Oxidation induced emissivity evolution of silicon carbide based thermal protection materials in hypersonic environments

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\textbf{ABSTRACT}

The emissivity of typical SiC-based thermal protection materials was measured \textit{in-situ} at a wide temperature range (800 ~ 2300°C) inside a plasma wind tunnel that was capable of simulating hypersonic environments on-ground. Based on it, the evolution mechanism dominated by dynamic oxidation was discussed. The results suggest an emissivity of \textit{C}/SiC 0.84 ~ 0.88 at 858 ~ 1502°C, prior to “temperature jump”. If “temperature jump” emerged, the emissivity was decreased rapidly to ~0.76. The emissivity drop was explained by the microstructural transition of the oxidized surfaces that were triggered by the dissipation of SiO\textsubscript{2} oxide scale at 1600 ~ 1900°C. Similar emissivity evolution was observed in SiC/SiC after “temperature jump”. The effect of temperature on the emissivity of ZrB\textsubscript{2}-SiC was more pronounced. It was increased from ~0.73 to ~0.98 at 1009 ~ 1297°C, and was plateaued at 1298 ~ 1497°C, ~0.98. This was a consequence of the formation of higher percentage SiO\textsubscript{2}-rich layers. However, due to the dissipation of SiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}, the emissivity of ZrB\textsubscript{2}-SiC was declined at higher temperatures, from ~0.98 (~1497°C) to ~0.85 (~1768°C).

\textbf{1. Introduction}

Thermal protection system (TPS) is a shield of hypersonic vehicle serving in near space or reentry environments, in order to withstand severe aerodynamic heating from atmosphere [1–5]. Among the widely used TPS materials, SiC-based composites are currently a main material class equipped at nozzle cones and sharp leading edges of the hypersonic vehicles. They are capable of resisting ultrahigh temperatures and simultaneously maintaining the aerodynamic shapes [6–8]. The excellent anti-oxidation property arises by the formation of a continuous oxide scale in oxidized atmospheres, and the main compound formed on the SiC-based composite is SiO\textsubscript{2} [2]. SiO\textsubscript{2} is formed by passive oxidation of SiC at >800°C and can survive up to 1600 ~ 1900°C, depending on the partial pressure of oxygen [9]. This peculiarity has limited the service temperature of traditional carbon fiber and SiC fiber reinforced SiC matrix composites (labeled C/SiC, SiC/SiC) ≤1900°C [4,10,11]. Novel oxide scales (including ZrO\textsubscript{2}, HfO\textsubscript{2}, et al.) are the focus of current studies to extend their temperature tolerances in flight condition [12,13]. This has forwarded the development of SiC-based ultrahigh temperature ceramics (UHTCs), i.e. ZrB\textsubscript{2}-SiC, ZrB\textsubscript{2}-SiC-ZrC, et al [2,13].

The as-formed oxide scale not only defines the temperature tolerance but also dominates the catalytic and radiative behavior of the SiC-based composite in flight condition, both are critical thermal processes of TPS occurring on the oxidized surfaces [14–17]. Catalycity is a chemical-heating process and is mainly determined by recombination of atomic O and N existing in the plasma environments [16,18]. Previous studies show that a fully catalytic surface could increase up to 50% the heat flux with respect to a low catalytic surface [15]. Unlike the catalytic effect, radiation is a thermal-dissipation process, and the dissipated heat is a function of surface temperature (T) and emissivity (e) [19]. Generally, a lower catalycity and a higher emissivity are desired to decrease the aero-heating temperatures of TPS under service [20]. For the SiC-based composites, the as-formed SiO\textsubscript{2} is such a material that has a catalytic efficiency on the order of 10\textsuperscript{-3}, and emissivity =0.9 [15,16]. The radiative behavior of the SiC-based composite may differ, depending on the microstructures of the oxidized surfaces at various temperatures [21]. Measuring the spectral emissivity of SiC-based composite in flight condition is important but is still a challenging and expensive task. The application of a plasma wind tunnel equipped with an emissivity measurement system is a proper

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solution, as high-enthalpy and high-speed plasmas can be generated inside, and the emissivity is measured \textit{in-situ} in an equivalent “flight condition” on ground.

