STRUCTURAL-PHASE STATE OF NANOCOMPOSITE ZrB\textsubscript{2}-MoSi\textsubscript{2} COATINGS FOR CARBON/CARBON COMPOSITES DEPOSITED BY A NEW MULTI-CHAMBER DETONATION ACCELERATOR

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Abstract

The ZrB\textsubscript{2}-MoSi\textsubscript{2} coating modified by Y\textsubscript{2}O\textsubscript{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 \(\mu m\). The powder containing 41 mol.% of ZrB\textsubscript{2}, 5 mol.% of MoSi\textsubscript{2}, 1 mol.% of Y\textsubscript{2}O\textsubscript{3} and 53 mol.% of Al (1-25 \(\mu m\)) 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\textsubscript{2}-MoSi\textsubscript{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\textsubscript{2}-MoSi\textsubscript{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\textsubscript{2}, fcc-Al, m-ZrO\textsubscript{2} and m-SiO\textsubscript{2}. ZrB\textsubscript{2}-MoSi\textsubscript{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 \(\mu m\).

Keywords: Multi-chamber detonation accelerator, ZrB\textsubscript{2}-MoSi\textsubscript{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 thermophysical 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 500°C 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\textsubscript{2}, ZrSiO\textsubscript{4}, SiO\textsubscript{2}-SiC, ZrB\textsubscript{2}-SiC [4-7]. A new multi-chamber gas-dynamic accelerator (MCDS) was proposed to spray ZrB\textsubscript{2}-MoSi\textsubscript{2} coatings in this study [8-10]. ZrB\textsubscript{2}-MoSi\textsubscript{2} nanocomposite coating containing 1 mol.% of Y\textsubscript{2}O\textsubscript{3} and 53 mol.% of Al. Including silicide into ZrB\textsubscript{2} can significantly promote the oxidation protection ability of ZrB\textsubscript{2} coating because of a stable compound silicate glass layer formation [11]. Y\textsubscript{2}O\textsubscript{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$_2$O$_3$ 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, [m$^3$/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 $\mu$m. ZrB$_2$-MoSi$_2$ coating has uniform and dense microstructure with porosity lower than 1%, and has a good adhesion to the substrate.

![Figure 3](image-url) 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 $\mu$m. (Figure 4b).
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.

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$_2$O$_3$ 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 partially 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 in an oxidizing atmosphere at high temperatures.

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