Dynamic oxidation mechanism of carbon fiber reinforced SiC matrix composite in high-enthalpy and high-speed plasmas

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Abstract: This work employed an inductively coupled plasma wind tunnel to study the dynamic oxidation mechanisms of carbon fiber reinforced SiC matrix composite (C_f/SiC) in high-enthalpy and high-speed plasmas. The results highlighted a transition of passive/active oxidations of SiC at 800–1600 °C and 1–5 kPa. Specially, the active oxidation led to the corrosion of the SiC coating and interruption of the SiO₂ growth. The transition borders of active/passive oxidations were thus defined with respect to oxidation temperature and partial pressure of atomic O in the high-enthalpy and high-speed plasmas. In the transition and passive domains, the SiC dissipation was negligible. By multiple dynamic oxidations of C_f/SiC in the domains, the SiO₂ thickness was not monotonously increased due to the competing mechanisms of passive oxidation of SiC and dissipation of SiO₂. In addition, the mechanical properties of the SiC coating/matrix and the C_f/SiC were maintained after long-term dynamic oxidations, which suggested an excellent thermal stability of C_f/SiC serving in thermal protection systems (TPSs) of reusable hypersonic vehicles.

Keywords: thermal protection system (TPS); ceramic matrix composite; oxidation mechanism; plasma wind tunnel; mechanical property

1 Introduction

The quest for higher Mach number and longer service time of hypersonic vehicles has advanced the development of novel thermal protection system (TPS) to resist severe aerodynamic heating. Among them,

carbon fiber reinforced SiC matrix composite (C_f/SiC) is considered as a promising candidate applied at sharp leading edges, nose cones, etc., due to its low density, high mechanical property, and excellent oxidation resistance [1,2]. Generally, the surface of the C_f/SiC is sealed by a dense thermal barrier coating (TBC), to protect carbon fibers from direct exposure in heating flows as well as to block inner diffusions of oxidized species [3–6]. The commonly used TBC material is still SiC, as it has the minimal thermal mismatch

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between the coating and matrix [7–9]. Previous studies show that the C_f/SiC with SiC coatings can resist ultrahigh temperatures up to ~1750 °C in re-entry environments of hypersonic vehicles [7,10,11]. Beyond the critical temperature, the C_f/SiC may experience severe ablation, due to dissipation of SiC coating which interrupts the thermal balance at the oxidized surface and leads to abrupt “temperature jump” [7]. Inductively coupled plasma wind tunnel is the main ground facility to simulate re-entry environment by generating a high-power electromagnetic field to the inside air. The activated flow temperature is generally beyond 3000 K, leading to complete dissociation of O₂ to atomic O. Recombination of atomic O on the oxidized surface (catalytic effect) is one of the main mechanisms releasing chemical heat to the TPS [12–14].

Except for the catalytic effect, dynamic oxidation occurring on the surface is another chemical behavior of TPS in re-entry environments. Referred to C_f/SiC, the dynamic oxidation is mainly dominated by the interaction of SiC coating with the oxidized species, i.e., atomic O in high-enthalpy and high-speed plasmas. However, the current study on oxidation mechanism of SiC is still limited in static environments where the flow speed is very low, and the main oxidized species is O₂ [15]. In the simulated environment, passive and active oxidations of SiC are observed, and the latter is prone to occur at higher temperatures and lower partial pressures of O₂ [16]. The transition of active/passive oxidation is the key to confine the service boundary of SiC based materials and has been widely determined by thermochemical modeling and experimental validities [11,16–20]. Due to the diversities of the models or the experimental facilities employed, the obtained transition border varies, and very few is determined in on-ground simulated environments, i.e., high-enthalpy and high-speed plasmas [11,18,20].

This work contributes to study the dynamic oxidation behavior of SiC coatings on a typical C_f/SiC TPS employing a 1 MW inductively coupled plasma wind tunnel available at China Aerodynamics Research and Development Center (CARD, China). The wind tunnel is capable of generating high-enthalpy and high-speed plasmas at reduced pressures, i.e., 1–5 kPa in this work. A wide heat flux range of 0.25–2.00 MW/m² was tailored to trigger oxidations of C_f/SiC at 800–1600 °C in the wind tunnel, which covered the typical service boundary of the material. Based on the detailed characterizations of the sub-surface microstructures,

the dynamic oxidation mechanism of SiC as a function of oxidation temperature and plasma pressure was firstly discussed. After that, the transition borders of passive/active oxidations were determined, and the dissipation behavior of SiC coating in each domain was discussed. Finally, two typical plasma flow states were chosen and were employed to oxidize the C_f/SiC (with SiC coating) for 1, 5, and 10 times, after which the mechanical properties of SiC coatings/matrix and C_f/SiC were quantified by nanoindentation and uniaxial tension. The multiple plasma exposures were essential to ascertain the dynamic oxidation behavior and the thermomechanical stabilities of C_f/SiC, to shed light on potential applications of TPS in reusable hypersonic vehicles.

