

## Effect of the Content of Molybdenum Disilicide on the Microstructure and Phase Transformations of $ZrB_2$ - $MoSi_2$ -10Al Coatings upon Annealing in Air

V.M. Beresnev<sup>1</sup>, I.Yu. Goncharov<sup>2,3,\*</sup>, M.G. Kovaleva<sup>2</sup>, M.N. Yapryntsev<sup>2</sup>, O.N. Vagina<sup>2</sup>,  
V.Yu. Novikov<sup>2</sup>, V.V. Sirota<sup>3</sup>, Yu.N. Tyurin<sup>4</sup>

<sup>1</sup> V.N. Karazin Kharkiv National University, 4, Svobody Sq., 61000 Kharkiv, Ukraine

<sup>2</sup> Belgorod National Research University, 85, Pobedy St., 308015 Belgorod, Russia

<sup>3</sup> Belgorod State Technological University named after V.G. Shoukhov, 46, Kostyukov St., 308012 Belgorod, Russia

<sup>4</sup> E.O. Paton Electric Welding Institute, NASU, 11, Bozhenko St., 03650 Kyiv, Ukraine

(Received 09 November 2021; revised manuscript received 02 December 2021; published online 20 December 2021)

The advantages of carbon/carbon (C/C) composites are low density, high heat capacity, resistance to thermal shock, low coefficients of friction and linear expansion, etc. However, their use in oxygen-containing environment at high temperatures is only possible with special protective heat-resistant gas-tight coatings, which prevent the access of oxygen to carbon. In this work,  $ZrB_2$ -based composite coatings with different contents of  $MoSi_2$  were fabricated on the surface of C/C composites by a Robotic complex for detonation spraying of coatings equipped with a multi-chamber detonation accelerator (MCDS). Flat specimens ( $10 \times 10 \times 5$  mm<sup>3</sup>) of 3D C/C composites (density 1.9 g/cm<sup>3</sup>) were used as substrates. The evolution of the microstructure and phase composition of  $ZrB_{2-x}MoSi_2$  ( $x = 24, 35, 45$  wt. %)-10Al coatings were analyzed with differential scanning calorimeter, X-ray diffractometry (in situ HT-XRD) and scanning electron microscopy at temperatures from 25 to 1400 °C (normal atmosphere and pressure). During analysis, it was observed that m-SiO<sub>2</sub> and ZrSiO<sub>4</sub> appear at 960 °C. Also, upon reaching the temperature 1235 °C, cubic zirconia and mullite are formed in  $ZrB_{2-x}MoSi_2$ -10Al coatings. In  $ZrB_{2-x}MoSi_2$ -10Al coatings at a temperature of 1400 °C, an increase in the  $MoSi_2$  content in the initial coating leads to almost complete disappearance of the cubic phase of zirconium dioxide, and the mullite content increases. It was found that the microstructure of the coating changed with an increase in the  $MoSi_2$  content after oxidation at 1400 °C from a dense to a "more defective".  $ZrB_{2-24}MoSi_2$ -10Al coating has a uniform dense microstructure in comparison with coatings containing 35 and 45 wt. % of  $MoSi_2$ . It is contributed to its good oxidation-resistant property at high temperature.

**Keywords:** Carbon/carbon composites,  $ZrB_2$ - $MoSi_2$ , Multi-chamber detonation accelerator, Microstructure, In situ HT-XRD.

DOI: [10.21272/jnep.13\(6\).06013](https://doi.org/10.21272/jnep.13(6).06013)

PACS numbers: 68.37.Hk, 68.37.Yz

### 1. INTRODUCTION

Recently, much attention has been paid to the development of processes and means of surface protection of carbon-carbon (C/C) composites from high-temperature oxidation. On the surface of C/C composites, single-layer, multilayer and composite heat-resistant coatings are formed in various ways [1-3]. One of the approaches to protecting the surface of C/C composites from high-temperature oxidation is the use of refractory boron-containing or aluminoborosilicate glasses as a matrix, in which to increase heat resistance particles of silicides, carbides, borides of metals of groups IV-VI are additionally added [4, 5].

The use of glass melt of different compositions reinforced with refractory particles of different nature and quantity provides great opportunities for regulating the properties of the main layer of protective coatings, as well as for controlling the process of coating formation. The melt of the glass matrix provides wetting of the filler particles and the substrate, reducing the porosity of the composition and healing of defects [6].

