description of the theoretical model and computer calculations for the parameters of porous medium densification by the method of radially moving pyrolysis zone relating the final density of compacted materials with their sizes, structure and densification modes.

The aim of this study is to obtain an effective estimation of the C–C composite performance under extreme conditions, to fulfill a series of investigations into the filler matrix phase composition influence on the composite corrosion, as well as the temperature influence on the erosion and ablative resistance of C–C composite.

### 1. MAIN PRINCIPLES OF C–C COMPOSITE FORMING BY THE METHOD OF THERMOGRADIENT AND GAS-PHASE DENSIFICATION

The current C–C composite technology is based on the thermal decomposition of hydrocarbon gases.

Gas-reagent – methane (CH<sub>4</sub>) diffuses into pores between fibers and is heated up to temperature T<sub>P</sub> – temperature of the starting process of methane destruction into hydrogen and carbon [2]. At the same time around methane a relatively narrow pyrolysis zone is formed with the temperature in the range from T<sub>K</sub> to the threshold temperature T<sub>n</sub> of the onset of gas-phase pyrocarbon deposition reactions.

The deposition reaction occurs only in this narrow pyrolysis zone. The temperature in the rest of the area, by the preform radius, is lower and there is no pyrocarbon deposition.

The process of pyrocarbon deposition in the C–C composite pores occurs in layers, especially on the surface of reinforcing fibers [4]. Fig. 1 represents the microstructure of a pore in the reinforced frame after pyrocarbon deposition. As is seen from the above figure, the pyrocarbon deposition can occur by separate layers (see position A, Fig. 1), as well as in the form of a globular structure (see position B, Fig. 1). The mechanism of pyrocarbon layer deposition on the fiber surface, in our opinion, is close to the epitaxial growth mechanism and is, in fact, similar to the formation of graphene layers. Similar and related techniques of graphene layer formation, when the gas mixture decomposes on the surface of different materials, are discussed by many of the authors (1, 4, 5).

Layer-by-layer deposition of such layers allows one to fill almost completely the pores in the material that promotes the formation of the C–C composite structure with high characteristics of physical properties.

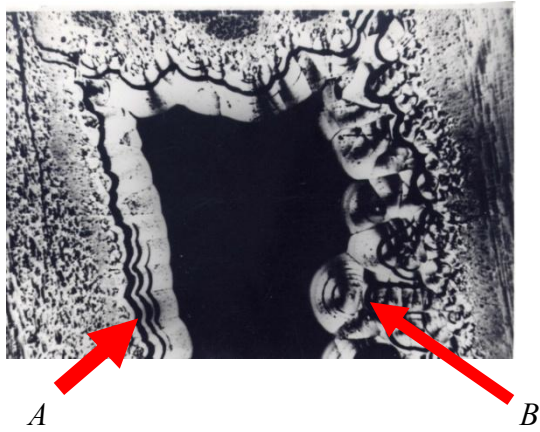


Fig. 1. Microstructure of a pore in C-C composite

The competing process of layered deposition is the process of globular structure formation. This process is very similar to the fullerene formation (see position B, Fig. 1). As is seen from Fig. 1, even under pyrolysis condition two matrix growth mechanisms can be implemented simultaneously.

## 2. INVESTIGATION OF C-C COMPOSITE CORROSION RESISTANCE

As noted above C-C composite materials have a high chemical resistance in the most corrosive media and can be used for making elements of various chemical devices and machines, elements of existing and promising reactor designs, such as salt reactors.

To study a simultaneous impact of various aggressive factors on C-C composites, experiments were carried out to evaluate the effect of the coolant salt simulator and of the air on the container made of C-C composite.

For this purpose, a series of model containers was made, one of which was filled with a mixture of NaF+ZrF<sub>4</sub> salt (10.5:42).

The container was filled up to the cover. The container was not sealed. The output data for the model container are shown in Table 1.

The diagram of the experiment is shown in Fig. 2.

The container (see pos. 2, Fig. 1) was installed on the thin C-C composite plate (see pos. 3, Fig. 1) in the middle of the carbon-carbon heater (see pos. 1, Fig. 1). The heater was installed between the graphite block in the AGAT-1.6 installation. Temperature was controlled by the XA-thermocouple in the quartz case. The experiment was carried out in the air with the open installation doors and switched-on exhaust ventilation (to create a flow).