2 Materials and experiments

2.1 As-received material and structural characterization

The C_f/SiC was fabricated by traditional precursor infiltration and pyrolysis (PIP) technique, using polycarbosilane (PCS) as precursor of SiC matrix and three-dimensional (3D) stitched carbon fiber fabrics as reinforcements (volume fraction ≈ 35%). The pyrolysis temperature was ~1200 °C [21]. Prior to the PIP process, a thin layer of pyrocarbon interphase was fabricated at the fiber/matrix interface by chemical vapor deposition (CVD), in order to tailor its bonding strength [22,23]. The density of the as-fabricated C_f/SiC was ~2.2 g/cm³ by Archimedes method and the open porosity was ~9% after ≥ 14 PIP cycles. As the carbon fibers were prone to oxidize at a low temperature (~400 °C) and the open porosities could be channels for oxygen diffusion, a SiC coating was further sealed on the surface of C_f/SiC by CVD to protect its inner microstructure. A methyltrichlorosilane (MTS, CH₃SiCl₃) was used as precursor and H₂ as carrier gas. The flow rate of both was 10:1. The deposition temperature was 1000 °C and the pressure was ~5.0 kPa. The total deposition time was up to 40 h. This yielded a coating thickness of ~20 μm, as shown in Fig. 1(a). Noted that the coating thickness might vary ±5 μm, depending on the flow state during the CVD process. Due to the difference in the PIP and CVD techniques, the crystalline structures of SiC matrix and SiC coating were different. As characterized by the transmission electron microscope (TEM; FEI Talos 200X, Czech Republic), the SiC

coating was crystalline, having high density of stacking faults, while the SiC matrix was amorphous.

2.2 Dynamic oxidation experiments in plasma wind tunnel

1 MW inductively coupled plasma wind tunnel was used to evaluate the dynamic oxidation behavior of the as-fabricated C_f/SiC. The wind tunnel was advantageous of generating high-enthalpy and high-speed plasmas by applying a high power electromagnetic field in the arc generator. The inside plasmas were formed by dissociation of air and were mainly composed of O, O₂, N, N₂, etc. The configuration of the wind tunnel can be accessed in Ref. [24]. The main plasma parameters involved enthalpy (H_0), heat flux (q_{cw}), flow pressure (P), flow density (ρ), velocity (U), and percentages of atomic O and N (C_O and C_N). They were determined by a standard flow reconstruction protocol developed for the 1 MW plasma wind tunnel [25]. q_{cw} and P were firstly measured by a copper slug (TU1 type, purity $\geq 99.97\%$, O content $\leq 0.003\%$) and a pitot pressure probe (DMP331, 0–60 kPa, 0.01% full scale, Germany), respectively. Figures S1 and S2 in the Electronic Supplementary Material (ESM) supplement typical configurations of copper slugs and pitot pressure probe used in the 1 MW plasma wind tunnel. Specially, the copper slug was embedded in a reference alloy that had the same dimension as the testing sample. The spatial thermal conduction between the copper slug and the reference alloy was blocked by a thermal-insulation material. Thus, the thermal conduction was assumed in one dimension. The copper slug was exposed to the heating flows for a very short time (< 1 s), during which the temperature of copper slug was continuously measured by a K-type thermal couple, and q_{cw} was calculated by Eq. (1):

$$q_{cw} = \rho_{Cu} \times C_p \times l \times \frac{\Delta T}{\Delta \tau} \quad (1)$$

where ρ_{Cu} , C_p , and l are the density, specific heat, and length of the copper slug, respectively. ΔT is the temperature increment during exposure time $\Delta \tau$.

After that, the measured q_{cw} and P were used as inputs for computational fluid dynamic (CFD) simulations to determine the rest flow parameters (H_0 , ρ , U , C_O , and C_N). The key parameter for CFD calculation was the power efficiency ($\lambda = 0-1$), which was unknown and determined by the following protocol. (1) The flow state in arc generator was firstly calculated by coupling Navier–Stokes (N–S) and Maxwell equations, given power of arc generator (Q) and mass flow of air (q), and assuming a value of λ ; (2) once finished, q_{cw} and P in front of copper slug were again calculated using the configurations of mixing chamber and conical nozzle as boundary conditions; (3) iterating the above process until the calculated q_{cw} and P equaled to the experimentally measured by copper slug. In this way, λ was determined and H_0 , ρ , U , C_O , and C_N were finally output. This standard protocol has been widely used in other plasma wind tunnels, i.e., VKI Plasmatron Wind Tunnel in Belgium [26].

