STRUCTURAL CARBON-CARBON MATERIALS FOR ACCELERATOR-DRIVEN SYSTEMS

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The paper presents results of investigations of the compatibility of carbon-carbon composite materials with molten sodium fluoride – zirconium fluoride mixture in the presence of molten lead and its fluoride. The investigations have been carried out both without irradiation and with irradiation with an electron beam of 10 MeV energy and 5 kW power (current density 0.5 mA/cm2) on a linear electron accelerator LPE–10 (LINAC–10). It has been shown that this material is impermeable to the above compounds. Does not interact with them. And does not break down on temperature cycling from room temperature to 700 °C. The mechanical properties of carbon-carbon composites have been investigated by the nanoindentation method. It has been found that neither long contact with molten fluoride mixture nor irradiation affects the mechanical properties of this material.

INTRODUCTION

The conceptual design of accelerator-driven reactors envisages the use of mainly structural materials based on carbon and metal alloys [1]. The function of carbon materials is to moderate thermal neutrons and ensure long-duration continuous delivery of the products to be fissioned to the reaction zone by means of a molten salt mixture-carrier and to remove the compounds formed from it.

Carbon-carbon materials with different reinforcement: carbon fabrics and composites based on graphite powders were used in the research. Carbon-carbon composites are characterised by a high mechanical strength, chemical stability, heat-shock resistance, resistance to reaction media of various compositions and enable operation in a wide temperature range (over 3000 °C). The technology developed by the Research Center "KIPT", for producing carbon materials enable making articles of various shapes and size. Thermal-gradient vapour-phase methods of tightening with pyrocarbon enable producing composites with low open porosity (of several per cent), which makes carbon-carbon composites almost impermeable to the molten salt and metallic phase.

During the operation of accelerator-driven reactor, nuclear transformation products: rare-earth fluorides, isotopes and fluorides of transition elements (Nb, Mo, Tc, Ru, Ag, Te, etc) will accumulate in the molten salt mixture-carrier of transmutation products. They will be uniformly distributed over all reactor systems. Besides, isotopes of rubidium, cesium, strontium, barium, zirconium, iodine will accumulate with time in the fuel mixture. The isotopes $^{131,135}I$ are a source of formation of neutron poison-xenon. Metals with high negative electrode potential (alkaline and rare-earth elements) decrease the corrosion stability of carbon materials in salt melts, transition metals (Nb, Mo) can cause formation of carbides, tellurium is surface-active towards metal alloys and causes intercrystalline corrosion.

The chemistry of molten salt blanket is today at the initial stage of investigations. Under real conditions, the structural materials of reactor will be in contact nor with a pure sodium fluoride - zirconium fluoride mixture but with a mixture containing the above elements and compounds. In view of this, the study of the properties of carbon-carbon materials in molten fluoride mixtures that simulative fuel compositions and in liquid - metal coolants is an urgent task not only in respect of cognition but also in respect of practice.

The paper presents results of studies of the compatibility of carbon-carbon composite materials with molten sodium fluoride - zirconium fluoride mixture and liquid-metal coolants: lead, lead-bismuth eutectic and bismuth.

EXPERIMENTAL PROCEDURE

Structural carbon-carbon materials were tested for compatibility with molten NaF (50.5 mol%) – ZrF_4 (49.5 mol%) mixture in a hermetically sealed container under dry argon. The mixture of the above composition has a melting point of 520 °C. Its specific weight at 700 °C is 3.26×10^3 kg/m^3, heat conductivity 2.1 J/cm·deg, Prandtl number 2.72, viscosity 5.7 Cp coefficient of volume expansion 3.36×10^{-4} deg^{-1}. The choice of this composition of the mixture-carrier of the products that are subjected transmutations was determined by the existing technology for the processing of spent park, spent fuel is fluorinated to extract uranium, zirconium tetrafluoride, which is part of the fuel element jacket of operating light-water reactors, forming the basis of fluorination products. If sodium fluoride is a added to this mix-

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ture in a 1:1 molar ratio, the NaF – ZrF_4 composition formed will fit the requirements to molten-salt fuel compositions and will be a good carrier of spent-fuel fission products [2].

