Deposition of heat-resistant coatings based on the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system for protection of non-metallic composite materials in high-speed high-enthalpy gas flows

I P Lifanov, A N Astapov and V S Terentieva

Moscow Aviation Institute (National Research University)
125993, Russia, Moscow, Volokolamskoe highway, 4

E-mail: leaf.un.off@gmail.com

Abstract. The work demonstrates possibility of formation of coatings based on the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system by the slip-firing method. During oxidation, the coatings form heterogeneous oxide film resistant to high-speed high-enthalpy gas flow due to generation of refractory ZrO$_2$ framework filled with borosilicate glass doped with zirconium dissolved in it. The advantages and disadvantages of the coatings in the system under study are presented.

1. Introduction
Carbon-carbon and carbon-ceramic composite materials (CFC and CMC), belonging to the class of nonmetallic composite materials, are among the most promising heat-resistant materials. Though, their low resistance to oxidation at temperatures above 450 °C necessitates their protection, which is especially important for the modern aviation and space industry.

In the development of heat-resistant coatings operated in a high-speed gas flow, considerable attention is paid to compositions based on ultra-high-temperature ceramics, which combine refractoriness with high heat resistance [1]. Coatings based on the systems ZrB$_2$-SiC, ZrB$_2$-SiC-TaSi$_2$, ZrB$_2$-SiO$_2$, SiC-ZrB$_2$-MoSi$_2$, ZrC-SiC, ZrC-MoSi$_2$, etc. are known. The protective action of the most of them is based on the formation of zirconium oxide ZrO$_2$ ($T_{mel} = 2715$ °C), which plays the role of a refractory framework with borosilicate glass, which fills the pores and microcracks in the coating. These two components together represent an oxide layer that effectively suppresses the diffusion of oxygen to the unoxidized part of the coating, and, at the same time, is resistant to mechanical entrainment by the gas flow. The typical operating temperature of the described coatings is 1700 °C and more.

The object of this work is heat-resistant coatings in a new ZrSi$_2$-MoSi$_2$-ZrB$_2$ system, which combines the above-described mechanism of heat resistance with the possibility of applying coatings by an effective slip-firing method, which is possible because of the presence of zirconium disilicide ZrSi$_2$ ($T_{mel} = 1620$ °C). Earlier, work was carried out on the synthesis and study of the mechanisms of oxidation of compact ceramics based on the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system in air at 1650 °C [2].

2. Experimental part
Materials for the subsequent formation of the coatings were prepared using thermal magnesium self-propagating high-temperature synthesis. Raw materials comprised powders of silicon oxide SiO$_2$, zirconia ZrO$_2$, molybdenum trioxide MoO$_3$, and boric anhydride B$_2$O$_3$ of high purity. Pure magnesium
powder of the MPF-3 brand was used as a reducing agent. Ceramic powders in the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system with different ratios of structural components were synthesized from the initial oxide powders (see table 1) through exothermic redox reactions and subsequent etching of magnesium oxide with HCl. The process of synthesis of ceramics in the system under study is described in more detail in [3].

Coatings were applied by the slip-firing method on samples of a promising CMC of the C/SiC class, which were cylinders 30 mm in diameter and 8 mm in height. Slurry suspensions were prepared by mixing the obtained powders in a solution of colloxylon in amyl acetate, which acted as a binder. Application was carried out with a brush or dipping, followed by drying and vacuum firing to temperatures of 1680–1700 °C. Additionally, process of joint layer-by-layer deposition of suspensions based on synthesized powders and elemental silicon powder were investigated.

Gas-dynamic bench tests were carried out in NIO-8 FSUE TsAGI (Russia, Zhukovsky) on a 240 kW induction plasmatron equipped with a high-temperature wind tunnel VAT-104. The sample was mounted on a ceramic holder, coaxial with the output nozzle of the plasmatron so that the working surface of the sample was perpendicular to the direction of gas flow. Gas flow parameters: speed $M = 5.5$–6.0 Mach, pressure in front of the samples 1.0–3.5 kPa, enthalpy 45–50 MJ/kg, degree of air dissociation 85–90 %. An increase in the average surface temperature of the samples $T_m$ during the firing experiments was carried out by a stepwise increase in the stagnation pressure in the preheater $P_0$ from 10 to 30–35 kPa. The temperature was recorded with a VS-CTT-285/E/P-2001 pyrometer at a wavelength of 890 nm, taking into account the correction for the spectral emissivity of the coating, estimated in the interval of $0.4 ≤ ε ≤ 0.7$.

Methods for studying coatings and powders included scanning electron microscopy with energy dispersive spectroscopy of the sample surface before and after testing, as well as cross-sections (Phenom XL microscope with an integrated EDS detector, Phenom-World, Netherlands). X-ray diffraction (XRD) was performed on an ARL X'tra diffractometer (Thermo Fisher Scientific, USA) with a Cu Kα copper anode.