In this work, the as-fabricated C_f/SiC was machined to two shapes for the dynamic oxidation experiments. The first was a cylinder flat specimen, having ~ 25 mm in diameter and ~ 4 mm in thickness, and the other was a “dog-bone” like tensile specimen, having a ~ 3 mm $\times$ 3 mm cross-section and ~ 20 mm gauge length. The former was embedded in a porous silica and was assembled in a water-cooled holder. The configuration is supplemented in Fig. S3 in the ESM. The inner diameter of the sample holder was ~ 50 mm, about 2 times higher than that of the cylinder sample. This sample holder was designed for the 1 MW plasma wind tunnel to obtain identical flow states in front of the cylinder flat specimen [27]. This was important for post analysis of the oxidized microstructure of C_f/SiC after dynamic oxidation. A conical nozzle with 80 mm inner diameter was used to transport the heating flow to the chamber. By tailoring the power of arc generator and the vacuum system in the wind tunnel, the heat flux ranged of 0.25–2.00 MW/m², and the stagnation pressure was 1–5 kPa. The oxidation time was 500–2000 s.

The “dog-bone” specimen was also used for the wind tunnel experiment, but with the main purpose of studying its thermomechanical stability after multiple

Fig. 1 (a) Cross-sectional microstructure of the as-fabricated C_f/SiC in scanning electron microscopy; (b) crystalline microstructure at the coating/matrix interface by TEM observation.

plasma exposure. A similar water-cooled holder (inner diameter ~60 mm) was used to fix the “dog-bone” specimen in the wind tunnel, as shown in Fig. S4 in the ESM. The “dog-bone” specimen was also embedded in porous silica for spatial thermal insulation. In order to generate a homogeneous plasma flow, a large conical nozzle with ~120 mm diameter was used. The “dog-bone” specimens were repeatedly oxidized for 1, 5, and 10 times at constant flow states (i.e., $q_{cw} \approx 0.35$ and 0.65 MW/m^2). The stagnation pressure was fixed at ~2.5 kPa. The dynamic oxidation time during each exposure was 300 s.

During the dynamic oxidation tests, the surface temperatures of both cylinder flat and “dog-bone” specimens were measured by two independent infrared pyrometers (LumaSense IGAR 12-LO, 550–2500 °C, ± 20 °C accuracy, Germany), and the real-time visual recording was acquired by a high-definition digital dual camera.

2.3 Mechanical measurements at micro- and macro-scale

The mechanical properties of the “dog-bone” specimens after dynamic oxidations were quantified by uniaxial tension inside a scanning electron microscope (SEM; ZEISS EVO 18, Germany) equipped with a Kammrath & Weiss tensile module (maximum load of $\pm 5 \text{ kN}$, Germany). The tensional load was applied at a constant displacement rate ($\sim 5 \text{ }\mu\text{m/s}$) until fracture of the specimen. The real-time deformation of the “dog-bone” specimens was also monitored *in-situ* in the SEM. Based on the measured load and displacement, the engineering stress and strain were finally calculated.

Nanoindentation was also performed to measure the mechanical properties of SiC matrix and SiC coating after dynamic oxidation experiments. The tests were performed inside a NanoTest Vantage system (Micro Materials, Inc., USA) equipped with a diamond Berkovich indenter. As a finely polished surface was required for the nanoindentation experiment, the oxidized cylinder flat and “dog-bone” specimens were wire-cut vertically to the oxidized surface and were polished by diamond grinding (down to $\sim 1 \text{ }\mu\text{m}$). Indentation loading was applied on individual SiC coating and SiC matrix with constant peak load (200 mN), which yielded a penetration depth of 600–650 nm. The loading time was 10 s and unloading time was 5 s. Prior to unloading, the indenter was held at peak load for 5 s to release the creep deformation and to ensure a

pure elastic deformation during unloading. More than 10 repeated nanoindentation experiments were performed on each sample to reduce the testing error. The Young's modulus and hardness of the SiC coating and SiC matrix were finally calculated based on the Oliver and Pharr model [28].

