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# Microstructure evolution and phase transformation of ZrB<sub>2</sub>-45MoSi<sub>2</sub>-10Al coating at high temperature

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**Abstract.** The ZrB<sub>2</sub>-45MoSi<sub>2</sub>-10Al coating was prepared by a Robotic complex for detonation spraying of coatings equipped with a multi-chamber detonation accelerator on surface of carbon/carbon composites without adhesion sublayer. The coating has a lamella-type structure typical for gas-thermal coatings, well connected with C/C composite substrate without sublayer, and composed of m-ZrO<sub>2</sub>, t-ZrO<sub>2</sub>, t-MoSi<sub>2</sub>, some h-ZrB<sub>2</sub>, and c-Al phases. Heat treatment of the samples at 1500 °C for 1, 3 and 6 h was carried out in air. The effect of heat treatment on the microstructure and phase composition of the ZrB<sub>2</sub>-45MoSi<sub>2</sub>-10Al coating was investigated by X-ray diffraction and scanning electron microscopy. The c-ZrO<sub>2</sub> and h-( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) were formed after oxidation at 1500 °C for 6 h. The uniform distribution of ZrO<sub>2</sub> ceramic particles and the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> enhanced the thermal stability of the coating. The coating after heat treatment (1, 3 and 6 h) exhibited structure without cracks and low porosity. The dense microstructure of the coating contributed to its good oxidation-resistant property at high temperature.

## 1. Introduction

The widespread use of carbon/carbon (C/C) composites is still significantly constrained by their extremely low or insufficient heat resistance in oxygen-containing media [1]. In vacuum and inert media, carbon materials are efficient up to 3000°C, however, in an air atmosphere they oxidize (burn out) already at temperatures of 350-500 °C. Reliable protection against high-temperature oxidation can significantly expand the temperature-time intervals of C/C composites application, and in most cases it is the only possible way to realize their heat-resistant characteristics and functional properties. The destruction of materials can be prevented by creating a protective heat-resistant gas-tight coating on the surface of the C/C composites, preventing the access of oxygen to carbon [2-4], such as ZrSiO<sub>4</sub>, C/SiC, SiO<sub>2</sub>/SiC, ZrB<sub>2</sub>-SiC, ZrB<sub>2</sub>-MoSi<sub>2</sub>, yttrium silicate, coating, etc [5, 6] by various methods, including pack cementation, slurry method, chemical vapor deposition, atmospheric plasma spraying and thermal spray, etc. [7, 8].

One of the widespread approaches to the selection of the composition of the main layer of the high-temperature coating is the selection of the composition of refractory compounds that are in the viscoplastic state during the operation of the product. This state is achieved by using refractory boron or aluminoborosilicate glasses as a matrix, into which reinforcing particles of silicides, carbides, borides (less often oxides and nitrides) of Group IV – VI metals are additionally introduced to increase the heat resistance. The use of precursors of the ZrB<sub>2</sub> – MoSi<sub>2</sub> system is promising for this class of coatings [9, 10].



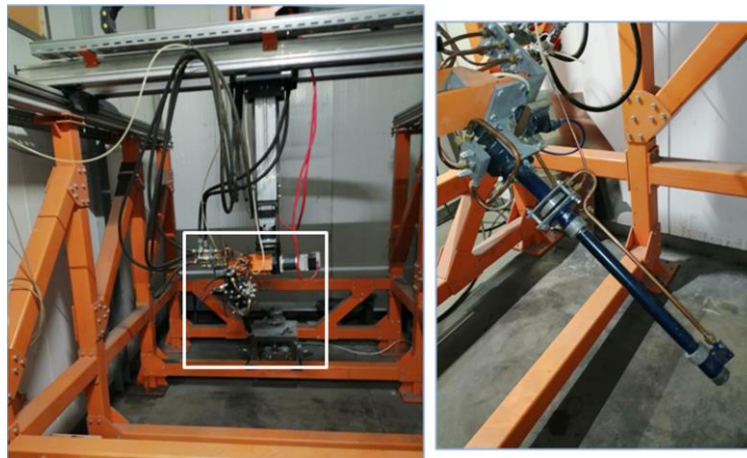
In this study, a  $ZrB_2-45MoSi_2-10Al$  coating was chosen as the oxidation protective coating for C/C composites. The microstructure evolution and phase transformation in the  $ZrB_2-45MoSi_2-10Al$  coating during annealing treatment at 1500 °C were investigated.