One of the directions of increasing the effectiveness of the protective effect of glass-ceramic coatings includes developments based on the formation of a heat-resistant layer of composite coatings through the reaction synthesis of a glass phase in air that encapsulates

the initial refractory components and inhibits the diffusion of oxygen deep into the protected material [6].

The production of the coatings under consideration is based on the formation of a glass phase by reaction synthesis in the process of heat treatment in air of oxygen-free compounds [7] or more complex compositions of refractory oxides, oxygen-free ceramics, and glass-forming elements (Si, B, Ge, etc.) [8, 9]. The heat-resistant coatings synthesized in this way are complex multicomponent systems and are a composite of a strong refractory matrix formed by sintered ceramic particles and a plastic glass phase that fills interfacial regions, pores, cracks, and capillary channels in the matrix and forms a protective oxide layer during oxidation. Non-oxidized components interacting with oxygen during high-temperature operation replenish the coating with glass phase and other oxides, playing a regenerating role. The variation of the chemical composition and regulation of the processes of chemical and phase transformations during the synthesis of the base layer provide ample opportunities for targeted control of the coating structure and allow sufficiently high operating temperatures [6].

Within the framework of this study, gas-thermal technologies with the use of a multi-chamber detonation accelerator were applied to the formation of glass-ceramic thermostable composite coatings  $ZrB_{2-x}MoSi_2$

\* [goncharov@bsu.edu.ru](mailto:goncharov@bsu.edu.ru)

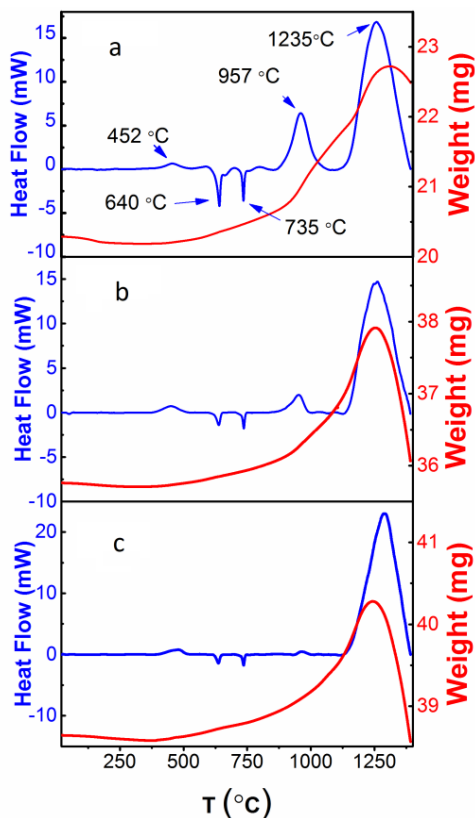
( $x = 24, 35, 45$  wt. %)-10Al (denoted as  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al) on the surface of C/C composites without an adhesion sub-layer. The microstructure evolution and phase transformation in the  $ZrB_2$ - $x$ MoSi<sub>2</sub> ( $x = 24, 35, 45$  wt. %)-10Al coating during annealing treatment from 25 to 1400 °C were investigated.

## 2. EXPERIMENTAL DETAILS

The coatings were deposited using a Robotic complex for detonation spraying of coatings equipped with a multi-chamber detonation accelerator (MCDS) [10-12] with a barrel length of 500 mm and a throat diameter of 16 mm [13]. The flow rate of the fuel mixture components (m<sup>3</sup>/h) was as follows: oxygen (4.0\*/3.6\*\*), propane + butane (0.75\*/0.68\*\*) and air (0.12\*/0.12\*\*) (\*cylindrical combustion chamber, \*\*combustion chamber in the form of a disk).

Free-standing coatings with a thickness of 250-300 μm were deposited on the substrate and peeled off for characterization.

The microstructure evolution and phase transformation in the coating during annealing treatment were investigated using a combined TGA/DSC/DTA analyzer SDT Q600 (TA Instruments), scanning electron microscopy with energy-dispersive spectroscopy Nova NanoSEM 450 (SEM) and a Rigaku Ultima IV powder X-ray diffractometer with CuKα radiation, equipped with an SHT-1500 high-temperature attachment. A Rigaku SHT-1500 chamber with a Pt sample holder was used to collect the data for  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al coating in air within 25-1400 °C with a heating rate of 10 °C/min.