2.4 Microstructure characterization

After the dynamic oxidation experiments, the oxidized surface of the SiC coating was characterized by SEM. The in-depth oxidized microstructure was also characterized, but by a high-resolution SEM (HR-SEM) technique combined with focused ion beam (FIB) cross-sectioning in an FEI Helios 600i dual-beam system. Thin TEM foils were also milled from the oxide surface by FIB and were characterized by TEM, to gain insight into the grain structure of the SiO_2 layers. The compositional information of the SiO_2 layer was acquired by an energy dispersive spectroscope (EDS; Oxford, UK) equipped inside the SEM or TEM. Note for the “dog-bone” specimens, the characterization was performed at the stagnation point, where the surface temperature, pressure, and heat flux were measured. The mesoscale microstructures of the C_f/SiC after dynamic oxidation were further characterized by the optical microscope (ZEISS, Axio Imager A2m, Germany) and the micro-computational tomograph (μCT , Bruke, Germany). In the former case, the C_f/SiC samples after dynamic oxidation were wire-cut and were finely polished, using epoxy to protect the oxidized surface.

3 Results and discussion

3.1 Oxidation temperature vs. heat flux

Cylinder flat specimens were firstly tested in the plasma wind tunnel at a wide heat flux range ($0.25\text{--}2.00 \text{ MW/m}^2$). In order to ascertain the pressure dependent oxidation behavior, the dynamic oxidations were performed at fixed pressures, i.e., ~1, ~2, ~3, and ~5 kPa. Figure 2 plots the temperature evolution of the oxidized surface during the wind tunnel experiments. In high-enthalpy plasmas, the surface temperature is dependent on the thermal equilibrium between convection, conduction, radiation, chemical heating, etc., based on Eq. (2):

$$q_{\text{tra,g}} + q_{\text{rad,g}} + q_{\text{chem,g}} = q_{\text{con,l}} + q_{\text{rad,l}} \quad (2)$$

where $q_{\text{tra,g}}$ and $q_{\text{rad,g}}$ are the heat gained by transfer and radiation from the heating flows, respectively [24].

Fig. 2 Surface temperature evolution of C_f/SiC cylinder flat specimens with oxidation temperature at varying heat fluxes and at (a) ~1 kPa, (b) ~2 kPa, (c) ~3 kPa, and (d) ~5 kPa.

The sum of both is approximately equal to q_{cw} that is experimentally measured by copper slug. $q_{chem,g}$ is the chemical heat mainly generated by oxidation and recombination of atomic O and N, both occurring at the oxidized surface and is highly sensitive to the oxidized microstructures. $q_{con,l}$ is the heat dissipated by conduction in the material and $q_{rad,l}$ is the heat dissipated by surface radiation. The latter is a function of spectral emissivity of the oxidized surface (ε) and oxidation temperature (T) based on Eq. (3):

$$q_{rad,l} = \varepsilon \times \sigma \times T^4 \quad (3)$$

where σ is the Stefan–Boltzmann constant. Therefore, the measured temperature was the iterations between heat gain and heat loss during dynamic oxidations. q_{cw} was a key flow parameter dominating the surface temperature. For example, at ~1 kPa, given q_{cw} of ~0.25 MW/m², the surface temperature rapidly was increased to ~835 °C in 150 s, and remained at the temperature level at longer oxidation. Increasing q_{cw} to ~0.56 and ~0.92 MW/m², the averaged surface temperatures increased to ~1100 and ~1270 °C, respectively. The stabilized temperatures (averaged

values) at various pressures were plotted against q_{cw} , and are shown in Fig. 3. The plot highlighted the dominant role of q_{cw} on the oxidation temperature. At the same level of heat flux, the surface temperature was similar. The observed discrepancy at different pressures was explained by: (1) the measurement error of the oxidation temperature. In this work, the surface temperature was measured by two independent

Fig. 3 Evolution of surface temperature of C_f/SiC with heat flux in the plasma wind tunnel.

pyrometers, and the maximum error can be 50 °C. (2) The measurement error of q_{cw} . Based on previous experiments, the measured q_{cw} was sensitive to the surface roughness, which was a parameter difficult to control. (3) The difference in the oxidation behavior. A higher stagnation pressure aided passive oxidation, but retarded active oxidation [29]. Its effect on dynamic oxidation was complicated and was discussed in detail in Section 3.2. Noted that the responding surface temperature ranged from 800 to 1600 °C, covering the typical service temperature of C_f/SiC in TPS.