The rate constant of heterogeneous recombination of atoms $K_w$ at the active centers of the coating surface was determined from the difference between the heat flux density to a reference and to the test coatings. As the reference, we used samples of a C/SiC composite coated with MAI D5, for which the rate constant of heterogeneous recombination was determined earlier [4].

3. Results

The phase composition of the synthesized powders for coating application is given in table 1.

| Powder composition | ZrSi$_2$ (Cmcm) | MoSi$_2$ (I4/mmm) | ZrB$_2$ (P6/mmm) | ZrSi (Cmcm) | Si (Fd-3m) |
|--------------------|-----------------|-------------------|------------------|------------|----------|
| № 1                | 53.6            | 27.7              | 15.3             | -          | 3.4      |
| № 2                | 44.3            | 17.7              | 35.8             | -          | 2.2      |
| № 3                | 21.5            | 18.1              | 48.6             | 11.8       | -        |

The formation of the coating from powder № 3 does not occur in the investigated range of firing temperatures. This is explained by the minimum content of ZrSi$_2$ melting matrix phase in this composition, which appeared to be insufficient for the sintering of the coating. Coatings from powders of compositions № 1 and № 2, as well as from the same powders with additional layers of elemental silicon were successfully formed. The last two will further be designated № 1 + Si and № 2 + Si, respectively. The structure of the coatings (see figure 1) includes refractory particles of zirconium diboride ZrB$_2$ ($T_{melt} = 3245$ °C) and molybdenum disilicide MoSi$_2$ ($T_{melt} = 2020$ °C), located in a relatively low-melting matrix of zirconium disilicide ZrSi$_2$ ($T_{melt} = 1620$ °C). In the coatings with the addition of silicon, thin layers of elemental Si are observed ($T_{melt} = 1414$ °C).
Figure 1. Microstructures of the formed coatings of composition № 1 (a) and № 2 + Si (b).

The results of gas dynamic tests for coatings № 1, № 1 + Si are shown in figure 2. All coatings withstood at least 800 seconds in a flow with the surface maximum temperature rise of more than 2000 °C. The silicon-doped coatings generally showed less performance and a tendency to spontaneously rise in temperature (ignition), at which point the test was interrupted.

Microstructure of the coatings after the gas dynamic tests is shown in figure 3. Coatings № 1 and № 2 form thick dense oxide layers based on ZrO$_2$ during the oxidation, while oxide layers of coatings № 1 + Si, № 2 + Si are thin and loose.

Figure 2. Fire bench tests of the C/SiC samples with coating № 1 (a) and № 1 + Si (b): 1 – stagnation pressure in the preheater; 2 – estimated temperature interval, according to the degree of blackness of $0.4 \leq \varepsilon \leq 0.7$; 3 – sample appearance after test.
Figure 3d shows voids formed in coating №1 + Si at the boundary of the outer oxidized layer with SiO₂ matrix and the inner one with Si matrix. Figure 3c shows highly dispersed precipitates of ZrO₂ in the glass.

Values of the catalyticity of the coatings, determined at different temperatures are shown in Table 2. The XRD analysis of the samples after testing showed that the oxide layer is based on zirconia with a monoclinic crystal lattice.

Figure 3. Cross-sectional morphology of the coatings after the fire bench tests: a – microstructure of coating №2, ×1000; b – microstructure of coating №1 + Si, ×2000; c – highly dispersed precipitates of ZrO₂ in the SiO₂ matrix phase, ×20000; d – voids in the structure of coating №2 + Si at the interface of the inner and outer layers, ×1000.
Table 2. Rate constant of heterogeneous recombination of oxygen and nitrogen atoms $K_w$.

| Coating | Temperature $T_0$, K | Constant $K_w$, m/s | Coating | Temperature $T_0$, K | Constant $K_w$, m/s |
|---------|----------------------|----------------------|---------|----------------------|----------------------|
| № 1    | 1500-1700            | 1,6±1                | № 2    | 1500-1700            | 1±1                  |
| № 1    | 1750-2000            | 5±2                  | № 2    | 1870                | 3±1                  |
| № 1    | 2000-2200            | 6±3                  | № 2    | 2000                | 5±2                  |
| № 1 + Si | 1500-1700          | 1,3±1                | № 2 + Si | 2100             | 7±2                  |
| № 1 + Si | 1750-1870          | 3±1                  | № 2 + Si | 2300             | 11±3                 |
| № 1 + Si | 1900-1990          | 4±1                  | № 2 + Si | 1500-1800        | 1,5±1                |
| № 1 + Si | 2250              | 10±4                 | № 2 + Si | 1870-1930        | 3±1                  |
| № 1 + Si | 2450              | 13±4                 | № 2 + Si | 2100             | 7±3                  |

4. Discussion

The formation of the refractory ZrO$_2$ oxide framework filled with borosilicate glass can be described by reactions (1)–(3):

$$
\begin{align*}
\text{ZrSi}_2 + 3\text{O}_2 & \rightarrow \text{ZrO}_2 + 2\text{SiO}_2, \\
2\text{ZrB}_2 + 5\text{O}_2 & \rightarrow 2\text{ZrO}_2 + 2\text{B}_2\text{O}_3, \\
\text{xSiO}_2 + y\text{B}_2\text{O}_3 & \rightarrow \text{xSiO}_2:y\text{B}_2\text{O}_3.
\end{align*}
$$