Carbon-carbon composite materials and articles made of them (rectangular container with cover) were tested for temperature cycling (heating - cooling - heating) from room temperature to 650 °C. Ampoules, which were additionally tightened with pyrocarbon and on whose surface a protective film of pyrocarbon was deposited, were also used for investigations. A eutectic sodium fluoride - zirconium fluoride mixture was filled into each ampoule (≈50 % of useful volume), and temperature cycling was performed. After weighing and visual examination of the ampoule, lead was filled into it, and temperature cycling was repeated. After examining the state of the ampoule once more and weighing, lead fluoride (5 wt% of the mass of the eutectic filled) was added to it, and the investigation was repeated. Un the presence of the lead compounds, then surface tension of lead decreases, and it becomes able to easily penetrate into porous materials. The experiments were made to find out whether the carbon-carbon ampoules are impermeable to molten salt and metallic phases. Samples which were irradiated in a melt above composition at 650 °C on a linear electron accelerator LPE-10 (LINAC-10) with 10MeV energy and 5 kW power (current density 0.5 mA/cm^2) were also.

The change in the constitution of salt compositions and carbon-carbon materials was determined by chemical, X-ray phase, atomic absorption analyses. The atomic absorption analysis was performed on a Pionicum SP-9 spectrophotometer, the IR spectroscopic studies were carried out an a Specord 80 M device, the X-ray microanalysis and visual examination of the surface state of the samples under investigation were performed on a PEMMA-101M scanning electron microscope - microanalyzer.

The mechanical properties of carbon-carbon composites were determined by the nanoindentation method on a Nano Indenter-II nanohardness tester (MTS Systems). The investigations were carried out using a Berkovich triangular indenter at a load of 50 mN (≈ 5 gf) and at a constant loading rate, which was 0.5 and 2 mN/s. The impressions spaced 50 μm apart were made on each sample. The hardness and elastic modulus were determined from the depth of impression by the Oliver and Pharr technique [3].

RESULTS AND DISCUSSION

The results of the investigations carried out are listed in Table 1. Container №11 was tightened with pyrocarbon.

Table 1

Results of tests of carbon-carbon containers for molten salt and metallic phase tightness

Container №	Number of cycles	Total time (h)	Mass of the ingredients filled (g)			Temperature (°C)	Mass loss (%)
			Eutectic	Lead	PbF_2		
4	6	35	20.0	–	–	650	
4	2	12	20.0	–	–	750	0.1
4	4	31	20.0	91.12	–	750	0.6
4	4	31	20.0	91.12	1.0	750	0.6
5	3	20	20.0	–	–	650	0.2
5	1	8	20.0	–	–	700	
5	4	31	20.0	70.0	-	650	1.5
5	4	31	20.0	70.0	1.0	650	0.13
11	3	21	20.0	–		750	0.7
11	3	28	20.0	67.0	–	700	0.15
11	3	24	20.0	67.0	1.0	700	0.3

Container №4 was heated six times from room temperature to 650 °C; the total time of isothermal soaking was 35 h. It was heated twice to 750 °C. The soaking time at the above temperature was 12 h. When cooled an ingot of eutectic mixture was easily separated from the container. A visual examination showed the container walls to be not wetted by the melt. The mass loss of the sample “container – fluoride mixture” was approximately 0.1 %. After making necessary measurements, lead was added to the same container, and heating to 750 °C and cooling performed four times. The total time of isothermal soaking was 31 h. The inner surface of the carbon-carbon article remained with out visible changes. The mass loss of the whole system was 0.6 %. No saturated of the container with the salt melt or lead was detected. Lead fluoride (5 wt%) was also added to the same container. After heating from room temperature to 750 °C and cooling performed four times and isothermal soaking for 31 h, the mass loss was 0.6 %/ No saturation of the carbon-carbon composite with the salt and metallic phases was detected visually.

Container №4 was used in long-duration (700 h) continuous studies of the compatibility of hastelloy of composition B with carbon-carbon materials and a molten sodium fluoride - zirconium fluoride eutectic under the short-circuit conditions of the galvanic couple composite – nickel-molybdenum alloy at 650 °C. Just after reaching the predetermined temperature conditions, the circuit current was 210 μA (105 μA/cm^2 for nickel-molybdenum alloy). The initial emf was 0.22 V. The sign “–” was on nickel-molybdenum alloy. In the seventh day, the current dropped to 8-9 μA and did not practically change subsequently throughout the period of tests. A visual examination showed that the ampoules retained its appearance and shape. No salt infiltration was detected. The total mass loss was 8.4 %, mainly owing salt phase sublimates (the cap of the ampoule was not screwed in because electrical leads were inserted into it), which condensed on the cold surfaces of the hermetically sealed reactor. The current drop in the electric circuit indicates that the surface of the electrodes is passivated with time, and their corrosion decreases.

