STRUCTURAL-PHASE STATE OF NANOCOMPOSITE ZrB_2-$MoSi_2$ COATINGS FOR CARBON/CARBON COMPOSITES DEPOSITED BY A NEW MULTI-CHAMBER DETONATION ACCELERATOR

[1]Vseslav NOVIKOV, [1]Marina KOVALEVA, [1,3]Igor GONCHAROV, [1]Maxim YAPRYNTSEV, [2]Yuri TYURIN, [3]Viacheslav SIROTA, [1]Olga VAGINA

[1]Belgorod State National Research University, Belgorod, Russian Federation,
novikov_v@bsu.edu.ru

[2]E.O. Paton Electric Welding Institute NASU, Kyiv, Ukraine

[3]Belgorod State Technological University named after V.G. Shoukhov, Belgorod, Russian Federation

https://doi.org/10.37904/nanocon.2019.8657

Abstract

The ZrB_2-$MoSi_2$ coating modified by Y_2O_3 and Al was prepared on a carbon/carbon composite substrate by a new multi-chamber detonation accelerator (MCDS). The thickness of deposited coatings ranged about 90-130 μm. The powder containing 41 mol.% of ZrB_2, 5 mol.% of $MoSi_2$, 1 mol.% of Y_2O_3 and 53 mol.% of Al (1-25 μm) has been used as the feedstock material to deposit a dense layer. The structural-phase state of the coatings was characterized by X-ray diffraction and scanning electron microscopy with energy-dispersive spectroscopy. The ZrB_2-$MoSi_2$ coating was well-adhered with carbon/carbon composites. The coating displayed compact microstructure with porosity lower than 1%. It was established that phase composition of ZrB_2-$MoSi_2$ powder under the influence of high temperatures and the atmosphere of detonation products changes with the formation of a complex heterogeneous structural-phase state in the coatings. As-sprayed coating consisted of t-$AlZrO_2$, fcc-Al, m-ZrO_2 and m-SiO_2. ZrB_2-$MoSi_2$ coatings are characterized by the presence of nanodispersed particles. The most of the powder particles were melted and formed lamellar-like structure typical for thermally sprayed coatings. But small amount of partially-melted areas has non-uniform structure, ranging from lamella to sphere with a size range of 0.05-1.5 μm.

Keywords: Multi-chamber detonation accelerator, ZrB_2-$MoSi_2$ coatings, carbon/carbon composites, microstructure

1. INTRODUCTION

Carbon-carbon composites are the most potential materials for high temperature applications due to its excellent mechanical and thermosphysical properties (low density, low coefficient of thermal expansion and improved mechanical properties at high temperatures above 2000 °C) [1-3]. However, in spite of its attractive mechanical and thermal properties at high temperatures, their poor resistance to an oxidizing atmosphere beyond 500ºC limits their performances as the high-temperature structural materials. One of most widely used methods for improving carbon-carbon composites oxidation resistance is to apply such coatings as $MoSi_2$, $ZrSiO_4$, SiO_2-SiC, ZrB_2-SiC [4-7]. A new multi-chamber gas-dynamic accelerator (MCDS) was proposed to spray ZrB_2-$MoSi_2$ coatings in this study [8-10]. ZrB_2-$MoSi_2$ nanocomposite coating containing 1 mol.% of Y_2O_3 and 53 mol.% of Al. Including silicide into ZrB_2 can significantly promote the oxidation protection ability of ZrB_2 coating because of a stable compound silicate glass layer formation [11]. Y_2O_3 was successfully used as a stabilizer of high temperature tetragonal and cubic modification of zirconia [12]. Aluminum was added as a bond for the oxidizing agent during of the spraying and creating "plastic" lamellae and nano-dispersed inclusions, which will relieve internal stresses. The microstructure, elemental and phase composition of coating were investigated in the present work.

2. EXPERIMENTAL

2.1. Materials

The powder containing 41 mol.% of ZrB_2, 5 mol.% of $MoSi_2$, 1 mol.% of Y_2O_3 and 53 mol.% of Al (1-25 µm) (**Figure 1**) has been used as the feedstock material to deposit a dense layer on the carbon/carbon composites substrate.