Oxidation of molybdenum disilicide proceeds selectively and can be described by reactions (4)–(7). MoSi$_2$ particles and their oxidation products, which are present in the form of bright particles in figure 3a,b, are encapsulated in the oxide layer and have the highest heat resistance (they remain the last under-oxidized element in the oxide layer).

$$
\begin{align*}
5\text{MoSi}_2 + 7\text{O}_2 & \rightarrow 7\text{SiO}_2 + 3\text{MoSi}_3, \\
3\text{MoSi}_2 + 5\text{O}_2 & \rightarrow 5\text{SiO}_2 + 2\text{MoSi}, \\
\text{MoSi}_2 + 2\text{O}_2 & \rightarrow 2\text{SiO}_2 + \text{Mo}, \\
\text{MoSi}_2 + 3\text{O}_2 & \rightarrow 2\text{SiO}_2 + 2\text{MoO}_2, \\
\text{SiO}_2(l) & \rightarrow \text{SiO}_2(g)↑, \\
\text{B}_2\text{O}_3(l) & \rightarrow \text{B}_2\text{O}_3(g)↑, \\
\text{SiO}_2(g) + \text{Si}(l) & \rightarrow 2\text{SiO}(g)↑, \\
2\text{MoO}_3(l) + 2\text{O}_2(g) & \rightarrow 10\text{MoO}_3(g)↑ + 6\text{SiO}_2(l), \\
2\text{MoO}_2(g) + \text{O}_2(g) & \rightarrow 2\text{MoO}_3(g)↑.
\end{align*}
$$

Gas formation also occurs in the system, according to reactions (8)–(12). Probably, it is the formation of gaseous SiO that is the reason for the occurrence of voids at the interface of layers with a matrix based on SiO$_2$ and Si. This leads to accelerated degradation of coatings № 1 + Si and № 2 + Si.

The temperature dependence of the coating surface catalyticity (table 2) allows to establish correlation between the oxidation mechanism stages and temperatures. It can be seen that as the temperature rises above 1750 °K, $K_w$ increases, which corresponds to the evaporation of low-catalytic borosilicate glass and the exposure of the highly catalytic ZrO$_2$ framework. This process is significantly intensified upon reaching 2100–2300 °K, leading to a further increase in temperature, as well as to the fact that the zirconia phase predominantly remains in the oxide layer, which is consistent with the XRD data and microstructures shown in figure 3.

The main reason for the degradation of coatings № 1 and № 2 is oxidation of the ZrSi$_2$ matrix and evaporation of the protective layer of borosilicate glass, which leaves a porous framework of ZrO$_2$ permeable to oxygen.

The favorable factors that determine the performance of coatings in the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system include:
formation of heat-resistant heterogeneous oxide film;
- dissolution of ZrO$_2$ in borosilicate glass, which increases the viscosity of the glass phase. Increase in viscosity, in turn, mitigates oxygen diffusion and reduces the rate of glass evaporation [1];
- formation of heat-resistant particles based on molybdenum, which entangle oxygen diffusion;
- high melting temperature and low thermal conductivity of the oxide framework based on ZrO$_2$, which protects the inner layers.

5. Conclusions
The possibility of heat-resistant coatings formation in the ZrSi$_2$-MoSi$_2$-ZrB$_2$ system by slip-firing method has been experimentally confirmed. During oxidation the coatings form heterogeneous oxide film, consisting of refractory ZrO$_2$-based framework filled with borosilicate glass doped with zirconium dissolved in it. The main factor limiting the performance of the coatings is the relatively rapid oxidation of ZrSi$_2$ matrix and internal gas formation at the SiO$_2$ – unoxidized silicides interface with the generation of gaseous silicon monoxide SiO.

Acknowledgments
The work was carried out within the framework of a grant from the Russian Science Foundation (Agreement No. 19-79-10258 of 08.08.2019).

References
[1] Ren Y, Qian Y, Xu J, Zuo J and Li M 2019 Ceramics International 45 15366–74 DOI: 10.1016/j.ceramint.2019.05.030
[2] Astapov A N, Pogozhev Yu S, Prokofiev M V, Lifanov I P, Potanin A Yu, Levashov E A and Vershinnikov V I 2019 Ceramics International 45 6392–404 DOI: 10.1016/j.ceramint.2018.12.126
[3] Astapov A N, Pogozhev Yu S, Lemesheva M V, Rupasov S I, Vershinnikov V I, Lifanov I P and Rabinskiy L N 2019 Russian Journal of Non-Ferrous Metals 60 710–9 DOI: 10.3103/S1067821219060026
[4] Zhestkov B E and Shtapov V V 2016 Industrial Laboratory. Diagnostics of Materials 82 58–65 (in Russian)