The effect of the products of interaction between lanthanum trifluoride and zirconium in a molten sodium fluoride - zirconium fluoride mixture (simulative fuel mixture) on the short-circuit current, emf and electrical resistance of the galvanic couple carbon-carbon composite - hastelloy was also studied. The temperature was 600 °C, and the time was 300 h.

In contrast to the previous system, the sign "+" manifested itself on hastelloy. The initial emf was 0.19 V, the short-circuit current was 5 μA, and the resistance was 1.73 Ω. At the end of the experiment (257 h), the shot-circuit current was 0.07 μA, and the resistance was 41 Ω.

Thus, change in fuel mixture composition can greatly affect the corrosion mechanism of structural materials. In the last case, hastelloy was in the melt under cathodic protection. Short-circuit currents of these systems can be used to evaluate the corrosion stability of structural materials since they are proportional to corrosion currents of each galvanic couple elements.

Experiments similar to those with container №4 describe above (except long-duration experiment with nickel-molybdenum alloy short-circuit conditions) were carried out with other ampoules. Moreover, the stability of carbon-carbon structural materials under heating to 650 °C in air for 10 h was determined in some experiments. As a result of the investigations carried out it has been found that under such conditions, the container deforms mainly at the top. The cap of the container cannot be screwed out. The mass loss averaged 17.6 – 18.0 %.

Investigations of the salt phase after soaking with carbon-carbon containers have been carried out by the IR spectroscopy. The IR spectra of sodium fluoride – zirconium fluoride eutectic soaking in containers under argon remain unchenged, being the same as those of the original mixture. In the IR spectra of NaF – ZrF_4 eutectic heated in air to 600 °C for 3 h in a carbon-carbon crucible, extra bands at 850 and 1100 cm^{-1} appear, which characterize Zr—O vibration in ZrO_2 formed (Table 2).

1. Table 2

2. Position of absorption bands in the IR spectra of the main systems under investigation

System	Conditions		IR spectra of zirconium fluorides, *ν* (cm^{-1})	IR spectra of various compounds, (ν см$^{-1}$)
	t, (°C)	τ, (h)		
Container №4	25			Solid line
Container №5 and fluoride melt	560	7	300, 360, 425, 450, 500, 530, 600	
ZrF_4-$NaF_{eut.}$ +Ar (Container №5)	800	7	300, 310, 365, 420, 475, 515, 560	
ZrF_4-$NaF_{eut.}$ +O_2 (Container №5)	600	3	300, 310, 365, 420, 480, 515, 600	700, 850, 1100 Zr-O-F
ZrF_4-$NaF_{eut.}$+O_2 (контейнер №4)	600	3	300, 400, 485, 525	625, 850,1100 Zr-O
ZrF_4-$NaF_{eut.}$+Ar + Pb (Container №4)	750	8	300, 360, 425, 480, 525, 570	
ZrF_4-$NaF_{eut.}$+Ar + 20% Pb+10% PbF_2 (Container №4)	650	5	425, 470, 525, 600	280, 330 Pb-F
ZrF_4-$NaF_{eut.}$+Ar + 20% Pb (Container №5)	650	8	300, 460, 520, 600	360, 850 Zr-0-F
ZrF_4-$NaF_{евт.}$+Ar + 20% Pb+30% PbF_2 (Container №5)	700	8	300, 400, 460, 500, 515, 600	370, 850 Zr-0-F
ZrF_4-$NaF_{eut.}$+Ar + 20% Pb+10% PbF_2 (crucible №5)	650	15	300, 360, 420, 500, 580	
Galvanic couple – hastelloy under short-circuit conditions	800	5	310, 370, 430, 485, 590	
– «» –	600	20	300, 360, 465, 520, 590	
– «» –	600	100	285, 330, 370, 420, 450, 500, 520,585	
– «» –	600	200	270, 300, 375, 425, 450, 490, 580	
– «» –	600	350	270, 295, 380, 400, 480, 515, 600	
– «» –	600	500	270, 295, 360, 425, 480, 520, 590	

The results obtained indicate that carbon -carbon composite materials are impermeable to molten salt and metallic phases in the case of a long (over 700 h) contact with them both without irradiation and with electron beam irradiation, and that they can be used in designs of accelerator-driven reactor.