This work makes full advantage of a 1 MW inductively coupled plasma wind tunnel (available at CARDC, China) and carries out systematic emissivity measurement of three typical SiC-based TPS materials (including C$_6$/SiC, SiC$_x$/SiC and ZrB$_2$-SiC) over a wide temperature range (800 ~ 2300°C). Based on this, the dominant mechanism leading to the temperature-dependent emissivity evolution is discussed by correlating the measured results with the microstructures of oxidized surfaces. Unlike the previous work that mainly measures the emissivity in static environment [16,20–23], this work highlights the emissivity measurement of SiC-based composite \textit{in-situ} in high-enthalpy and high-speed plasmas. In this way, dynamic oxidation proceeds simultaneously, and the as-formed oxide scale can be a mechanism altering the radiation behavior. The information may shed light on the fundamental understanding of the radiative behavior and help to feed the aero-heating computations of SiC-based thermal protection materials in flight condition.

2. Materials and experiments

2.1. Material fabrication techniques

The C$_6$/SiC and SiC$_x$/SiC were fabricated by precursor infiltration and pyrolysis (PIP) technique [24]. Firstly, 3D weaved carbon and SiC fiber fabrics were infiltrated in a polycarbolosilane solution (with 50 wt% xylene) in vacuum. After adequate infiltration, the infiltrated fiber fabrics were pyrolyzed at 1200°C for 1 h (in Ar atmosphere) to yield transitions of polycarbolosilane to SiC. The porosity in the SiC matrix and among the fiber fabrics was minimized by repeating the PIP process, until the gained mass after each cycle was <1%. The densities of both C$_6$/SiC and SiC$_x$/SiC were =2.2 g/cm$^3$. In addition, the ZrB$_2$-SiC was consolidated by hot-pressing sintering technique using commercial ZrB$_2$ and SiC powders (>99% purity, volume fraction ratio 4:1) as raw materials. The average particle size of ZrB$_2$ was 2 μm and that of SiC 0.5 μm. The powders were hot-pressed at 1950°C and at 30 MPa for 60 min in Ar atmosphere, to achieve an approximate dense microstructure (density =5.5 g/cm$^3$). A carbon fiber reinforced carbon matrix composite (C$_6$/C) was also added in this work for reference. It was fabricated by chemical vapor deposition of propylene and carbonization of phenolic resin on T700 weaved carbon fiber fabrics. Its density was =1.7 g/cm$^3$. After the fabric processing, the raw C$_6$/C, C$_6$/SiC, SiC$_x$/SiC and ZrB$_2$-SiC were machined to hemisphere shapes (diameter =20 mm) for further wind tunnel experiments. Due to the weak oxidation resistance of carbon fibers, the surfaces of C$_6$/SiC hemisphere specimens were further sealed by a CVD-SiC coating to protect its interior microstructures. Detailed coating protocol was introduced elsewhere [4].

2.2. Surface temperature measurement

A 1 MW inductively coupled plasma wind tunnel (CARDC, China) was employed to simulate the high-enthalpy and high-speed plasma environments where the high-temperature emissivity was measured. Its detailed configuration can be accessed in Ref [25]. The wind tunnel generates the plasma flows with the enthalpy 5 ~ 55 MJ/kg, the nominal flow speed 0.5 ~ 2 Mach and the flow pressure 1 ~ 30 kPa, by modulating its arc power, mass flow of air, nozzle configuration and pump system. In this study, the surface temperature is a key parameter for the high-temperature emissivity measurement. Based on the thermodynamics law, it is determined by iterations of the heat gained and dissipated at the gas/solid interfaces by:

$$q_{\text{con},g} + q_{\text{rad},g} + q_{\text{chem},g} = q_{\text{con},i} + q_{\text{rad},i}$$  \hspace{1cm} (1)

Here, $q_{\text{con},g}$ and $q_{\text{rad},g}$ are the heat received by conduction and radiation from the generated plasmas [25]. $q_{\text{chem},g}$ is the chemical heat generated by oxidation and catalytic effects, both are highly sensitive to the surface microstructure. As $q_{\text{chem},g}$ was challenging to acquire for each material, the input cold wall heat flux ($q_{\text{cw}}$) was experimentally determined by a copper slug (TU1 type, purity $\geq$99.97%, O content $\leq$0.003%) that had the same aerodynamic shapes of the hemisphere samples. $q_{\text{con},i}$ is the heat dissipated by the conduction in the material and $q_{\text{rad},i}$ is the heat dissipated by surface radiation. The latter is a function of $\varepsilon$ and $T$ based on:

$$q_{\text{rad},i} = \sigma \varepsilon T^4$$  \hspace{1cm} (2)

Here, $\sigma$ is the Stefan-Boltzmann constant.

