High-Temperature Laminated Ceramic Material HfC-ZrB2-SiC-ZrO2 for the Development of the Arctic and Siberia

A G Burlachenko1,2, Yu A Mirovoy3, S P Buyakova1,2, E S Dedova3 and S N Kulkov1,2
1 National Research Tomsk State University, Tomsk, 634050, Russia
2 Institute of Strength Physics and Materials Science SB RAS, Tomsk, 634055, Russia
E-mail: burlachenkoag8@gmail.com

Abstract. Ultra-high-temperature ceramics based on zirconium diboride and silicon and hafnium carbides are presented as composites with ceramic matrix and oxidation-resistant surface. Relatively low density, high strength at extreme temperatures and operability at oxidative environment with temperature up to 2000°C make these materials useful for aerospace construction and power engineering. HfC-ZrB2-SiC-ZrO2 systems are presented, structural analysis and the results of temperature tests in high-enthalpy gas are provided. It was demonstrated that high resistance of HfC-ZrB2-SiC-ZrO2 system to high-temperature corrosion is achieved owing to formation of protective oxide layer with variable composition. A key area for the use of the material in the Arctic is the organization of heat-shielding structures in the oil and gas industry.

1. Introduction
One of the most promising aims of modern materials science is development of composite materials demonstrating resistance to high-temperature heat flows and having operation temperatures up to 2500°C [1–3]. Among the promising high-temperature composites, oxygen-free ceramics deserved significant attention. Their advantages are low density, outstanding operating temperature, chemical inertness, corrosion and crack resistance, high strength, etc. [2–4]. ZrB2-based ceramics are the most interesting amongst high-melting materials. SiC-doped ZrB2 ceramics demonstrate high thermal and chemical stability, in particular – oxidative resistance in extreme temperatures [1–6]. In last decades, a large amount of studies is focused at these high-melting compounds. However, composite functional-graded materials which possess various functional properties are of great interest. The present article describes the results of fabrication of heat-protective multilayered ceramic material with hierarchical structure organized by reduction of heat conductivity from top to bottom side. Such principal provides high heat insulation in extreme conditions. ZrB2-SiC compounds were selected as a basic material for the composite. HfC coating was applied as a layer with the highest melting temperature (3890°C). ZrO2 was chosen for bottom layer as a material with abnormally low heat conductivity. Combination of properties of the mentioned compounds in multilayered material makes it promising in the sphere of aerospace construction.

2. Materials and methods
ZrO2 (4 wt. % of Y2O3), ZrB2 and SiC powders were used as primary components. Application of HfC coating was conducted using magnetron sputtering of Hf target in methane atmosphere.
Multilayered ceramic composites were obtained by hot-pressing at a temperature of 1800 °C and pressure of 35 MPa. Duration of isothermal treatment was 30 minutes. Phase composition and crystal structure parameters were studied using X-ray diffraction with CuKα irradiation, 0.05° scanning step and 5 seconds exposure. Structure of the obtained materials was studied using Tescan VEGA 3 scanning electron microscope. Thermal treatment of HfC-ZrB2-SiC-ZrO2 composite materials for studies of oxidation and ablation resistance in high-enthalpy flow of dissociated air was conducted in Plasmotron EDG-200M apparatus.

Strength of the obtained materials was determined by diametral compression method using Instron test machine. Tensile strength under diametral compression (rupture) was calculated according to the following formula:

\[
\sigma = \frac{0.636P}{d \times h}
\]

where: \( P \) – maximum load, \( d \) – sample diameter, \( h \) – thickness.

3. Results and discussion

Obtained HfC-ZrB2-SiC-ZrO2 multilayered composite is shown in Fig. 1. The layers are deposited on the principle of heat conductivity lowering from the top to bottom one with lowest gradient of thermal expansion coefficient. Top side of the sample is presented by ZrB2-SiC layer with HfC coating, the bottom one is made of ZrO2.

![SEM images of ZrB2 – SiC layer with 20 vol.% of SiC coated with HfC and bottom ZrO2 layer of HfC-ZrB2-SiC-ZrO2 system are shown in Fig. 2.](image)

Table 1. Composition and temperature characteristics of material layers.

| Layer Composition | \( \alpha_L, 10^6 \times \text{K}^{-1} \) | \( \lambda, \text{W/m} \times \text{K} \) |
|-------------------|---------------------------------|-----------------|
| Front layer HfC   | 6.1                             | 17              |
| ZrB2-SiC          | 5.2                             | 65              |
| Rear layer, ZrO2  | 10.4                            | 2.3             |

Figure 1. Structure of the multilayered HfC-ZrB2-SiC-ZrO2 composite material (a); macro photo of the sample (b).
Analysis of the structural state of the studied composites revealed that obtained HfC-ZrB2-SiC-ZrO2 materials possess homogenous distribution of SiC particles in ZrB2-SiC layer. HfC coating on the ZrB2-SiC layer was found uniform on all samples. XRD patterns of the top layer of HfC-ZrB2-SiC-ZrO2 heat-protective material with HfC coating are provided in Fig. 3.