The investigations of mechanical properties, which have been carried out by the nanoindentation method, corroborate this conclusion. Carbon-carbon composites (sample 1) and a carbon-carbon composite which was additionally tightened with pyrocarbon and had a protective film of pyrocarbon on the article surface (sampler 2) were studied. In sample 1, two phases have been found on the lateral microsection: fibers and binding material. Observation with a microscope revealed no impressions on samples since this material has a high ability for the elastic restitution of the original shape. This is indicated by loading-unloading curves (Fig 1).

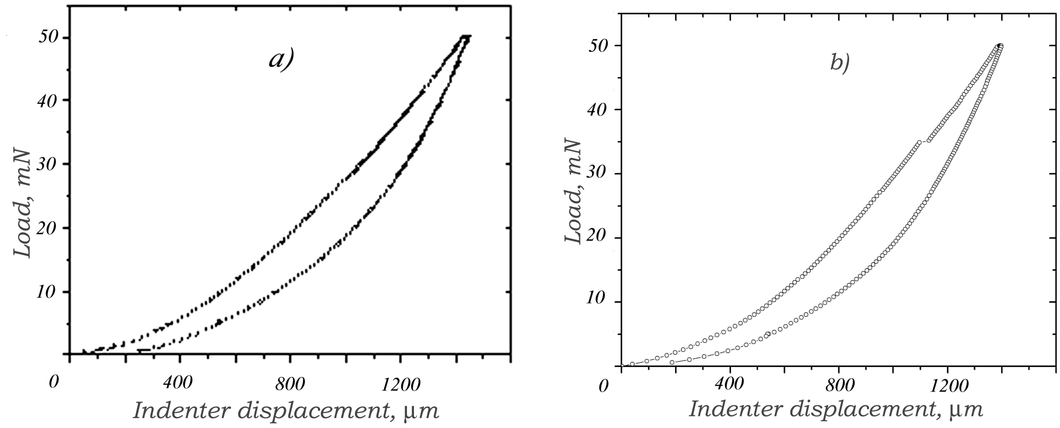

Fig. 1. Loading and unloading curves for carbon-carbon composite materials without contact with fluoride melt and without irradiation: a – sample not tightened with pyrocarbon; b – sample tightened with pyrocarbon

During unloading, loading and unloading curves generally diverge. For the samples under investigation, these curves first diverge and then converge again, and the indentation almost fully disappears an complete unloading. Dependences of this characteristic were observation earlier for glassy carbon [4]. The hardness and elastic modulus of the fibers and binding material in sample 1 differ only slightly (Table 3). This indicates the mechanical properties to be isotropic. The hardness and elastic modulus of sample 2 are higher. This sample is characterized by a sharp increase in the depth of impression on loading. This change may be due just to the vapor-deposited pyrocarbon film. There are good reasons to believe that this material is a variety of glassy carbon (amorphous carbon in which sp^2 bounds predominate).

Table 3

Mechanical properties of carbon-carbon composite materials

3. Sample	4. Elastic modulus (Gpa)	5. Hardness (Gpa)
6. Sample 1 (binding material)	*7.* 17±2	*8.* 2.83±0.14
9. Sample 1 (fiber)	*10.* 19±1	*11.* 2.11±0.23
12. Sample 1 (fiber)	*13.* 17±0	*14.* 1.72±0.38
15. Sample 2 (fiber)	*16.* 20±2	*17.* 2.72±0.35

18.

The hardness and elastic modulus of sample 1 differ only slightly, indicating the mechanical properties to be isotropic. The sample tightened with pyrocarbon has a higher elastic modulus. This sample is characterized by a sharp increase in the depth of impression on loading. The loading and unloading cures for irradiated samples are shown in Fig. 2.