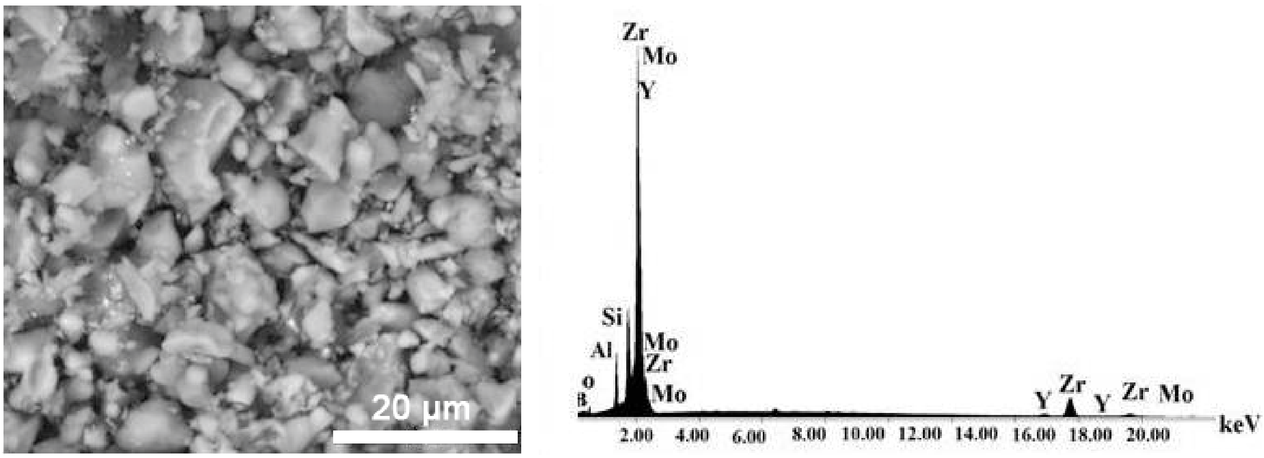


Figure 1 SEM micrograph (back-scattered electron mode) and elemental composition of composite powder

2.2. Apparatus and Procedure

Vertically mounted, multi-chamber, gas-dynamic accelerator (MCDS) with a barrel length of 500 mm was employed to deposit the ZrB_2-$MoSi_2$ nanocomposite coatings in this study. The realized detonation regime of the combustion of the gas mixture in two chambers has a special profile in MCDS. The automated equipment (**Figure 2**) consists of: 1 - device for spraying, 2 - standard powder feeder with a feed rate of up to 3 kg/h, 3 - a standard low-pressure (max. 0.3 MPa) gas panel, 4 - an automated control system for the technological process, 5 - an automated manipulators for moving MCDS and 6 - a specimen holder.

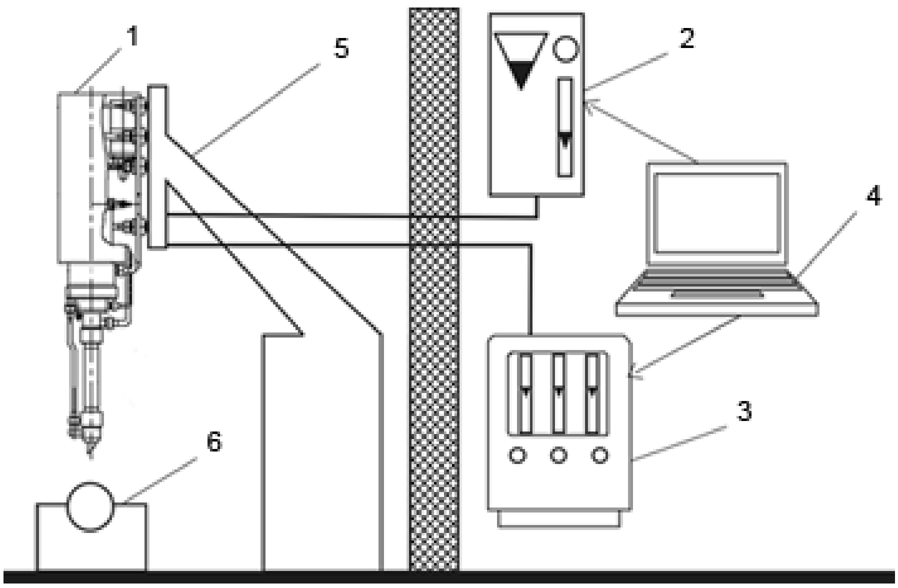


Figure 2 Equipment for deposition of the ZrB_2-$MoSi_2$ coating.

The spray parameters used for deposition of ZrB_2-$MoSi_2$ coating are listed in **Table 1**.