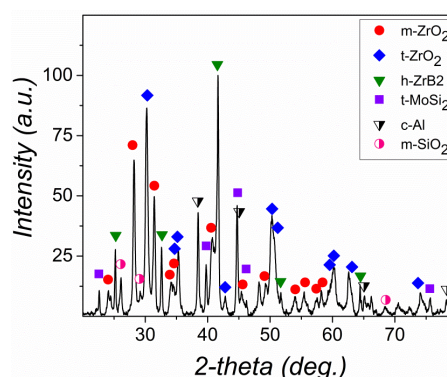
**Fig. 1** – TGA-DSC curves at room temperature to 1400 °C of  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al coating:  $x = 24$  (a), 35 (b), 45 (c)

## 3. RESULTS AND DISCUSSION

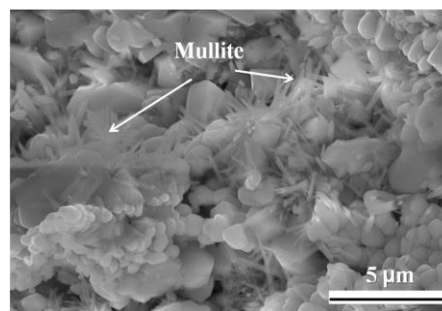
The program for air treatment of coatings was formed taking into account the data obtained using the combined TA Instruments SDT-Q600 Simultaneous TGA/DSC (Fig. 1).

In the temperature range from 25 to 960 °C,  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al coatings have a similar qualitative phase composition and consist of tetragonal ( $t$ -ZrO<sub>2</sub>) and monoclinic ( $m$ -ZrO<sub>2</sub>) zirconia, monoclinic silicon oxide ( $m$ -SiO<sub>2</sub>), hexagonal zirconium diboride ( $h$ -ZrB<sub>2</sub>), tetragonal molybdenum disilicide ( $t$ -MoSi<sub>2</sub>), and cubic aluminum ( $c$ -Al) (Fig. 2).

Complete oxidation of the starting materials takes place at annealing temperatures above 960 °C. At a temperature of ~960 °C, mullite with a rhombic crystal lattice ( $3Al_2O_3 \cdot 2SiO_2$ ) begins to form in the coating (the finest intertwined needle-shaped crystals penetrating the glass phase) (Fig. 3).



**Fig. 2** – X-ray diffraction pattern of the  $ZrB_2$ -24MoSi<sub>2</sub>-10Al coating from 25 to 960 °C

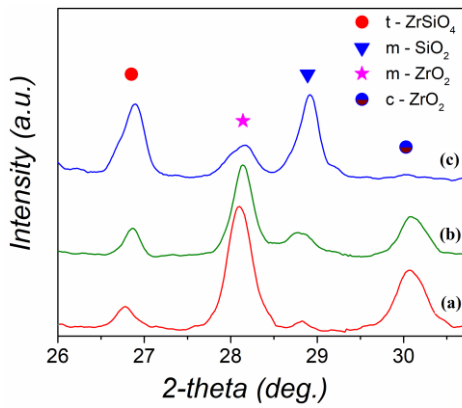


**Fig. 3** – SEM-BSE micrograph of the fractured surface of the  $ZrB_2$ -24MoSi<sub>2</sub>-10Al coating after treatment at 960 °C

An increase in the MoSi<sub>2</sub> content leads to a change in the phase composition of  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al coatings at an annealing temperature of 960 °C (Fig. 4): the content of zirconium orthosilicate ZrSiO<sub>4</sub> increases; the amount of  $m$ -SiO<sub>2</sub> increases sharply; the content of  $t$ -ZrO<sub>2</sub> during the formation of free  $m$ -SiO<sub>2</sub> decreases to a minimum value (the intensity of the reflections of the corresponding  $t$ -ZrO<sub>2</sub> is close to the background value of the intensity).

It was found that at a temperature of 1235 °C a two-phase material is formed in the coating, consisting of cubic zirconium dioxide and mullite (Fig. 5).