In this work, two independent pyrometers (550 ~ 2500°C, with ±20°C precision) were used to measure the temperatures of the hemispheres: one was pointed at the stagnation where the heat flux was maximized and the other was at the position of the emissivity measurement, as schematically shown in Figure 1. The latter was used to correlate the oxidation temperatures with the radiation signals that were acquired by a transform infrared spectroscopy (FTIR, Bruker Vertex80, wavelength range: 0.3 ~ 10 μm and resolution 2 cm$^{-1}$). The FTIR acquired the infrared spectral energy from the hemisphere surface that was aero-heated by the plasmas in the wind tunnel. Note the measured temperature was a “colorimetric” temperature ($T_d$) acquired at the working wavelength of the pyrometer (labeled $\lambda$, 1.52 ~ 1.64 μm). The
In the text, the divergence of $T_\infty$ with the "actual" temperature ($T$) depends on the consistency of the emissivity at 1.52 $\mu$m by:

$$\frac{1}{T} - \frac{1}{T_\infty} = \frac{\ln\varepsilon_{\lambda_2} - \ln\varepsilon_{\lambda_1}}{c_2(\lambda_1 - \lambda_2)}\lambda_1\lambda_2$$

In this equation, $c_2$ is the second radiation constant, $\approx 1.43879 \times 10^4$ $\mu$m$^2$K. $\varepsilon_{\lambda_1}$ and $\varepsilon_{\lambda_2}$ are the emissivity at $\lambda_1$ (1.52 $\mu$m) and $\lambda_2$ (1.64 $\mu$m) at temperature $T$. Though they are unknown, once $\varepsilon_{\lambda_1} \approx \varepsilon_{\lambda_2}$, $T_\infty \approx T$.

In order to acquire $\varepsilon$ at a wide temperature range, in this work stepped wind tunnel experiments were carried out on the C/C, SiC/SiC, C/SiC and ZrB$_2$-SiC hemispheres, at each step the surface temperature was stabilized for a few seconds and the radiation characteristics were acquired instantaneously at the measured temperatures. Figure 2 (a) plots typical thermal responses of the C/C and SiC/SiC during the stepped wind tunnel experiments. E.g. for the C/C, the surface temperature was stepped increased from $\approx 1000$ to $\approx 2115^\circ$C by increasing $q_{cw}$ from $\approx 0.85$ to $\approx 3.37$ MW/m$^2$. Unlike the C/C, the SiC/SiC, C/SiC and ZrB$_2$-SiC are all SiC-based composites and a "thermal instability" may emerge at higher $q_{cw}$ due to abrupt changes in the surface oxidized microstructures [26]. The mechanism may interrupt the thermal balance, thus triggering an abrupt "temperature jump". As shown in Figure 2 (a), the "temperature jump" of the SiC/SiC emerged when raising $q_{cw}$ from $\approx 2.52$ to $\approx 2.68$ MW/m$^2$. During the process, the surface temperature was rapidly increased from $\approx 1406$ to $\approx 2297^\circ$C in a few seconds. Similar "temperature jump" phenomena emerged at $\approx 1750^\circ$C in the C/SiC [4], and in our wind tunnel it was triggered when increasing $q_{cw}$ from $\approx 3.68$ to $\approx 4.74$ MW/m$^2$, as shown in Figure 2 (b). For the ZrB$_2$-SiC, the oxidation temperature was continuously increased, and thermal balance was hardly achieved when increasing $q_{cw}$ from $\approx 2.98$ to $\approx 3.45$ MW/m$^2$. As will be shown later, the oxide scale at the temperature range is continuously evolved, which leads to an evident temperature-sensitive emissivity in the plasma environment. This may be a mechanism interrupting the thermal balance and leading to the temperature increase.