After charging the installation the assembly was heated to 600 °C/min with a rate of 60 °C/min and held at this temperature for 30 min and then the heating was turned off. Within 30 minutes, the crucible was cooled to 100 °C then the assembly was dismantled for the visual inspection of the container and weighed. The visual inspection of the container has shown that the salt was melted and took a characteristic metallic luster. After the inspection and weighing of the container, the assembly was placed into the chamber and the heating cycle was continued.

Table 1  
Output data on the model container with NaF+ZrF<sub>4</sub> salt mixture

Weight of assembled container, g	86.84
Weight of container itself, g	64.32
Weight of cover, g	22.52
Weight of salt mixture, g	34.565
Weight of container with salt, g	98.88
Weight of container with cover and salt, g	121.41

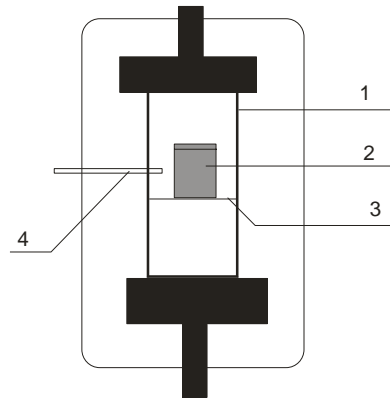


Fig. 2. Diagram of experiment: 1 – Carbon-carbon heater; 2 – container; 3 – thin C-C composite plate; 4 – thermocouple XA

The heating was carried out at a rate of 120...150 °C/min to a temperature of 600...700 °C.

After 9 cycles of heating and cooling, the container was removed from the assembly to carry out visual inspection and weighing. The inspection has shown that there was no leakage of the salt mixture. On the outer surface of the container there were small burnout marks.

After the inspection and weighing, the assembly was again placed into the chamber to continue the heating-cooling cycles. After 4 cycles the heater failed. Then the heater was replaced and another 6 cycles of heating-cooling were carried out. After 20 cycles a visual inspection of the container has shown that the burnout of the container was rated as critical (at a depth of 5 mm). It should be noted that because of the outer part burnout it was impossible to open the container without breaking. In general, the container maintained its integrity and efficiency, the salt mixture leaking did not occur. Table 2 gives the data on the dynamics of the container and cover weight changes. As can be seen from the table, the number of cycles is 20 with a total time of the crucible cooling in the oxidizing atmosphere at 600...700 °C for 10 hours.

After each weighing the change in the weight of both the crucible with salt mixture and the cover was observed. Taking into account that the cover did not come into contact with salt, the cover weight loss occurred only due to the process of oxidation in the air. Thus, the covers in the crucibles were used as control material samples to estimate the rate of burnout due to the oxidation.

Table 2

Data on the corrosion resistance of C-C composite container with NaF+ZrF<sub>4</sub> salt in the air at 600 to 700 °C

Cycle	Weight of cover, g	Weight of assembly, g	Weight loss, %	
			cover	assembly
0	22.52	121.41	0	0
1	22.461	121.13	0.26	0.23
10	21.737	117.72	3.48	3.04
20	–	112	–	7.75

As is seen from the data given in Fig. 2, the weight loss of the container material occurs only due to the oxidation of the material in the air, mainly from the outer surface of the container.

During the complete experiment the C-C composite container ensured the safety of the salt mixture (model heat carrier). After the experiment was over, the container was cut. Fig. 3 shows a section of the container with a frozen salt melt.



Fig. 3. Section of the container with a frozen melted salt after 20 “heating-cooling” cycles

It is seen from the figure that there is no wall destruction of the container with molten salt mixture, and the salt mixture penetration into the container walls is not observed. Thus, this experiment confirms the high corrosion resistance of C-C composite in relation to the model heat carrier even under emergency conditions. The main factor having an influence on the performance of composite materials under emergency conditions is the oxidation process on the outside of the atmosphere.

As noted above, the carbon-carbon composite material consists of the carbon fiber and matrix. To estimate the effect of the phase composition of the matrix and filler on the C-C composite corrosion resistance we have prepared a layered composite in which a layer with a high matrix content (75...80 %) alternated with layers in which the matrix content was 50 % [6]. This approach made it possible to estimate effectively the matrix influence on the composite ultimate resistance to the burnout. The external view of the test sample after oxidation in the muffle furnace at 900 °C is represented in Fig. 4.