3.2 Effect of plasma pressure on dynamic oxidation

The effect of plasma pressure on the dynamic oxidation of C_f/SiC was explored by characterizations of the oxidized surface. The information was important implication on the oxidation mechanisms of SiC in high-enthalpy plasmas. Figure 4 shows the microstructural evolution of the oxidized surface after dynamic oxidation at ~1 kPa. At $q_{cw} \approx 0.56 \text{ MW/m}^2$ and lower q_{cw} , the surface temperature was ≤ 1100 °C, and the oxidized surface was smooth without observation of coating corrosion (Fig. 4(a)). EDS detections on the oxidized surface further evidenced the existence of a continuous SiO₂ oxide scale covering on the SiC coating. Representative EDS spectra are supplemented in Fig. S5 in the ESM. The SiO₂ layer was successfully

observed by HR-SEM on an FIB milled cross-section. As shown in Fig. 4(b), a thin layer of SiO₂ formed on the SiC coating after dynamic oxidation at ~1100 °C for 2000 s. The SiO₂ oxide scale was formed by passive oxidation of SiC with atomic O [25]:

Though the oxidation time was up to 2000 s, the thickness of the SiO₂ layer was quite low, averaging ~150 nm. Comparable values were obtained at lower temperatures, i.e., ~835 and ~990 °C. Noted that the as-formed SiO₂ was in a dense microstructure at ≤ 1100 °C, which was essential to block inner diffusions of oxidized species. Increasing oxidation temperature (by increasing q_{cw}) altered the oxidized microstructures, e.g., after oxidation at ~1175 °C for 2000 s, the SiC coating on the C_f/SiC surface was evidently corroded. As shown in Fig. 4(c), large number of pits with micro-sizes were formed on the oxidized surface. Despite this, SiO₂ oxide scale was still formed at ~1175 °C (Fig. 4(d)), suggesting the occurrence of passive oxidation. However, the growth of the oxide layer was interrupted by the formation of pores (Fig. 4(d)). The corrosion of SiC coatings at ~1175 °C was a consequence of active oxidation of SiC with atomic O:

and with SiO₂ at SiC/SiO₂ interface [10]:

As the reactions mainly occurred at the SiC/SiO₂ interfaces, the gaseous SiO was released to the environment crossing the SiO₂ layer. This must be the mechanism leading to the formations of pores in the SiO₂ layer. Noted that the corrosion was more severe at ~1275 and ~1375 °C, as evidenced in Figs. 4(e) and 4(f). In the latter case, the SiC coating was significantly corroded, and the size of the formed pits was much higher (several tens of micrometers). This evidenced a more severe active oxidation at higher temperatures. Reminded that the thickness level of SiO₂ could be a factor altering the passive/active oxidation mechanisms. The thicker the SiO₂, the lower the partial pressure of atomic O (P_{O}) at the SiC/SiO₂ interface. In this case, active oxidation was triggered based on Eqs. (5) and (6). As the thickness level of the as-formed SiO₂ was extremely low in this work, its effect was not dominant.

The transition of passive-to-active oxidation was also observed at ~3 kPa. Figure 5 shows the microstructural evolution of the as-formed SiO₂ layer at varying

Fig. 4 Surface microstructural evolution of C_f/SiC after dynamic oxidation at ~1 kPa: (a, b) ~1100 °C for 2000 s, (c, d) ~1175 °C for 2000 s, (e) ~1270 °C for 1500 s, and (f) ~1370 °C for 1000 s.

Fig. 5 Microstructures of SiO₂ layers formed at ~3 kPa: (a) ~1107 °C for 2000 s, (b) ~1283 °C for 2000 s, (c, d) ~1400 °C for 1000 s, and (e, f) ~1530 °C for 600 s.

temperatures (1107–1530 °C) at ~3 kPa. At ~1107 °C, the as-formed SiO₂ was still in a dense microstructure (Fig. 5(a)), manifesting the occurrence of passive oxidation. The oxide thickness was measured of ~307 nm after 2000 s oxidation. The value was fostered, compared to that at ~1100 °C and ~1 kPa (Fig. 4(b)). This was expected as higher partial pressure of atomic oxygen facilitated passive oxidation of SiC, based on Eq. (4). When the oxidation temperature further increased to ~1283 °C, passive oxidation proceeded, but active oxidation was also triggered, as evidenced by the formation of pores in the SiO₂ layer (Fig. 5(b)). The critical temperature triggering active oxidation at ~3 kPa was higher than that at ~1 kPa (~1283 vs. ~1175 °C). Passive/active oxidations still co-existed at ~1400 °C. However, at ~1400 °C, the SiO₂ began to melt (due to low melting point), which partly healed the pores formed due to active oxidation (Fig. 5(c)). Noted that the melting temperature in such lower pressures and high-enthalpy plasmas was generally lower than the melting point of pure SiO₂ in ambient environment. Melting of SiO₂ was also supported by the formation of SiO₂ spheres on the oxidized surface (Fig. 5(d)). When SiO₂ melted, the diffusion activity of oxidized species accelerated in the SiO₂, and this led to a higher oxidation rate. At this temperature, the average thickness of SiO₂ was measured ~259 nm after 1000 s oxidation. The dynamic oxidation was evidently