## 2. Materials and methods

$ZrB_2-45MoSi_2-10Al$  coating was obtained on the surface of C/C composites using by a Robotic complex for detonation spraying of coatings (IntelMashin LLC, Russia) equipped with a multi-chamber detonation accelerator (MCDS) [11-14] (Figure 1).  $ZrB_2$ ,  $MoSi_2$ ,  $Y_2O_3$ , Al micro-powders (Russia) were used for applying  $ZrB_2-45MoSi_2-10Al$  coating. The powders were sieved on the fractions (<20 microns). Then mechanical mixing and homogenization of the powders was carried out in planetary mill with balls made of zirconium oxide in alcohol for 24 hours. Then the powder mix was dried in a drying cabinet (100°C, 6 h). All operations were performed in the air.

The technology of detonation spraying of industrial coatings is characterized by economy and environmental friendliness, since the plasma components used are not substances hostile to the environment. The physical essence of the detonation coating technology using a multi-chamber detonation accelerator (MCDS) is the collision of fine particles heated and accelerated in a supersonic flow of combustion products with a solid substrate. The MCDS provides a high speed of > 1600 m/s and a compact powder jet of up to 100 g/s, with a ceramic spraying capacity of up to 1 kg/h. The process of coating formation is carried out in layers, using the effects of collective interaction between the powder jet and the surface, which determines its high quality. The high speed of dispersed materials ensures their plastic deformation, nanostructuring and the creation of thin lamellae (thickness 4-8 microns) [11-14].

The parameters of the coating spray are listed in Table 1.



**Figure 1.** Robotic complex for detonation spraying of coatings (IntelMashin LLC, Russia) equipped with a multi-chamber detonation accelerator (MCDS).

**Table 1.** Spraying parameters of coating.

Spray distance, mm	Barrel length, mm	Barrel diameter, mm	Powder feed rate, g/h	Flow rate of fuel mixture components, m <sup>3</sup> /h			Oxygen/fuel ratio
				Oxygen	C <sub>3</sub> H <sub>8</sub> +C <sub>4</sub> H <sub>10</sub>	Air	
80	500	16	600	*4.00 / **3.60	*0.75 / **0.68	*0.12 / **0.12	5.3
*Cylindrical form combustion chamber. **Combustion chamber in the form of a disk							

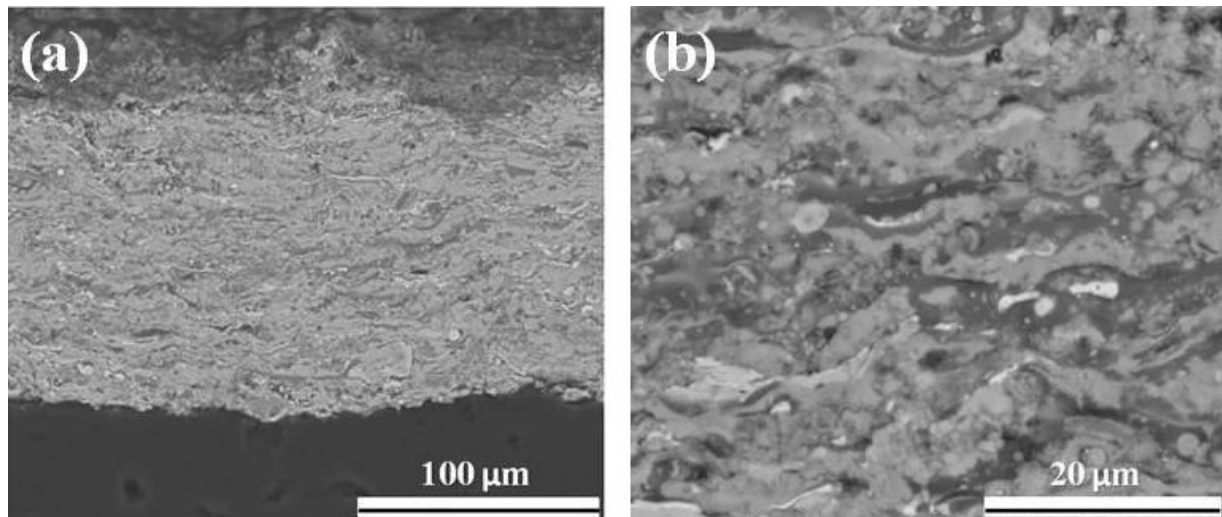
5 wt.%  $Y_2O_3$  acts as a stabilizer of high-temperature tetragonal and cubic modification of zirconia [13-15].