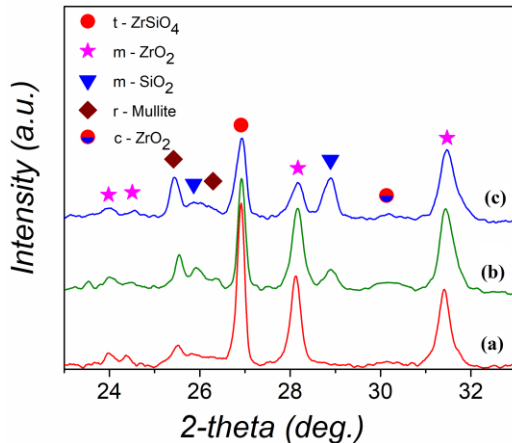
Also, an increase in the content of MoSi<sub>2</sub> in  $ZrB_2$ - $x$ MoSi<sub>2</sub>-10Al coatings at an annealing temperature of 1235 °C (Fig. 5) leads to a decrease in the content of



**Fig. 4** – X-ray diffraction patterns of the  $ZrB_2-xMoSi_2-10Al$  coating:  $x = 24$  (a), 35 (b), 45 (c) at 960 °C

cubic zirconium dioxide with a simultaneous increase in the content of the monoclinic phase of zirconium dioxide and zirconium orthosilicate. The main phase is mullite.

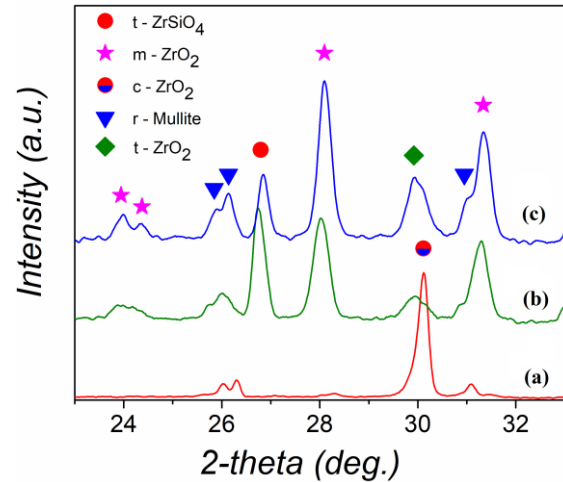
The broad exothermic peak in the temperature range 1235-1400 °C on the DTA curves (Fig. 1) corresponds to the final formation of the coating structure.



**Fig. 5** – X-ray diffraction patterns of the  $ZrB_2-xMoSi_2-10Al$  coating:  $x = 24$  (a), 35 (b), 45 (c) at 1235 °C

The qualitative phase composition of coatings with different content of MoSi<sub>2</sub> at 1400 °C is similar, but the quantitative ratio of the phases changes. The content of the cubic phase of zirconium dioxide decreases and the content of mullite increases. From the analysis of the intensity distribution of reflexes corresponding to c-ZrO<sub>2</sub>, it can be seen that when the MoSi<sub>2</sub> content in

coatings reaches 45 wt. %, there is a sharp decrease in the cubic phase of the zirconium dioxide content (Fig. 5). The m-ZrO<sub>2</sub> and t-ZrSiO<sub>4</sub> phases are also retained in the coating, which can be explained by the insufficient time of the annealing process under the conditions of this analysis.