accelerated compared to the case at lower temperatures. Active oxidation became dominant at even higher temperatures, i.e., ~1530 °C. As shown in Figs. 5(e) and 5(f), an extremely thin layer of SiO₂ was still formed at this temperature (thickness < 100 nm after 600 s oxidation), due to the retardation of passive oxidation at such high temperatures. As a comparison, active oxidation was significantly promoted, as evidenced by the massive formations of pores in the SiO₂ layer and pits in the SiC coating. In the selected region, the depth of pits was up to 1 μm (Fig. 5(e)), suggesting a dissipation process of SiC coating during the dynamic oxidation.

The active oxidation was further delayed at ~5 kPa. Figure 6 shows the microstructure of SiO₂ formed at ~1230, ~1352, and ~1507 °C. TEM was used here to acquire higher-resolution images of the SiO₂ layer. At ~1230 and ~1352 °C, the SiO₂ oxide layer was still in a dense microstructure, evidencing a passive oxidation process at ≤ 1352 °C. The as-formed SiO₂ was in an amorphous microstructure, which was expected considering the quite short oxidation time in the plasma wind tunnel. Similar to the case at ~3 kPa (Figs. 5(e) and 5(f)), the active oxidation of SiC was also triggered at ~1507 °C, leading to pore formations on the oxidized surface (Fig. 6(c)). Interestingly, the SiO₂ oxide scale was not continuous at this temperature (Fig. 6(d)), and this was possibly a consequence of massive outward escape of gaseous SiO.

Fig. 6 Microstructures of SiO₂ layers formed at ~5 kPa: (a) ~1230 °C for 1500 s, (b) ~1352 °C for 800 s, and (c, d) ~1507 °C for 600 s.

3.3 Transition of passive/active oxidation

Based on Wagner's model which related Fick's diffusion law and thermodynamic equilibrium [18], the transition border of passive/active oxidation was defined by re-plotting the partial pressure of atomic oxygen with reciprocal temperature (Kelvin), as shown in Fig. 7. Here, O_2 was assumed fully dissociated and N_2 was not in the boundary layer, considering the extreme high temperatures inside (> 3000 K). Based on the experimental data in Fig. 7, three domains were defined: active domain, transition domain, and passive domain. In the active domain, severe active oxidation of SiC occurred, signified by evident SiC corrosion, without formation of SiO_2 oxide scale. This was the case at ~ 1370 °C (~ 1 kPa). In comparison, the passive domain defined the dominant process of passive oxidation, which was indicated by a dense microstructure of SiO_2 layer (i.e., ≤ 1100 °C at ~ 1 kPa, ~ 1107 °C at ~ 3 kPa, etc.). Finally, in the transition domain, both passive and active oxidations co-existed, and this was distinguished by the pore formations in the SiO_2 layers (i.e., ~ 1175 °C at ~ 1 kPa, ~ 1283 °C at ~ 3 kPa, etc.). This definition yielded the transition borders between each domain (the red and blue lines in Fig. 7). Compared with the transition borders obtained by static oxidation, our analyses, though approximations of experimental data, highlighted a broader active domain where active oxidation was triggered at moderate temperatures (1100 – 1600 °C) and at 1 – 5 kPa, e.g., a recent study on static oxidation of SiC evidenced passive oxidation purely occurred up to 1600 °C at ~ 3 kPa [30], whereas in the dynamic oxidation condition, a strong active oxidation was still observed at comparable temperatures and pressure conditions. This comparison suggested that

active oxidation of SiC occurred much easier in high-enthalpy and high-speed plasmas. Another key finding based on the defined transition border was that both active and passive oxidations can co-exist at moderate temperatures in high-enthalpy plasmas. The behavior could be only addressed by detailed observation of the as-formed oxide scale, especially at the border of passive and transition domains where active oxidation was weak. The results differed from a recent study by Momozawa *et al.* [18]. In their results, the transition domain was missed even in dynamic oxidation condition. Noted that due to the diversities in the experimental devices and oxidation conditions, the defined transition borders of SiC might vary among different researchers [11,18]. Despite this, our results highlighted the active/passive transitions of SiC in high-enthalpy and high-speed plasmas where the main oxidized species was atomic O.