Fig. 4. External view of the layered C-C- composite after oxidation at 900°C in the muffle furnace

In Fig. 4 you can see spirally wound C-C composite layers. The wide layers of 2 mm thick have a pyrocarbon matrix content of about 75...78 %, the thin layers, respectively, have a thickness of 0.5 mm, and the pyrocarbon content of 50 %. To make the preform in both layers graphite carbon fibers based on viscose were used. The investigations have shown that the composite burnout rate well correlates with the pyrocarbon matrix composition – layers with the increased pyrocarbon matrix content have a higher, in 2...4 times, resistance to the burnout in the air. This experiment obviously confirms that the corrosion resistance of the carbon-carbon composite material directly depends on the pyrocarbon matrix content in the composite. The matrix provides the necessary corrosion resistance, and fibers provide the mechanical resistance of the composite. So, by developing corrosion-resistant carbon-carbon composites one has a problem of finding an optimum fiber-matrix ratio in the composite.

### 3. INVESTIGATION ON THE CORROSION RESISTANCE OF C-C COMPOSITES WITH CERAMIC MATRIX AND PROTECTIVE COATING

Carbon-carbon composite materials, as is noted above, have chemical and temperature resistance, but their performance is very dependent on the external environment. In the air, the working temperature of carbon and graphite materials is limited to 450...550 °C [6–8]. The traditional way of increasing the resistance of C-C composites in the air is to deposit on their surface protective coatings, mainly of silicon-carbide, and to silicate them.

For this series of experiments cylindrical model samples from the C-C composite were prepared using the thermogradient gas-phase pyro-densification technologies. The preform was formed by winding carbon fabric layers onto graphite frame.

The preform density after winding was 0.62 to 0.64 g/cm<sup>3</sup>. Preforms were placed into the chamber of the AGAT-1.6 installation to fill them with pyrocarbon using direct resistive heating under the following conditions: during 1 hour the temperature in the preform surface was increased to 800 °C, then the temperature

reached 1100 °C at a rate of 30 °C, the samples were held for 1 hour and, after all, the heating was stopped. By this mode 5 pipes of  $\varnothing 55 \times \varnothing 29 \times 750$  mm were made. An average density of samples after densification was 1.35...1.38 g/cm<sup>3</sup>. From these pipes 20 samples of  $\varnothing 51 \times \varnothing 31$  mm, H = 130 mm were prepared.

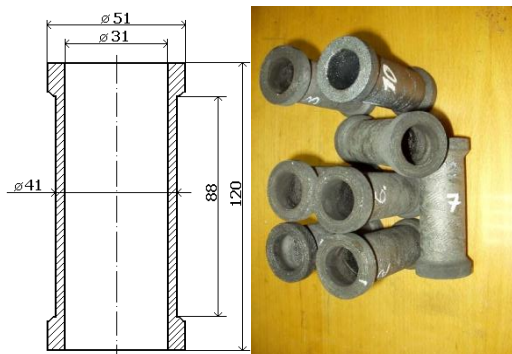


Fig. 5. Diagram and appearance of the samples

After the samples were prepared, they were certified with the use of hydrostatic investigations for determining the composite density and porosity. The results are shown in Table 3.

#### 4. SILICATION OF C-C COMPOSITE SAMPLES

Samples No 9–18 from Table 3 were selected to study the silication process. Samples No 1–8 (from pure C-C composite) were used as control samples. The silication procedure was carried out using the sprinkling method [9, 10]. The procedure of silication was carried out at temperature of 1500 °C, the duration of the process was 30 minutes. The silication of each sample was performed individually. After silication on the sample surface there were silicon buildups.

Additional annealing was carried out to remove the silicon bulges and to transform free silicon into carbide.