Figure 3. XRD patterns of the HfC-coated samples of HfC-ZrB2-SiC-ZrO2 composite front layer with SiC concentration of 15 (a) and 20 (b) % v/v.

Phase analysis of the XRD patterns of all samples showed the presence of ZrB2 reflexes. Moreover, low-intensity peaks corresponding to SiC were observed. HfC is presented by broad reflexes. That fact demonstrates nanostructural nature of the obtained coating.

Samples of HfC-ZrB2-SiC-ZrO2 material before and after 1000 seconds of high-enthalpy dissociated airflow exposure at a temperature of 2500°C are shown in Fig. 4. Formation of glasslike phase with ZrO2 particles was mainly observed. This is due to thermal-oxidative reactions with oxygen from high-temperature plasma. Surface structure is characterized by heterogeneous distribution of oxidation products. Mass increase after high-temperature exposure was found at 0.3 g, crater depth was found at +0.13 mm.
Figure 4. Top side of multilayer HfC-ZrB₂-SiC-ZrO₂ ceramic samples with SiC concentration of 20 % v/v: a) before and b) after high-temperature testing.

Fig. 5 represents XRD patterns of the surface of multilayered heat-protective HfC-ZrB₂-SiC-ZrO₂ ceramics with heat-resistant HfC coating after high-temperature testing. Reflexes corresponding to ZrO₂ monocline modification were observed. HfO reflexes possess low intensity.

Figure 5. XRD patterns of the samples after high-temperature testing with SiC concentration of 15 (a) and 20 (b) % v/v.

SEM images of the layers with SiC concentration of 15 and 20 % v/v after high-temperature testing are provided in Figure 6.
Figure 6. SEM images of the samples with SiC concentration of 15 (a) and 20 (b) % v/v after high-temperature testing.

From Fig.6a it is obvious that sample has char layer with small craters after ablation. It is possible that craters were formed due to melting and liquid layer boiling during the exposure to hot gas. With that, sample Fig. 6b has flawless structure after plasma exposure.

Tensile testing showed that tensile strength of the multilayered HfC-ZrB2-SiC-ZrO2 materials during diametral compression before high-temperature testing was at 49±4 MPa and after - 68±9 MPa. Increase of tensile strength is the evidence of self-healing processes in the materials.

Analysis of the break surface (Fig. 7) reveals no delamination of the heat-protective material after rupture test before and after the exposure to hypersonic high-enthalpy oxygen-containing plasma flow for 1000 seconds.

Figure 7. SEM images of the fracture surfaces: a) before and b) after high-temperature testing.
4. Conclusion
Multilayered heat-protective materials with decreasing (from top to bottom side) heat conductivity were obtained. After high-temperature testing, no destruction of any HfC-ZrB$_2$-SiC-ZrO$_2$ samples was observed.

It was found, that after high-temperature testing the strength of the obtained materials during diametral compression increased for 30%. That fact leads to the conclusion that self-healing processes take place in the developed composite materials.

Conducted studies confirm the potential of the obtained multilayered HfC-ZrB$_2$-SiC-ZrO$_2$ ceramic materials as a part of heat-protection in conditions of extreme temperatures.

Acknowledgments
This work was carried out according to the Program III.23.2.3. of Fundamental Scientific Research of the State Academies of Sciences for 2013-2020 and in the framework of the Program of increasing the competitiveness of TSU.

References
[1] Eakins E, Jayaseelan D D and Lee W E 2011 Toward oxidation-resistant ZrB$_2$-SiC ultra high temperature ceramics Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 42 878–87
[2] Fahrenholtz W G, Hilmas G E, Talmy I G and Zaykoski J A 2007 Refractory diborides of zirconium and hafnium J. Am. Ceram. Soc. 90 1347–64
[3] Medri V, Monteverde F, Balbo A and Bellosi A 2005 Comparison of ZrB$_2$-ZrC-SiC composites fabricated by spark plasma sintering and hot-pressing Adv. Eng. Mater. 7 159–63
[4] Mashhadi M, Khaksari H and Safi S 2015 Pressureless sintering behavior and mechanical properties of ZrB$_2$-SiC composites: Effect of SiC content and particle size J. Mater. Res. Technol. 4 416–22
[5] Justin J F, Jankowiak a. and J.F.Justin A J 2011 Ultra High Temperature Ceramics: Densification, Properties and Thermal Stability Aerosp. Lab J. 8 1–11
[6] Bongiorno A, Först C J, Kalia R K, Li J, Marschall J, Nakano A, Opeka M M, Talmy I G, Vashishta P and Yip S 2006 Bongiorno-ZrB$_2$SiC-MRSB06 31 9