Table 1 Parameters employed for deposition of ZrB_2-$MoSi_2$ coating by a new multi-chamber detonation accelerator

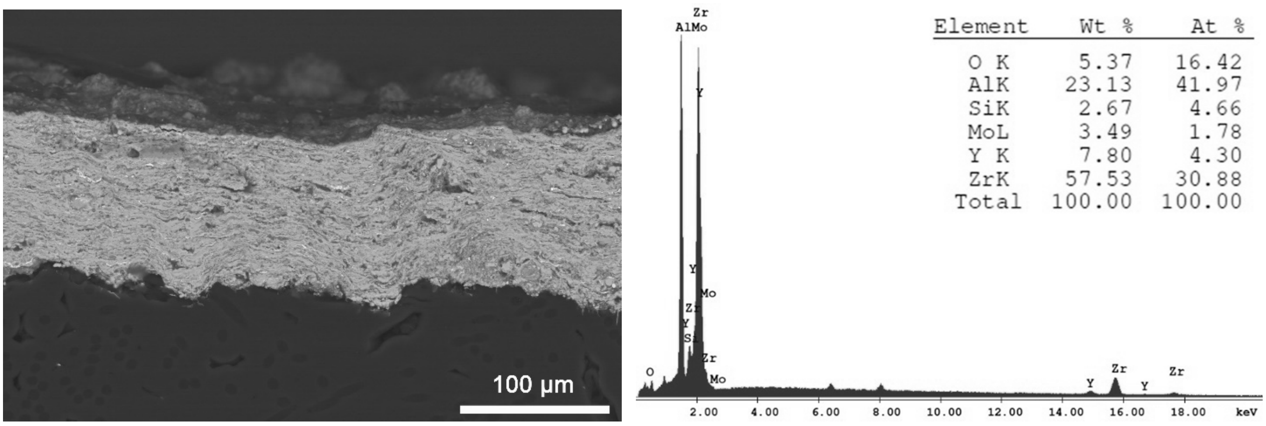
Flow rate of fuel mixture components, [m³/h]			Barrel length [mm]	Barrel diameter [mm]	Spray distance [mm]	Powder feed rate [g/h]	Frequency [Hz]
Oxygen	**Propane (30 %) + butane (70 %)**	**Air**					
4*/3.6**	0.75*/0.68**	0.12*/0.12**	500	16	80	600-700	20

*Cylindrical form combustion chamber. **Combustion chamber in the form of a disk

The cross-section of the coating was polished using abrasive SiC paper and diamond suspension to prepare the samples. The morphology of the polished cross-section of the coating was investigated by scanning electron microscopes (SEM) FEI Nova NanoSEM 450 and FEI Quanta 600 FEG with energy-dispersive spectroscopy (EDS). Porosity of the composite coating was measured by the metallographic method with elements of the qualitative and quantitative analysis of the pores geometry by using an optical inverted Olympus GX51 microscope. X-ray analysis was performed by the Rigaku Ultima IV diffractometer. Crystalline phases were identified by the ICDD PDF-2 (2008) powder diffraction database.

3. RESULTS AND DISCUSSION

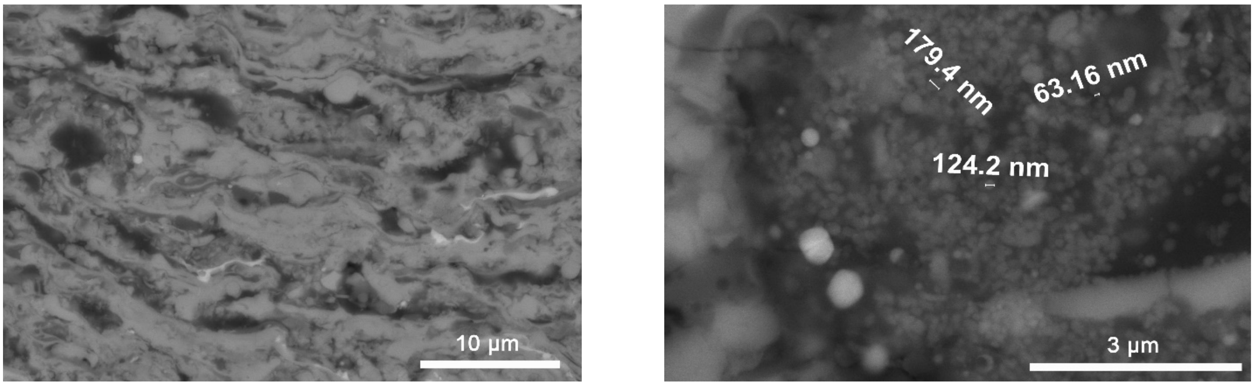
The cross-sectional morphologies and elemental composition of the ZrB_2-$MoSi_2$ nanocomposite coating are illustrated in **Figure 3**. The thickness of deposited coatings ranged from 90 to 130 μm. ZrB_2-$MoSi_2$ coating has uniform and dense microstructure with porosity lower than 1%, and has a good adhesion to the substrate.