Table 3  
Properties of C-C composite samples

No	Mass, g	Density by dimensions data, g/cm <sup>3</sup>	Density by hydrostatic weighing data, g/cm <sup>3</sup>	Open-porosity %	Picnometric density, g/cm <sup>3</sup>
1	108.535	1.24	1.29	15.7	1.53
2	115.86	1.33	1.36	12.1	1.55
3	110.54	1.28	1.30	13.5	1.51
4	114.515	1.31	1.33	13.7	1.55
5	116.92	1.34	1.37	12.2	1.56
6	114.385	1.31	1.34	15.0	1.58
7	117.97	1.36	1.39	13.8	1.61
8	113.695	1.31	1.32	13.0	1.52
9	105.7	1.22	1.26	16.6	1.51
10	121.58	1.39	1.40	12.6	1.61
11	112.76	1.29	1.33	15.9	1.58
12	97.15	1.12	1.15	22.7	1.49
13	115.585	1.24	1.29	14.9	1.51
14	116.615	1.36	1.39	13.3	1.60
15	96.225	1.11	1.13	24.1	1.49
16	106.83	1.25	1.29	14.1	1.51
17	112.24	1.24	1.27	15.5	1.50
18	110.635	1.32	1.35	13.2	1.55
19	115.11	1.32	1.35	12.3	1.54
20	108.45	1.25	1.28	15.0	1.50

The data on the test samples are given in Table 4. As is seen from the table, there is no significant increase in the mass and density of samples during silication, samples hold their shape and integrity during the silication process. The data confirm once again that pyrocarbon, deposited from the gas phase, is resistant to the silicon melt.

Table 4  
Summarized data on the C-C composite samples after densification, silication and additional heating

No	Initial data				Silication				Annealing			
	Mass, g	Density, g/cm <sup>3</sup>		P, %	Mass, g	Density, g/cm <sup>3</sup>		P, %	Mass, g	Density, g/cm <sup>3</sup>		P, %
		Appar.	Picnom			Appar.	Picnom			Appar.	Picnom	
1	2	3	4	5	6	7	8	9	10	11	12	13
10	121.58	1.39	1.61	12.6	136.86	1.58	1.63	3.3	136.38	1.52	1.72	11.65
11	112.76	1.29	1.58	15.9	134.66	1.57	1.59	1.1	127.55	1.57	1.85	15.44
12	97.15	1.12	1.49	22.7	141.85	1.66	1.68	1.2	129.83	1.50	1.79	16.42
13	115.59	1.24	1.51	14.9	150.57	1.67	1.68	0.9	141.32	1.54	1.71	9.81
14	116.62	1.36	1.60	13.3	133.25	1.58	1.59	0.6	128.16	1.55	1.73	10.49
15	96.23	1.11	1.49	24.1	147.30	1.75	1.83	4.5	142.64	1.64	1.93	14.86
16	106.45	1.25	1.51	14.1	137.9	–	–	–	131.94	1.55	1.71	9.08
17	111.82	1.24	1.50	15.5	150.47	–	–	–	141.92	1.55	1.73	10.39
18	110.34	1.32	1.55	13.2	131.7	–	–	–	127.85	1.49	1.70	12.36
19	114.77	1.32	1.54	12.3	–	–	–	–	–	–	–	–
20	108.08	1.25	1.50	15.0	–	–	–	–	–	–	–	–

#### 5. INVESTIGATION INTO C-C COMPOSITE RESISTANCE IN THE AIR

To determine the C-C composite corrosion resistance in the air we tested the samples prepared

without protective layer deposition by the silication method (No 1–8).

Investigations were carried out in the camera of the installation AGAT-1.6 with an open door (in the air). The photo of the experiment is shown in Fig. 6. The



experiment was performed at a temperature of 1000 °C on the sample surface.

Sample 1 was exposed to the air for 1 hour at 1000 °C. After turning off the heating the carbon burnout on the outer sample surface was determined by visual inspection (the thickness of the sample walls has been decreased by 30...60%).



Fig. 6. Photo of the experiment on the investigation into the erosion of C-C composite resistance in the air

The sample mass loss was 16 %. The sample was close to the destruction. Therefore the experiment was stopped. The sample No 9 processed by silication was exposed to the air at 1000 °C during total time of 7 hours (1 h, 3 h, 3 h 45 min). After the exposure in the air for 1 hour the mass loss was 3%; after 3 hours it was 3%; after 3 h 45 min it was 18%. After the total exposure of the sample in the air for 7 h 45 min at a temperature of 1000 °C the sample was destructed in the middle part. It should be noted that in the C-C composite samples, that did not not silicated, the material burnout started from the surface, and in the silicated samples the burnout occurred in the volume, the appearance and size of the sample did not changed until the moment of destruction. Fig. 7 shows the appearance of the samples after the tests.