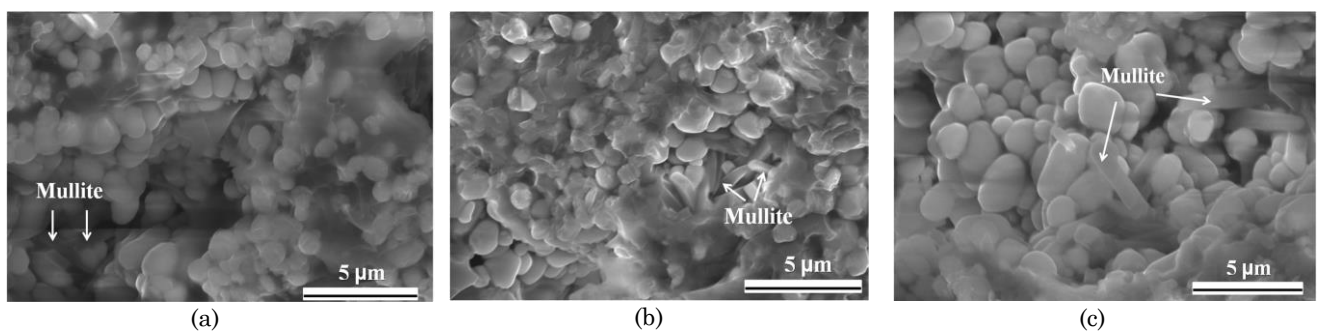


**Fig. 6** – X-ray diffraction patterns of the  $ZrB_2-xMoSi_2-10Al$  coating:  $x = 24$  (a), 35 (b), 45 (c) at 1400 °C

The microstructure of the  $ZrB_2-24MoSi_2-10Al$  coating after oxidation at 1400 °C is similar to that of  $ZrB_2-35MoSi_2-10Al$  and  $ZrB_2-45MoSi_2-10Al$  coatings.

However, pores and a large amount of mullite are observed in the structure of  $ZrB_2-35MoSi_2-10Al$  and  $ZrB_2-45MoSi_2-10Al$  coatings (Fig. 7b, c). This is explained by the one-sided diffusion of SiO<sub>2</sub> into the Al<sub>2</sub>O<sub>3</sub> grain; a pore forms in place of the SiO<sub>2</sub> grain.

A dense structure without cracks and pores forms in the  $ZrB_2-24MoSi_2-10Al$  coating (Fig. 7a). The densified microstructure is characterized by the presence of rounded and irregularly shaped grains (Fig. 7a). The close bond between the grains creates a barrier that effectively prevents the penetration of oxygen into the C/C surface. It was found that mullite is present in small amounts in the structure of the  $ZrB_2-24MoSi_2-10Al$  coating. Needle mullite in small amounts reinforces the glass phase, leading to increased refractoriness [8]. On the basis of Al<sub>2</sub>O<sub>3</sub> grains, a strong crystalline framework of mullite is formed, which, in the absence of a sufficient amount of the liquid phase, prevents sintering and pore closure.



**Fig. 7** – SEM-BSE micrographs of the fractured surface of the  $ZrB_2-xMoSi_2-10Al$  coating after treatment at 1400 °C:  $x = 24$  (a), 35 (b), 45 (c)

#### 4. CONCLUSIONS

In this paper,  $ZrB_2-xMoSi_2$  ( $x = 24, 35, 45$  wt. %)-10Al coatings prepared by a Robotic complex for detonation spraying of coating were oxidized from 25 to 1400 °C in air. The microstructure evolution and phase transformation in the coatings during annealing treatment from 25 to 1400 °C were investigated. The results showed that an increase in the  $MoSi_2$  content leads to a change in the structure and phase composition of the coatings during oxidation. It was found that up to a temperature of 960 °C, all coatings have the same phase composition. Cubic zirconium dioxide was formed for all coatings at 1235 °C, and its content decreased with increasing temperature and original  $MoSi_2$  content. It was found that with an increase in the  $MoSi_2$  content after oxidation at 1400 °C, the content of mul-

lite and pores in the coating increases. All these changes in the microstructure of the  $ZrB_2-xMoSi_2$  ( $x = 24, 35, 45$  wt. %)-10Al coatings can lead to decreased oxidation-resistant property at high temperatures.

#### ACKNOWLEDGEMENTS

This research was funded by the Russian Science Foundation (grant no. 19-19-00274). The work was carried out using the equipment of the Joint Research Center of Belgorod State National Research University «Technology and Materials» with the financial support of the Ministry of Science and Higher Education of the Russian Federation in the framework of agreement no. 075-15-2021-690 (unique identifier for the project RF-2296.61321X0030).