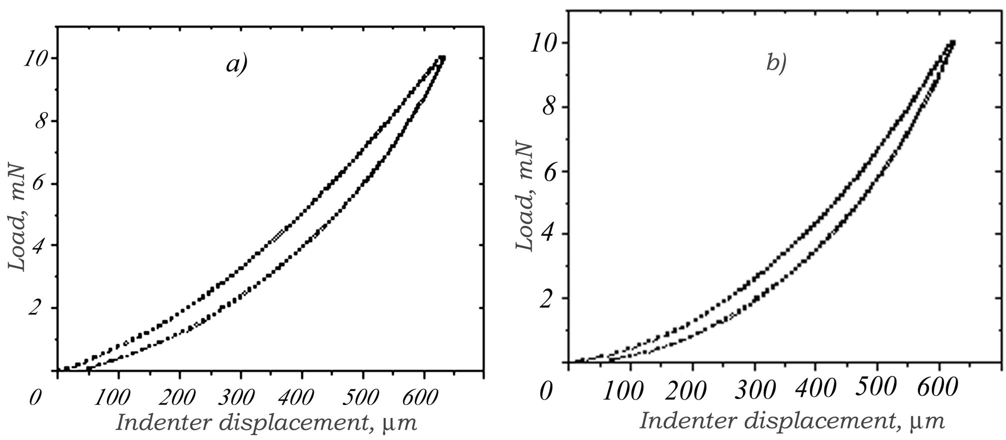

Fig. 2. Loading and unloading curves for carbon-carbon composite materials after electron beam irradiation in a sodium fluoride – zirconium fluoride melt for 700 h at 650 °C: (a) beam entance (5066 MeV/atom), (b) beam exit (64 MeV/atom)

And investigation of mechanical properties showed that either irradiation intensity or contact with molten fluoride mixture did not practically affect the hardness of this material within the above period of time. The hardness of the composite at the beam entrance was H = 2.0±0.3 GPa and at the beam exit H = 1.9±0.5 GPa.

CONCLUSIONS

As a result of the investigations carried out it has been found that carbon-carbon composite materials are resistant to molten sodium fluoride – zirconium fluoride mixture and lead. These materials withstand a long contact with molten salt and metallic phases at 650 °C, are impermeable to them, and are resistant to temperature cycling no chemical interaction with molten fluorides has been detected. Long contact with fluoride properties of carbon-carbon composites. The materials developed can be used in the designing of accelerator-driven reactors.

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УГЛЕРОД-УГЛЕРОДНЫЕ КОНСТРУКЦИОННЫЕ МАТЕРИАЛЫ ДЛЯ УПРАВЛЯЕМЫХ УСКОРИТЕЛЯМИ РЕАКТОРОВ

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Приведены результаты исследований совместимости углерод-углеродных композиционных материалов с расплавленной смесью фторидов натрия и циркония в присутствии расплавленного свинца и его фторида. Исследование выполнены как без облучением так и при облучении пучком электронов энергией 10 МэВ та мощностью 5 кВт (плотность тока 0.5 мА/см^2) на линейном ускорителе электронов ЛУЭ – 10 (LINAC–10). Показано, что данный материал в инертной атмосфере является непроницаемым для указанных выше соединений, не взаимодействует с ними и не разрушается при термоциклировании от комнатной температуры до 700 °С. Методом наноиндентирования изучены механические свойства углерод-углеродных композитов. Определено, что ни долгий контакт с расплавленной фторидной смесью, ни облучение не влияют на его механические свойства.

ВУГЛЕЦЬ-ВУГЛЕЦЕВІ КОНСТРУКЦІЙНІ МАТЕРІАЛИ ДЛЯ КЕРОВАНИХ ПРИСКОРЮВАЧЕМ РЕАКТОРІВ

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Приведені результати досліджень сумісності вуглець-вуглецевих композиційних матеріалів з розплавленою сумішшю фторидів натрію та цирконію в присутності розплавленого свинцю та його фториду. Дослідження виконані як без опромінення, так і при опроміненні пучком електронів енергією 10 МеВ та потужністю 5 кВт (густина струму 0,5 мА/см^2) на лінійному прискорювачі електронів ЛПЕ –10 (LINAC-10). Показано, що даний матеріал в інертній атмосфері є непроникним для зазначених вище сполук, не взаємодіє з ними та не руйнується при термоциклюванні від кімнатної температури до 700 °С. Методом наноіндентування досліджені механічні властивості вуглець-вуглецевих композитів. Встановлено, що ні тривалий контакт з розплавленою фторидною сумішшю, ні опромінення не впливають на його механічні властивості.