To increase the wettability of the surface of C/C composites Al powder was added to the initial powder mixture [16, 17].

The cross-section surfaces of the samples with coating were investigated using a scanning electron microscope (SEM) (Nova NanoSEM 450). The phase composition was determined by diffractometer Rigaku Ultima. A high-temperature furnace (LHT 04/17, Nabertherm GmbH) was used for the heat treatment of coating in air from 23 to 1500 °C for different time (1, 3 and 6 h).

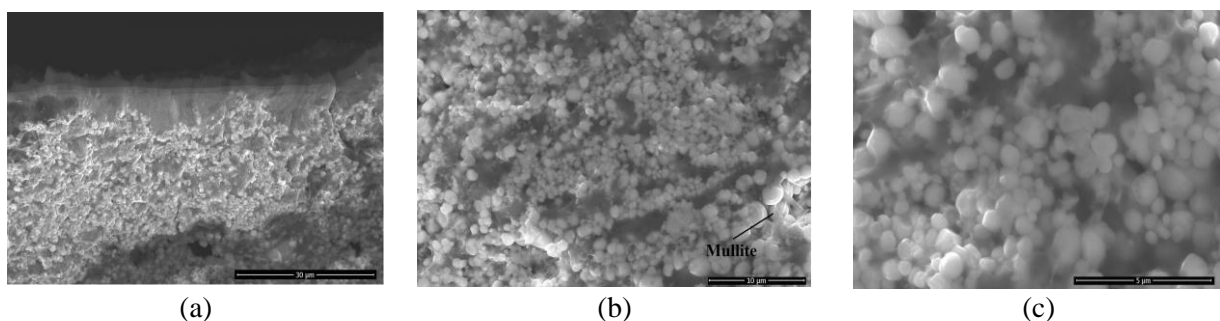
### 3. Results and discussion

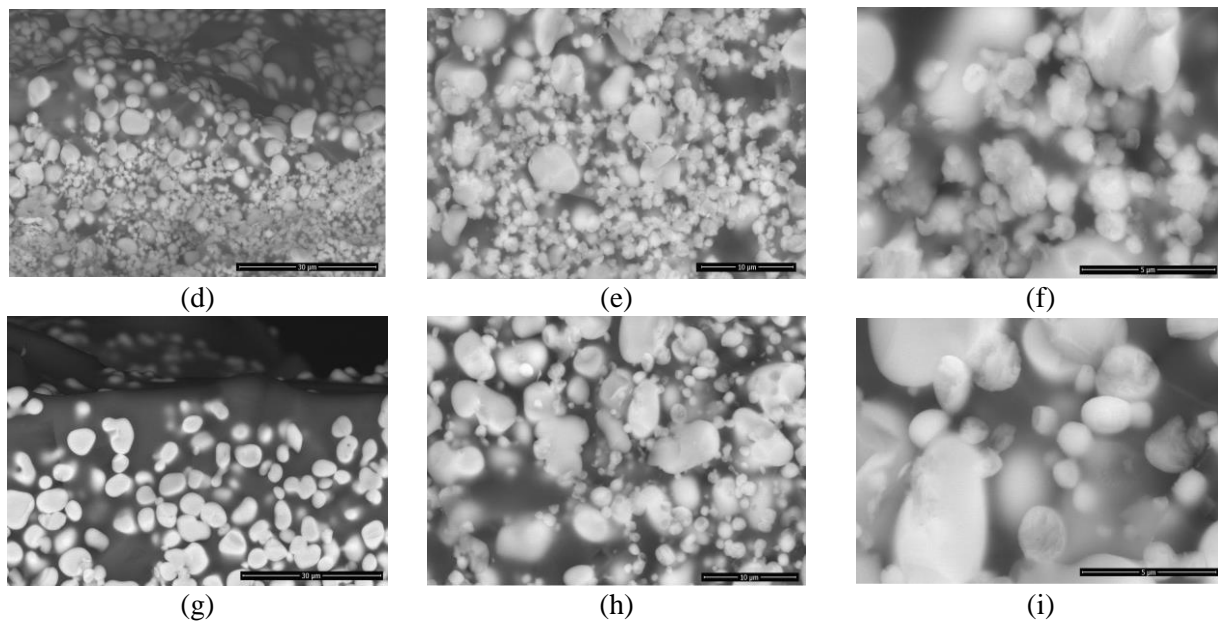
Thickness of the coating was 200  $\mu\text{m}$  (Figure 2, a). The coating shows a very dense microstructure consisting of well-flattened particles (Figure 2). Micro-cracks not found out. High rates of deformation of dispersed particles cause their fragmentation into smaller fragments and the formation of particles with characteristic sizes from 50 to 1000 nm. Thus, the fine fractions of the powder were heated, deformed to the state of thin lamellas, filled the space between the coarse particles, and formed a dense coating.