#### REFERENCES

1. J. Sheehan, K. Buesking, B. Sullivan, *Annu. Rev. Mater. Sci.* **24**, 19 (1994).
2. M. Lalit, *Sadhana* **28**, 349 (2003).
3. N. Jacobson, D. Curry, *Carbon* **44**, 1142 (2006).
4. H. Fritze, J. Jovic, T. Witke, C. Ruscher, S. Weber, S. Scherrer, R. Weiß, B. Schultrich, G. Borchardt, *J. Eur. Ceram. Soc.* **18**, 2351 (1998).
5. F. Smeacetto, M. Salvo, M. Ferraris, *Carbon* **40**, 583 (2002).
6. G. Devi, K. Rao, *Def. Sci. J.* **43** No 4, 369 (1993).
7. M.L. Grilli, D. Valerini, A.E. Slobozeanu, B.O. Postolnyi, S. Balos, A. Rizzo, R.R. Piticescu, *Materials* **14**, 1656 (2021).
8. W.Z. Zhang, Z. Yi, L. Gbologh, X. Xiang, B.Y. Huang, *Trans. Nonferrous Met. Soc. China* **21**, 1538 (2011).
9. X.R. Ren, H.A. Chu, K.Y. Wu, A. Zhang, M. Huang, C. Ma, H. Liu, P. Feng, *J. Eur. Ceram. Soc.* **41**, 1059 (2020).
10. M. Kovaleva, I. Goncharov, V. Novikov, M. Yapryntsev, O. Vagina, I. Pavlenko, V. Sirota, Y. Tyurin, O. Kolisnichenko, *Coatings* **9** No 12, 779 (2019).
11. M. Kovaleva, Y. Tyurin, N. Vasilik, O. Kolisnichenko, M. Prozorova, M. Arsenko, E. Danshina, *Surf. Coat. Technol.* **232**, 719 (2013).
12. N. Vasilik, Y. Tyurin, O. Kolisnichenko, *RU Patent* 2506341 (2012).
13. M. Kovaleva, M. Yapryntsev, V. Novikov, I. Pavlenko, O. Vagina, I. Goncharov, V. Beresnev, V. Sirota, Yu. Tyurin, *Proceedings of the 2019 IEEE 9th International Conference on Nanomaterials: Applications and Properties*, 01TFC51 (2019).

#### Вплив вмісту дисиліциду молібдену на мікроструктуру та фазові перетворення покриттів $ZrB_2-MoSi_2-10Al$ після відпалу на повітрі

I.Ю. Гончаров<sup>1,2</sup>, В.М. Береснев<sup>3</sup>, М.Г. Ковальова<sup>1</sup>, М.Н. Япринцев<sup>1</sup>, О.Н. Вагіна<sup>1</sup>, В.Ю. Новіков<sup>1</sup>, В.В. Сирота<sup>2</sup>, Ю.Н. Тюрін<sup>4</sup>

<sup>1</sup> Белгородський національний дослідницький університет, вул. Перемоги, 85, 308015 Белгород, Росія

<sup>2</sup> Белгородський державний технологічний університет імені В.Г. Шухова, вул. Костюкова, 46, 308012 Белгород, Росія

<sup>3</sup> Харківський національний університет імені В.Н. Каразіна, пл. Свободи, 4, 61000 Харків, Україна

<sup>4</sup> Інститут електрозварювання імені Є.О. Патона НАН України, вул. Боженка, 11, 03650 Київ, Україна

У роботі композитні покриття на основі  $ZrB_2$  з різним вмістом  $MoSi_2$  були виготовлені робототехнічним комплексом для детонаційного розпилення покриттів, обладнаним багатокамерним прискорювачем детонації (MCDS). Еволюцію мікроструктури та фазового складу покриттів  $ZrB_2-xMoSi_2$  ( $x = 24, 35, 45$  мас. %)-10Al аналізували за допомогою диференціального скануючого калориметра, рентгенівської дифрактометрії (in situ HT-XRD) та скануючої електронної мікроскопії при температурі від 25 до 1400 °C (нормальна атмосфера та тиск). Під час аналізу було помічено, що  $m-SiO_2$  та  $ZrSiO_4$  з'являються при 960 °C. Також при досягненні температури 1235 °C у покриттях  $ZrB_2-xMoSi_2-10Al$  утворюється фіаніт та муліт. В покриттях  $ZrB_2-xMoSi_2-10Al$  при температурі 1400 °C збільшення вмісту  $MoSi_2$  у вихідному покритті призводить до майже повного зникнення кубічної фази діоксиду цирконію, а вміст муліту збільшується. Встановлено, що мікроструктура покриття змінюється зі збільшенням вмісту  $MoSi_2$  після окислення при 1400 °C від щільної до "більш дефектної". Покриття  $ZrB_2-24MoSi_2-10Al$  має рівномірну щільну мікроструктуру в порівнянні з покриттями, якф містять 35 та 45 мас. %  $MoSi_2$ . Це сприяє його хорошій стійкості до окислення при високій температурі.

**Ключові слова:** Вуглець/вуглецеві композити,  $ZrB_2-MoSi_2$ , Багатокамерний прискорювач детонації, Мікроструктура, In situ HT-XRD.