The plot in Fig. 7 can be the guideline for C_f/SiC serving in high-enthalpy and high-speed plasmas. It is not suggested to use the material in the active domain, due to corrosion of SiC coatings. An example is the case oxidized at ~ 1370 °C and ~ 1 kPa (Fig. 4(f)). Figure 8(a) shows the cross-sectional view of this composite. Only after 1000 s oxidation, the SiC coating was fully dissipated, leaving the beneath C_f/SiC directly exposed to the heating flows. This suggested the failure of the C_f/SiC in this plasma condition. Noted that in traditional static heating, SiC could still survive for several hundreds of hours at similar conditions [30]. In the passive domains, due to the formation of a continuous SiO_2 oxide scale, the dissipation of SiC coating was negligible. Unlike the dissipation mechanism in the active domain, the dissipation of SiC occurred mainly by passive oxidation (Eq. (4)) and dissipation of the as-formed SiO_2 in the passive domain [7,10]. The competing process of these two mechanisms finally led to the dissipation of SiC. An example was presented in Fig. 8(b) where the SiC coating was well maintained after oxidation at ~ 1071 °C for 2000 s (by comparison with the lateral coating structure not exposed in the heating flow). This suggested an improved thermal-stability of SiC coating in passive domain compared to that in active domain. Similar phenomena were observed in the transition domain. In this domain, the dissipation of SiC coating was contribution of both active and passive oxidations of SiC and dissipation of SiO_2 layer. Despite this, the dissipation of SiC coating was still very weak, as typically presented in Fig. 8(c).

Fig. 7 Transition of active and passive oxidations: effect of temperature and partial pressure of atomic O.

Considering the negligible dissipation rate of SiC coating, it is concluded that the C_f/SiC could survive in both passive and transition domains in the high-enthalpy plasmas.

3.4 Effect of multiple plasma exposures on dynamic oxidation

When C_f/SiC is served in reusable TPS that might experience multiple plasma exposures, the quite high reliability necessitates a much safer service boundary of TPS. In order to study the thermal-stability of SiC coating and C_f/SiC after multiple plasma exposures, two typical flow states were chosen based on the passive/active transition borders and employed to

oxidize the C_f/SiC “dog-bone” specimens for 1, 5, and 10 times. During each exposure, the oxidation time was 300 s. Details of the experimental procedure are described in Section 2.2. Two flow states with q_{cw} of ~ 0.38 and ~ 0.65 MW/m² were employed, and the stagnation pressure was fixed at ~ 2.5 kPa. The averaged oxidation temperatures in both plasma conditions were ~ 1100 and ~ 1270 °C, respectively. Noted that both conditions were positioned in the passive and transition domains. The oxidation temperature evolutions of the “dog-bone” specimens during multiple plasma exposures are plotted in Fig. 9. During the process, C_f/SiC suffered not only long-term oxidation, but also strong thermal shock. Both were potential risks for reliability of the material serving in reusable TPS.

Fig. 8 Optical images of the SiC coatings on C_f/SiC after oxidation at (a) active domain (~ 1370 °C, ~ 1 kPa), (b) passive domain (~ 1071 °C, ~ 5 kPa), and (c) transition domain (~ 1283 °C, ~ 3 kPa).

Fig. 9 Surface temperature evolution of C_f/SiC “dog-bone” specimens at ~ 2.5 kPa at (a–c) ~ 0.38 MW/m² and (d–f) ~ 0.65 MW/m² with 1, 5, and 10 times plasma exposures, respectively.

Figure 10 compares the SiO_2 microstructure and its thickness evolution after multiple plasma exposures at ~ 1100 and ~ 1270 °C. At both temperatures, the grain structure of SiC was maintained even after 10-time exposures (up to 3000 s). In addition, the as-formed SiO_2 also remained amorphous, without observation of lamination during multiple exposures. At ~ 1100 °C, the oxide thickness was ~ 90 nm after 1-time exposure. It further increased to ~ 190 and ~ 240 nm after 5-time and 10-time exposures, evidencing a cumulative SiO_2 layer at ~ 1100 °C. As the formation of SiO_2 was competing contributions of passive oxidation and dissipation of SiO_2 , its thickness might not monotonously increase at longer oxidation time. This was the case at ~ 1270 °C. At this temperature, the maximized thickness was obtained after 5-time exposures, ~ 600 nm, higher than that after 1-time and 10-time exposures (~ 150 and ~ 400 nm, respectively). This was understood by the stronger barrier effect of SiO_2 after 5-time exposures which slowed down the passive oxidation and promoted SiO_2 dissipation in high-enthalpy plasmas.