### 2.3. High temperature emissivity measurement

At each $q_{cw}$ step, the infrared spectral signal ($\lambda_3$) emitted from the hemispheres was detected by the FTIR in a wavelength ranging from 3 $\mu$m to 5 $\mu$m (the main atmosphere band). As $\lambda_3$ at a given temperature and wavelength is only an indicating value of the FTIR system, a mathematical transformation is necessitated to transform $\lambda_3$ to radiation intensity ($I_{\lambda_3}$). In this work, their mathematical relation was polynomial fitted by a blackbody furnace (Mikron M490s, 600 $\rightarrow$ 3000$^\circ$C). The blackbody furnace was placed at the same...
position of the hemisphere (Figure 1). Based on the Planck’s law, the normal radiation intensity for a blackbody \( L_{bb} \) is a function of \( \lambda \) and \( T \):

\[
L_{bb} = \frac{c_1}{\pi\lambda^5} \cdot \frac{1}{e^{c_2/\lambda T} - 1}
\]  

(4)

Here, \( c_1 \) is the first radiation constant. \( c_1 = 3.7415 \times 10^8 \) W·μm\(^5\)/m\(^2\). The blackbody temperature was measured by the same pyrometers, and the indicating value of the radiation intensity (\( x_{bb} \)) was acquired by the same FTIR system. In this work, \( x_{bb} \) was measured at \( T \) ranging 800 ~ 2300°C and \( \lambda \) within 3 ~ 5 μm, and the corresponding \( L_{bb} \) was calculated based on equation (4). The mathematical relation between \( L_{bb} \) and \( x_{bb} \) at a given \( \lambda \) was thus polynomial fitted by:

\[
\log L_{bb} = a_0 + a_1 x_{bb} + \ldots + a_5 x_{bb}^5
\]  

(5)

The actual radiation intensity of the hemisphere specimen was further calculated by \( L_3 = f(x_3) \) based on equation (4). Figure 3 (a-c) plots the calculated radiation intensity of \( \text{C} / \text{SiC}, \text{SiC}/\text{SiC} \) and \( \text{ZrB}_2-\text{SiC} \) at 3 ~ 5 μm. Once \( L_3 \) is known, the spectral emissivity is finally calculated based on the definition of it (ratio of actual radiation intensity with that of blackbody):

\[
\varepsilon(\lambda, T) = \frac{L_3(\lambda, T)}{L_{bb}(\lambda, T)}
\]  

(6)

Figure 3 (d-f) plots the calculated spectral emissivity of the three materials at different temperatures. In the inserted sub-figures, we also attached the spectral emissivity of all materials at the working wavelength of the pyrometers (1.52 ~ 1.64 μm). At the working wavelength, it is identical at each measured temperature. This evidences the validity of the temperature measurement by the pyrometers.

Based on the measurement protocol, the emissivity of \( \text{C}/\text{SiC}, \text{SiC}/\text{SiC} \) and \( \text{ZrB}_2-\text{SiC} \) at 3 ~ 5 μm and at a given temperature were finally calculated by:

\[
\varepsilon_T = \frac{\int_{\lambda_1}^{\lambda_2} L_3(\lambda, T) d\lambda}{\int_{\lambda_1}^{\lambda_2} L_{bb}(\lambda, T) d\lambda}
\]  

(7)

where \( \lambda_1 \) and \( \lambda_2 \) are the lower and upper limit of the wavelength range (equal to 3 and 5 μm). Table 1 summarizes the flow states of the plasmas, the measured surface temperature and the emissivity of the \( \text{C} / \text{SiC}, \text{SiC}/\text{SiC} \) and \( \text{ZrB}_2-\text{SiC} \) at temperatures ranging 800 ~ 2300°C.