**Figure 2.** The cross-sectional SEM-BSE micrograph of the  $\text{ZrB}_2\text{-45MoSi}_2\text{-10Al}$  coating before treatment: low (a) and high magnification (b).

The changes in the microstructure and phase composition of the coating after treatment in air at 1500 °C were observed (Fig. 3, 4).





**Figure 3.** SEM-BSE micrograph of the fracture surface of  $ZrB_2-45MoSi_2-10Al$  coating after oxidation at different hours: 1 (a, b, c), 3 (d, e, f), 6 (g, h, i).

The m- $ZrO_2$ , t- $ZrO_2$ , t- $MoSi_2$ , and some h- $ZrB_2$  were identified in composite coating before the oxidation test (Fig. 4, a).

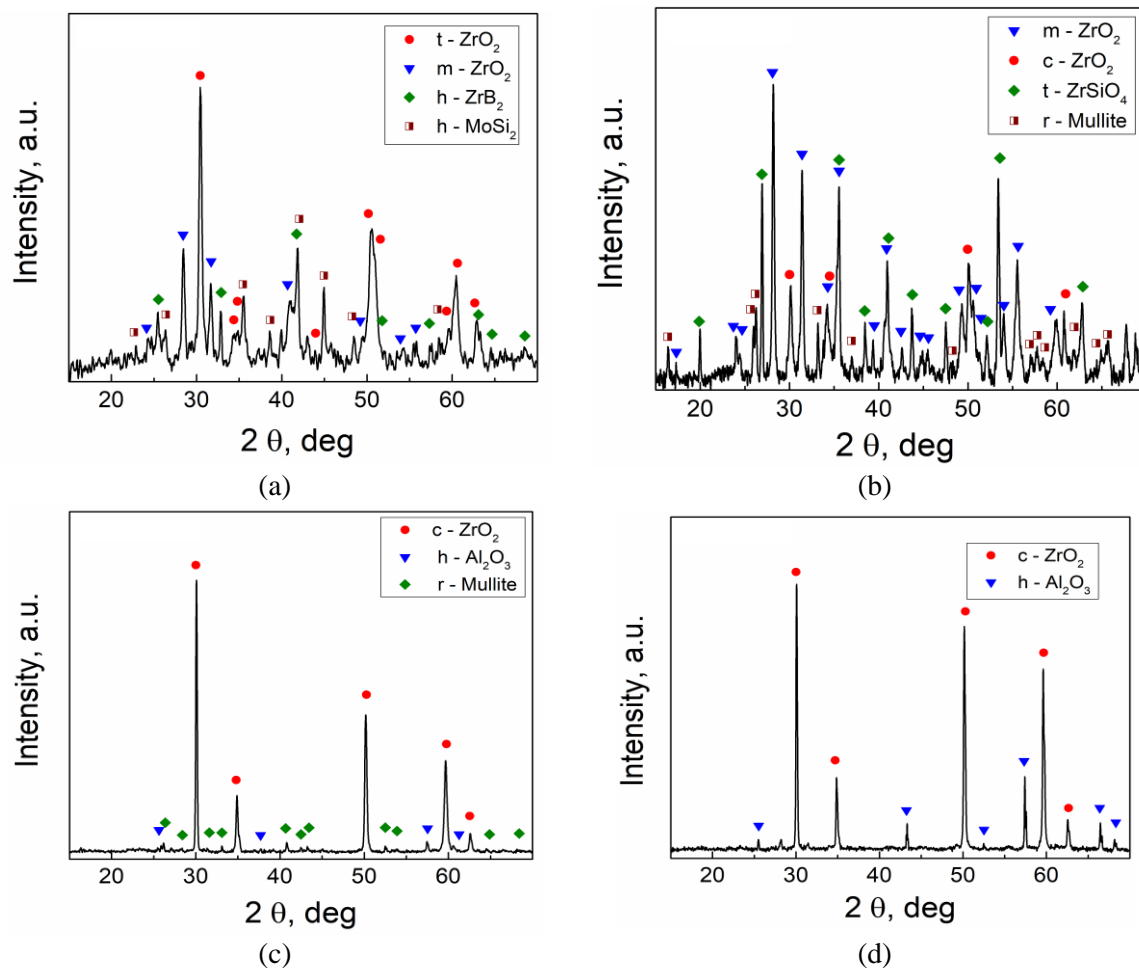
The XRD patterns of  $ZrB_2-45MoSi_2-10Al$  coating after oxidations at different hours (1, 3 and 6) are presented in Fig. 4, b-d. A silica glass with mullite, and zircon in small amounts was formed in of  $ZrB_2-45MoSi_2-10Al$  coating after oxidation at different hours (1, 3 and 6) (Fig. 3, a, d, g). White particles with a higher amount of zirconium oxide are embedded in the glassy matrix (Fig. 3, a, d, g), according to the XRD result.