Fig. 7. Appearance of the samples after corrosion tests in the air

Corrosion tests have shown that the samples prepared from C-C composite material with a silicon carbide coating have the corrosion resistance increased by a factor of 7 to 7.5 compared to the uncoated samples.

## CONCLUSIONS

Studies on the corrosion resistance of carbon-carbon composite materials in the corrosive media (salt NaF+ZrF<sub>4</sub> coolant) at 700% in the air flow have confirmed that C-C composites are resistant to the model heat-carrier even under accident temperature conditions, and the main factor responsible for C-C composite corrosion under these conditions is the composite material oxidation due to the contact with the air.

Investigations on the corrosion resistance of C-C composites have shown that the composite corrosion resistance is provided first of all by the matrix, and the reinforcing fibers provide the necessary mechanical resistance. The C-C composite burnout rate is in a good correlation with the pyrocarbon matrix content in the composite, the pyrocarbon matrix content increase by 25...30% increases the corrosive resistance of the composite by a factor of 2 to 4.

So, in the development of corrosion resistant C-C composite there is a problem which is reduced first of all to the selection of an optimum reinforced fiber-matrix ratio in the composite.

Experiments confirmed that the C-C composite silication by the methods developed in NSC KIPT allows one to increase the service life of products under simulated emergency conditions (in the air at temperature of 1000 °C) by a factor of 7 to 7.5.

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## **ИССЛЕДОВАНИЕ КОРРОЗИЦИОННЫХ СВОЙСТВ УГЛЕРОД-УГЛЕРОДНЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ**

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Проведены исследования коррозионной стойкости углерод-углеродных композиционных материалов (УУКМ) в агрессивных средах (модельный солевой теплоноситель  $\text{NaF}+\text{ZrF}_4$ ) при температуре 700 °С в потоке воздуха. Показано, что УУКМ является стойким по отношению к модельному теплоносителю даже в условиях аварийных температур, а основным механизмом, ответственным за коррозию УУКМ, есть механизм окисления композиционного материала при контакте с атмосферной средой. Проведенные исследования наглядно подтвердили, что скорость выгорания УУКМ четко коррелирует с содержанием в композите пироуглеродной матрицы, с повышением содержания матрицы в композите на 25...30% коррозионная стойкость возрастает в 2–4 раза. Таким образом, при разработке коррозионно-стойких УУКМ возникает задача выбора оптимального соотношения в композите волокна и матрицы. Экспериментально подтверждено, что силицирование УУКМ с использованием разработанных в НИЦ ХФТИ методов позволяет повысить ресурс работы изделий в моделируемых аварийных условиях в 7–7,5 раза.

## **ДОСЛІДЖЕННЯ КОРОЗІЙНИХ ВЛАСТИВОСТЕЙ ВУГЛЕЦЬ-ВУГЛЕЦЕВИХ КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ**

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Проведено дослідження корозійної стійкості вуглець-вуглецевих композиційних матеріалів (ВВКМ) в агресивних середовищах (модельний сольовий теплоносій  $\text{NaF}+\text{ZrF}_4$ ) при температурі 700 °С у потоці повітря. Показано, що ВВКМ є стійким по відношенню до модельного теплоносія навіть в умовах аварійних температур, а основним механізмом, відповідальним за корозію ВВКМ, є механізм окислення композиційного матеріалу при контакті з атмосферним середовищем. Проведені дослідження наочно підтвердили, що швидкість вигорання ВВКМ чітко корелює зі змістом у композиті піровуглецевої матриці, з підвищенням вмісту матриці в композиті на 25...30% корозійна стійкість зростає в 2–4 рази. Таким чином, при розробці корозійно-стійких ВВКМ виникає завдання вибору оптимального співвідношення в композиті волокна і матриці. Експериментально підтверджено, що силиціювання ВВКМ з використанням розроблених у НИЦ ХФТИ методів дозволяє підвищити ресурс роботи виробів у модельованих аварійних умовах у 7–7,5 разів.