2.4. Post characterizations of the oxidized surface

After the wind tunnel experiments, the surface microstructures of the oxidized hemispheres were characterized by scanning electron microscopy.
Table 1. Flow states, oxidation temperature and emissivity of \( \text{C}_4/\text{SiC}, \text{SiC}_4/\text{SiC} \) and \( \text{ZrB}_2/\text{SiC} \) in the 1 MW plasma wind tunnel.

| Material       | Pressure (kPa) | Heat Flux (MW/m²) | Enthalpy (MJ/kg) | Temperature (°C) | Emissivity (f < 3 μm) |
|----------------|---------------|-------------------|------------------|------------------|----------------------|
| \( \text{C}_4/\text{SiC} \) | 1.86          | 1.25              | 10.0             | 858              | 0.84                 |
|                | 2.53          | 1.22              | 9.2              | 1027             | 0.85                 |
|                | 3.28          | 2.09              | 12.7             | 1235             | 0.84                 |
|                | 3.79          | 2.98              | 16.3             | 1370             | 0.89                 |
|                | 4.38          | 3.68              | 18.7             | 1502             | 0.88                 |
| \( \text{SiC}_4/\text{SiC} \) | 2.47          | 4.74              | 24.3             | 2172             | 0.76                 |
| \( \text{ZrB}_2/\text{SiC} \) | 2.51          | 1.09              | 7.6              | 1120             | 0.91                 |
|                | 2.84          | 1.53              | 9.9              | 1215             | 0.92                 |
|                | 3.28          | 1.88              | 11.2             | 1305             | 0.93                 |
|                | 3.67          | 2.52              | 14.1             | 1406             | 0.92                 |
|                | 3.8           | 2.68              | 15.2             | 2297             | 0.75                 |
|                | 2.43          | 0.85              | 6.3              | 1009             | 0.73                 |
|                | 3.03          | 1.71              | 10.6             | 1165             | 0.88                 |
|                | 3.66          | 2.80              | 15.6             | 1298             | 0.98                 |
|                | 4.89          | 2.98              | 14.5             | 1497             | 0.98                 |
|                | 5.12          | 3.37              | 16.1             | 1627             | 0.95                 |
|                | 5.16          | 3.45              | 16.7             | 1768             | 0.83                 |

(SEM, ZEISS EVO18) and energy-dispersive spectroscopy (EDS, Oxford, UK). Note the characterizations were performed at the positions where the temperature and emissivity were measured, in order to build correlations between the emissivity and the oxidized microstructure in high-enthalpy flows.

3. Results and discussion

3.1. Surface microstructures of raw material

Figure 4 presents the typical surface microstructures of the as-fabricated \( \text{C}_4/\text{SiC}, \text{SiC}_4/\text{SiC} \) and \( \text{ZrB}_2/\text{SiC} \) hemispheres. The surface of \( \text{C}_4/\text{SiC} \) was mainly composed of a continuous SiC coating. Its thickness was ≥20 μm. As a comparison, the \( \text{SiC}_4/\text{SiC} \) was much rougher and was mainly composed of woven SiC fiber bundles and SiC matrix. Large porosities was still observed on the surface. As reported in an earlier work of our group, the observed porosities could be diffusion channels of oxidized species, leading to interior oxidations of SiC \( /\text{SiC} \) [11]. Unlike the typical continuous fiber reinforced composites, the \( \text{ZrB}_2/\text{SiC} \) showed a rather different microstructure. It was mainly composed of SiC and ZrB\(_2\) grains, having few porosities. The nominal volume fraction of SiC was =20%.