After oxidations at 1 h in the coating mullite with a rhombic crystal lattice of mullite of the composition  $Al_{2.35}Si_{0.64}O_{4.82}$  in small amounts begins to form (Fig. 3, b). The main phases at this temperature are m- $ZrO_2$  and c- $ZrO_2$ . Also, the zirconium orthosilicate phase (zircon -  $ZrSiO_4$ ) is formed in the coating.

After oxidations at 3 h the coating has the following composition: c- $ZrO_2$ , h- $Al_2O_3$  and mullite (Fig. 4, c). The content of mullite, according to X-ray phase analysis, is close to the detection limit (the intensity of reflections corresponding to mullite is close to the background intensity).

The XRD pattern of  $ZrB_2-45MoSi_2-10Al$  coating after the oxidation at  $1500^\circ C$  for 6 h is presented in Fig. 3, d. It can be seen that only c- $ZrO_2$  and h- $Al_2O_3$  were detected.

The microstructure of the  $ZrB_2-45MoSi_2-10Al$  coating after oxidation at 1 h is similar to that of the samples oxidized at  $1500^\circ C$  for 3 and 6 h. A dense without cracks and pores structure of coating is formed, however, there is mullite (the finest intertwined needle-shaped crystals penetrating the glass phase) in the structure of coating (Fig. 3, b). Needle mullite reinforces the glass phase, leading to increased refractoriness [17].



**Figure 4.** XRD patterns of the  $\text{ZrB}_2\text{-45MoSi}_2\text{-10Al}$  before (a) and after oxidation at different hours: 1 (b), 3 (c), and 6 (d).

#### 4. Summary

In this paper, a  $\text{ZrB}_2\text{-45MoSi}_2\text{-10Al}$  coating prepared by a Robotic complex for detonation spraying of coatings was oxidation at  $1500^\circ\text{C}$  for 1, 3 and 6 h. Coating was formed on the substrate surface without intermediate layers in the "carbon-containing materials – coating" system that perform barrier-compensation functions. Complex for detonation spraying has provided the conditions for formation of dense and uniform coating layers with high adhesion. The penetrative cracks and pores in the coating were not found before and after oxidation. The oxidized for 1 h  $\text{ZrB}_2\text{-45MoSi}_2\text{-10Al}$  coating mainly consist of c- $\text{ZrO}_2$ , m- $\text{ZrO}_2$ , and in small amounts mullite and zircon. It was found that h-( $\alpha\text{-Al}_2\text{O}_3$ ) was detected in  $\text{ZrB}_2\text{-45MoSi}_2\text{-10Al}$  coating after oxidation for 3 and 6 h. The  $\text{Y}_2\text{O}_3$  stabilized cubic phase (c- $\text{ZrO}_2$ ) is found in the coating after oxidation for 3 and 6 h also.

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