(a) (b)

Figure 3 SEM image of cross-section (a) and elemental composition (b) of the ZrB_2-$MoSi_2$ coating (back-scattered electron mode)

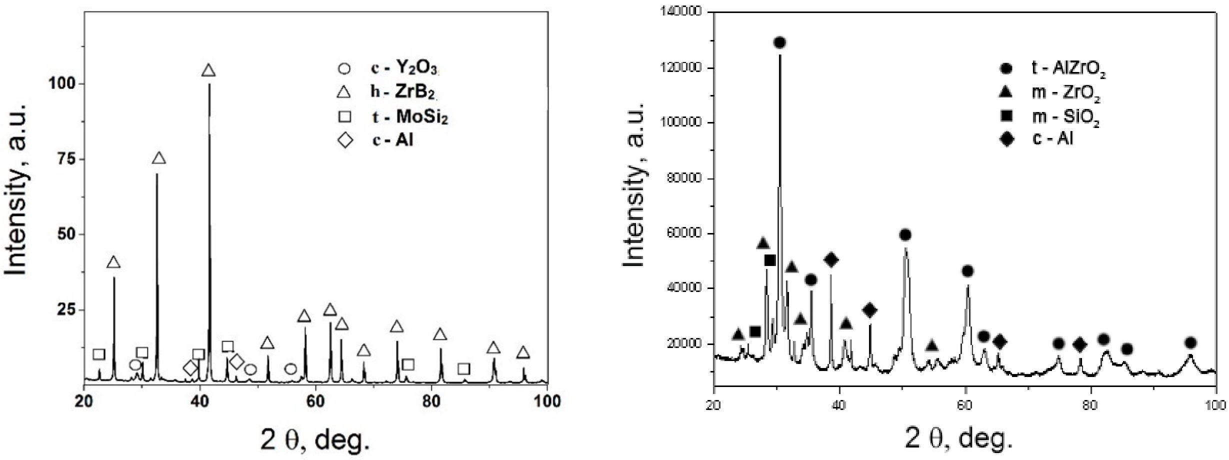
The cross-section images show two areas with different types of structure (**Figure 4**). The most of the powder particles were melted. It was found that the shape of the fully-melted area has typical for thermally sprayed coatings lamellar-like structure (**Figure 4a**). A partially-melted area consisting of unmelted non-uniform particles changes from lamella to sphere with a size ranged from 0.05 to 1.5 μm. (**Figure 4b**).



(a) (b)

Figure 4 SEM images of fully-melted (a) and partially-melted areas (b) of the ZrB_2-$MoSi_2$ coating (back-scattered electron mode)

Figure 5 shows the X-ray diffraction (XRD) of the ZrB_2-$MoSi_2$ powder and coatings.



(a) (b)

Figure 5 XRD patterns of the (a) ZrB_2-$MoSi_2$ powder, and (b) the ZrB_2-$MoSi_2$ coating

It can be seen that the powder was consisted of hexagonal ZrB_2, tetragonal $MoSi_2$, and cubic Y_2O_3 and Al phases (**Figure 5a**). Reported powders could be melted quickly and some part of powders react with oxygen in the air during the spraying process, Tetragonal $AlZrO_2$, cubic Al, monoclinic ZrO_2 and monoclinic SiO_2 were identified in the coating (**Figure 5b**). It was clearly shown that melted or semi-melted ZrB_2 and $MoSi_2$ particles reacted with oxygen in the surrounding environment during spraying process, led to formation of $AlZrO_2$, ZrO_2 and SiO_2. It should be noted that MoO_3(s) vaporizes at the same time as it is produced while MoO_3(g) possesses high vapor pressures at high temperatures.

4. CONCLUSION

Multi-chamber detonation accelerator (MCDS) was applied for deposition of the ZrB_2-$MoSi_2$ nanocomposite coating on carbon/carbon composites in this study. MCDS has provided conditions for formation of dense and uniform coating layers. These coatings have a lamellar-like structure typical for thermally sprayed materials with a small amount of partially-melted areas and non-uniform structure ranged from lamella to sphere with an average size from 0.05 to 1.5 µm. The melted powder partialy react with oxygen in the air during spraying led to formation of $AlZrO_2$, ZrO_2 and SiO_2. The results of this work open up new prospects for the further elaboration of new technologies for manufacturing protective coatings able to enhance the properties of carbon/carbon composites an oxidizing atmosphere at high temperatures.

ACKNOWLEDGEMENTS

The study was financial supported by the Russian Science Foundation, under grant No 19-19-00274. Studies were carried out on the equipment of the Joint Research Center «Technology and Materials» of Belgorod National Research University and the Center for High Technologies of Belgorod State Technological University named after V.G. Shoukhov.

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