3.2. Emissivity evolved with temperature

Figure 5 plots the emissivity (at 3 – 5 μm) of the \( \text{C}_4/\text{SiC}, \text{SiC}_4/\text{SiC} \) and \( \text{ZrB}_2/\text{SiC} \) as a function of surface temperature. Note “temperature jump” emerged in both \( \text{C}_4/\text{SiC} \) and \( \text{SiC}_4/\text{SiC} \) at 1600 ~ 1800°C, following which the surface temperature was rapidly increased to >2100°C (see Fig. 3). The emissivity of \( \text{C}_4/\text{C} \) was also added for reference. It was consistent at 1000 ~ 2115°C, 0.66 ~ 0.75. This is reasonable as the oxidized surface of the \( \text{C}_4/\text{C} \) was mainly composed of ablated carbon fibers and carbon matrix. The emissivity of \( \text{C}_4/\text{SiC} \) was higher, 0.84 ~ 0.88, prior to the “temperature jump”. However, it was decreased evidently to =0.76 when the “temperature jump” was triggered. As the emissivity is mainly dominated by the surface microstructures, this result implies a sudden change in the oxidized microstructures of \( \text{C}_4/\text{SiC} \) during the ”temperature jump”. The emissivity evolution of \( \text{SiC}_4/\text{SiC} \) is similar. Prior to the “temperature jump”, the emissivity was stabilized at 0.91 ~ 0.93, and after that it was decreased suddenly to =0.75. Note the measured emissivity of \( \text{C}_4/\text{SiC} \) and \( \text{SiC}_4/\text{SiC} \) after “temperature jump” were quite similar to that of \( \text{C}_4/\text{C} \). Unlike \( \text{C}_4/\text{SiC} \) and \( \text{SiC}_4/\text{SiC} \), the \( \text{ZrB}_2/\text{SiC} \) exhibits a highly temperature-dependent emissivity. As the surface temperature increased from ≈1009°C to ≈1298°C, the emissivity was monotonously increased from ≈0.73 to ≈0.98. After reaching a plateau at 1298 ~ 1627°C, it was further decreased and at ≈1768°C an ultimate emissivity, ≈0.83, was obtained. This implies a continuous microstructural

![Figure 4](image-url)
3.3. Correlation of emissivity with the oxidized microstructures

(1) For C/\text{SiC} and SiC/\text{SiC}

Based on the emissivity evolution, it is clear that “temperature jump” emerged in C/\text{SiC} and SiC/\text{SiC} can alter evidently their emissivity. Figure 6 thus compares the oxidized surface microstructures of both materials prior to and after “temperature jump”. For the C/\text{SiC}, a continuous SiO\textsubscript{2} layer could be formed on the SiC coatings by passive oxidation with atomic O [4]:

\[ \text{SiC(s)} + 3\text{O(g)} = \text{SiO}_2\text{(s)} + \text{CO(g)} \]  

Note the mechanism in the plasma environment differs from that occurred in static condition where the main oxidized species is still O\textsubscript{2}. Though atomic O was more active than O\textsubscript{2}, the as-formed SiO\textsubscript{2} layer prior to “temperature jump” was still quite thin. As typically shown in Figure 6 (a), after oxidation at \( \approx 1100^\circ\text{C} \) for 2000 s, the thickness of SiO\textsubscript{2} layer was only \( \approx 150 \) nm (the insert in Figure 6a). As the thin SiO\textsubscript{2} was almost transparent in the near-infrared range, its contribution to the C/\text{SiC} emissivity could be negligible. Therefore, the main microstructure dominating the emissivity of C/\text{SiC} prior to “temperature jump” was still SiC coating. Note our results differ from the static measurements, but agree well with those measured in similar plasma environments (i.e. emissivity of CVD-SiC measured by Pidan, et al.) [19,27].

An interesting observation is the sudden emissivity decrease of C/\text{SiC} when “temperature jump” is triggered. It is now widely accepted that the “temperature jump” phenomenon of SiC-based TPS emerges at 1600 \( \sim \) 1900°C due to the interruption of thermal balance on the oxidized surface and is mainly triggered by abrupt changes in the surface chemistry [4]. During the “temperature jump”, the active oxidation of SiC is also accelerated at higher oxidation temperatures by:

![Figure 5](image-url)  
Figure 5. Emissivity of C/\text{SiC}, SiC/\text{SiC} and ZrB\textsubscript{2}/\text{SiC} as a function of oxidation temperature measured in the 1 MW plasma wind tunnel.

![Figure 6](image-url)  
Figure 6. Typical surface microstructures of (a, b) C/\text{SiC} oxidized at \( \approx 1100^\circ\text{C} \) and \( \approx 2172^\circ\text{C} \), (c, d) SiC/\text{SiC} oxidized at \( \approx 1215^\circ\text{C} \) and \( \approx 2297^\circ\text{C} \).
\[ \text{SiC}(s) + 2\text{O}(g) = \text{SiO}_2(g) + \text{CO}(g) \]  
(9)

\[ \text{ZrB}_2(s) + 5\text{O}(g) = \text{ZrO}_2(s) + 2\text{B}_2\text{O}_3(l) \]  
(10)