3.5 Effect of dynamic oxidation on mechanical properties

It was wondering whether the mechanical properties of SiC matrix and SiC coating were altered or not after single/multiple dynamic oxidations in high-enthalpy plasmas. The information was important to evaluate the

reliability of C_f/SiC under service. Nanoindentation was thus performed to acquire the Young's modulus and the hardness of SiC coating and SiC matrix after dynamic oxidations at 1100 – 1500 °C. Figure 11(a) plots the typical nanoindentation force–displacement curves of both constituents in raw C_f/SiC . In response to ~ 200 mN indentation load, the averaged penetration depths of SiC coating and SiC matrix were ~ 600 and ~ 650 nm, respectively. The calculated Young's modulus of raw SiC coating was ~ 310 GPa, and the hardness was ~ 38 GPa. Both surpassed those of SiC matrix (~ 286 and ~ 35 GPa, respectively). The properties remained unchanged after dynamic oxidation at 1100 – 1500 °C, suggesting an excellent thermal stability of SiC matrix and coating in high-enthalpy plasmas.

The mechanical properties of C_f/SiC were further quantified on the “dog-bone” specimens after single/multiple plasma exposures, to ascertain its mechanical stability at macroscales. Figure 12(a) compares the stress–strain curves of C_f/SiC with that after single/multiple plasma exposures at 1100 – 1500 °C. In response to uniaxial tension, all “dog-bone” specimens exhibited an elastic deformation after establishment of full contact between the “dog-bone” specimen and the tensile grip. This was followed by a typical fracture behavior [31]. The tensile fracture was successfully captured by *in-situ* SEM observation of the “dog-bone” specimen, as shown in Figs. 12(b) and 12(c). The tensile strength

Fig. 10 Microstructures of SiO_2 layers oxidized on the SiC coating after multiple plasma exposures at (a–c) ~ 1100 °C and (d–f) ~ 1270 °C for 1, 5, and 10 times, respectively.

Fig. 11 (a) Representative force–displacement curves of SiC coatings and SiC matrix by nanoindentation; (b, c) hardness and Young’s modulus vs. oxidation temperature, respectively.

Fig. 12 (a) Stress–strain curves of C_f/SiC “dog-bone” specimens after oxidation at various temperatures; (b, c) surface morphologies prior to and after uniaxial tension, respectively; and (d, e) meso-structure of raw C_f/SiC and after 10-time plasma exposures at ~1275 °C, respectively.

of raw C_f/SiC was measured ~140 MPa. After single plasma exposure at 1100–1500 °C, the tensile strength was maintained. This was also the case after multiple plasma exposures at ~1100 and ~1275 °C (the green and blue lines in Fig. 12(a)). Specially, after 10-time exposures, the tensile strength was not degraded. The meso-structures of raw “dog-bone” specimen and after 10-time exposures at ~1275 °C were further characterized by μ CT. Figures 12(d) and 12(e) present two typical μ CT slices of the cross-sections of both samples. The distribution of mesoscale pores, even after 10-time exposures, was not evidently altered. As measured by μ CT, the derived total porosity was ~48.3% for raw C_f/SiC, and was ~47.7% after 10-time plasma exposures at ~1275 °C. The mesoscale analysis correlated well with the measured tensile strength, and evidenced strongly an excellent thermo-stability of C_f/SiC serving in reusable TPS.

4 Conclusions

In this work, the dynamic oxidation behavior of carbon fiber reinforced SiC matrix composite (C_f/SiC) was studied in a 1 MW inductively coupled plasma wind tunnel. The following main conclusions can be drawn based on the current study:

- 1) Passive and active oxidations of SiC occurred at 800–1600 °C in reduced plasma pressure (1–5 kPa). Passive oxidation led to the formation of a dense SiO₂ layer, while active oxidation was prone to occur at higher temperatures or lower plasma pressures. The latter resulted in corrosion of SiC coating and interruption of SiO₂ growth. Specially, at ~1 kPa, active oxidation was triggered at ~1175 °C, and severe SiC corrosion occurred at ~1370 °C. The critical temperature triggering active oxidation was ~1283 °C at ~3 kPa and ~1507 °C at ~5 kPa.

2) The transition borders of active/passive oxidations in high-enthalpy and high-speed plasmas were defined based on the dynamic oxidation behavior of SiC with respect to temperature and partial pressure of atomic O. In the active domain, the SiC coating was severely dissipated (i.e., the case at $\sim 1370^\circ\text{C}$ and $\sim 1\text{ kPa}$), while in the passive and transition domains, the dissipation rate of SiC was negligible.

3) During multiple dynamic oxidations of C_f/SiC , the as-formed SiO_2 thickness was not monotonously increased due to competing mechanisms of passive oxidation of SiC and dissipation of SiO_2 . In addition, the mechanical properties of the SiC coating/matrix and the C_f/SiC were maintained after long-term dynamic oxidations, which suggested an excellent thermal stability of C_f/SiC in high-enthalpy and high-speed plasmas.

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Electronic Supplementary Material

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