The SiC coating was thus severely dissipated, which exposed the beneath carbon fibers and SiC matrix directly to the heating flows. As shown in Figure 6 (b), after the “temperature jump” the SiC coatings on the C_/SiC vanished. In addition, the exposed carbon fibers were evidently sharpened by ablation and the SiC matrix was recessed. It seems that the dissipation rate of SiC matrix was higher than that of carbon fibers during the “temperature jump”. As a result, the uppermost material of the oxidized surface was still the needle-sharpened carbon fibers, at the roots of which were the recessed SiC matrix. This is an explanation of the comparable emissivity of the C_/SiC and C_/C after “temperature jump”.

Unlike the C_/SiC where the surface was sealed by a continuous SiC coating, the SiC_/SiC was not sealed and the oxidized surface was mainly made up by SiC matrix and SiC fibers, as shown in Figure 6 (c). When exposed in high-enthalpy plasmas, both constituents in SiC_/SiC were oxidized, forming a continuous SiO_2 layer prior to “temperature jump”. Despite that, the contribution of the as-formed SiO_2 to the SiC_/SiC emissivity could be negligible, due to its small thickness. The controlling microstructures are still the SiC fibers and SiC matrix exposed on the oxidized surface. As the oxidized surface of SiC_/SiC was rougher than that of C_/SiC, the emissivity might be enhanced by promotion of scattering and polarization of the electromagnetic waves by thermal radiation [28]. This explains the higher emissivity of SiC_/SiC than that of C_/SiC prior to “temperature jump” (=0.92 vs. =0.86).

As the dynamic oxidation in SiC_/SiC was still dominated by passive and active oxidations of SiC, the “temperature jump” emerged at higher temperatures, which raised the oxidation temperature rapidly to >2100°C. Figure 6 (d) shows a typical surface microstructure of SiC_/SiC after “temperature jump”. A similar needle-sharpened morphology of SiC fiber was still observed, evidencing a severe active oxidation process. Beneath the SiC fibers were the recessed SiC matrix. Note SiO_2 oxide scale was not again formed at such high temperature. An interesting observation is the emissivity decrease of SiC_/SiC after “temperature jump”, from =0.92 to =0.75. The emissivity level is also in accordance with that of C_/SiC and C_/C. This implies a consistent radiation behavior of the C_/SiC and SiC_/SiC if “temperature jump” is triggered.

(2) For ZrB_2-SiC

Unlike those in C_/SiC and SiC_/SiC, the oxidized microstructure of ZrB_2-SiC was rather complicated and was highly temperature dependent. At the temperature range studied, both SiC and ZrB_2 were oxidized, and specially, the latter took place by: The emissivity evolution of ZrB_2-SiC must be a consequence of the microstructural changes of the oxide scale formed at various temperatures. In order to ascertain the underlying mechanism, independent dynamic oxidation experiments were performed at 1100 ~ 2200°C in the 1 MW plasma wind tunnel, and post microstructures of the oxidized surface were characterized. Figure 7 shows the surface temperature evolutions of the ZrB_2-SiC at different heat fluxes. The inserted are typical surface microstructures after oxidation at different temperature and time. At a comparably low temperature (i.e. ≈1100°C), the oxidized surface was mainly occupied by a SiO_2-rich glass (mixture of B_2O_3 and SiO_2) and ZrO_2 skeletons after 200 s oxidation (Figure 7a). Both were byproducts of oxidations by equations (8) and (10). The SiO_2-rich glass was not continuous and some ZrO_2 was directly exposed to the heating flows. The thickness of the as-formed oxide scale was up to =10 μm [2]. The oxidation rate was much higher than those of C_/SiC and SiC_/SiC. This is expected, as the microstructure of the oxide scale in the ZrB_2-SiC is porous due to the evaporation of liquid B_2O_3 and the gaseous species (i.e. CO). This contrasts to the dense microstructure of the SiO_2 layer that is formed on those C_/SiC and SiC_/SiC, which strongly blocks the inner diffusion of the oxidized species. Therefore, the main contribution to the emissivity of ZrB_2-SiC at this temperature could be the as-formed SiO_2-rich glass and the ZrO_2 layer.

The oxidations of both SiC and ZrB_2 were accelerated at higher temperatures, and at ≈1340°C, after only 150 s oxidation a continuous SiO_2-rich glass layer was formed on the oxidized surface (Figure 7b). The oxide scale was in a multilayer microstructure, where the uppermost layer was the SiO_2-rich glass and the subsurface layer was mainly composed of a thick ZrO_2 [2]. In this case, the dominant microstructure determining the emissivity of ZrB_2-SiC might be changed.

As B_2O_3 and SiO_2 are prone to vaporize at higher temperatures, the SiO_2-rich glass formed on the ZrB_2-SiC surface can be evidently thinned at even higher temperatures. E.g. after oxidation at ≈1540°C for 200 s, the thick SiO_2-rich glass as observed at lower temperatures vanished, as shown in Figure 7 (c). Instead, a thin SiO_2 layer was formed on the surface, beneath it was a columnar structured ZrO_2 layer. In this case, the main contribution to the emissivity of the ZrB_2-SiC was the ZrO_2 layer. At even higher temperatures, the thin SiO_2 could be fully dissipated, thus exposing the beneath ZrO_2 to the heating flows (Figure 7d) [2].

The emissivity evolution of ZrB_2-SiC with temperature can be rationalized by the observed microstructural transitions of the oxide scale. The increased emissivity (from =0.73 to =0.98) at 1009 ~ 1298°C was mainly a consequence of accelerated oxidations of SiC
and ZrB₂, which formed a higher percentage of SiO₂-rich layer on the surface. At 1298 ~ 1497°C, the oxidized surface was mainly occupied by a thick SiO₂-rich glass. Considering the relative higher emissivity of SiO₂, the emissivity of ZrB₂-SiC at this temperature range was maximized, ≈0.98. Finally, due to the dissipation of SiO₂ and B₂O₃, the SiO₂-rich layer was evidently thinned at higher temperatures, which left a very thin SiO₂ layer on the uppermost surface, beneath it was a pristine ZrO₂ skeletons. Due to the relatively low emissivity of ZrO₂ (∼0.7 measured by Thermal Radiation Calorimetry) [29], the emissivity of ZrB₂-SiC was declined, from ≈0.98 (∼1497°C) to ≈0.85 (∼1768°C). Similar emissivity decrease of ZrB₂-SiC has been observed at ≥1600°C in static environments [21].

4. Conclusions
In this work, the emissivity of three typical SiC-based thermal protection materials (including C/SiC, SiC/SiC and ZrB₂-SiC) were measured at a wide temperature range (800 ~ 2300°C) in high-enthalpy and high-speed plasma environments. The underlying mechanism dominating the temperature-dependent emissivity was further discussed by correlating the measured results with the oxidized microstructures. The following main conclusions can be drawn based on current study:

(1) “Temperature jump” emerged in the C/SiC and SiC/SiC altered evidently their emissivity at high temperatures. For the C/SiC, prior to the “temperature jump”, the emissivity was averaged 0.84 ~ 0.88 (858 ~ 1502°C), and after that it was decreased to ≈0.76 (measured at ≈2172°C). Similar emissivity evolution was observed in the SiC/SiC. The emissivity drop was explained by the microstructural transition of the oxidized surfaces that were triggered by the dissipation of SiO₂ oxide scale at 1600 ~ 1900°C.

(2) The effect of temperature on the emissivity of ZrB₂-SiC was more pronounced, due to the sensitivity of surface microstructures with temperature. The
emissivity was increased monotonously from \(\approx 0.73\) to \(\approx 0.98\) at 1009 – 1297°C, due to the accelerated oxidations of SiC and ZrB\(_2\), which formed a higher percentage of SiO\(_2\)-rich layer. At 1298 – 1497°C, the surface was mainly occupied by a thick SiO\(_2\)-rich glass, thus the emissivity was maximized, \(\approx 0.98\). Finally, due to the dissipation of SiO\(_2\) and B\(_2\)O\(_3\), the contribution of ZrO\(_2\) was more significant at higher temperatures, which led to the decrease of emissivity, from \(\approx 0.98\) (\(\approx 1497°C\)) to \(\approx 0.85\) (\(\approx 1768°C\)).

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