

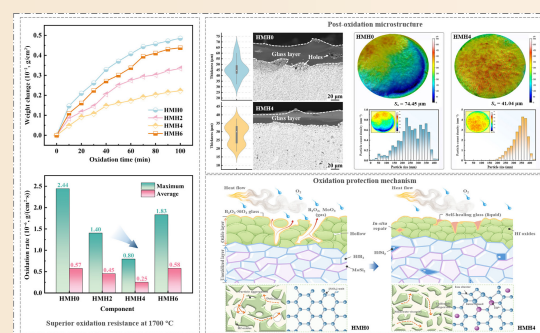
Oxidation-driven glass evolution enabling self-sealing protection in HfB₂-based boride-silicide coatings at high temperatures

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ABSTRACT: At high temperatures, oxidation is generally regarded as an unavoidable degradation process for ceramic protective coatings. Here, oxidation is shown to drive dynamic glass evolution and form a robust self-sealing barrier under extreme thermal conditions. An *in situ* alloyed boride-silicide composite coating is constructed, and the controlled incorporation of HfSi₂ is found to change oxide-scale development by providing additional Hf and Si sources during oxidation and promoting the early formation and continuous reconstruction of a highly sealing Hf-Si-O glassy layer. The optimized coating exhibits exceptional oxidation resistance at 1700 °C, with the oxygen permeability and carbon loss rate reduced by 61.67% and 75.26%, respectively, corresponding to an average protection efficiency of 99.94%. Mechanistically, oxidation-driven glass evolution seals pores and microcracks and slows inward oxygen diffusion, whereas appropriate HfSi₂ incorporation helps compact and stabilize the glassy layer, while excessive glass stiffening reduces high-temperature fluidity and weakens scale integrity. These findings provide a general design method for improving self-sealing oxidation protection at high temperatures.

KEYWORDS: high-temperature oxidation; self-sealing barrier; oxidation-driven glass evolution; *in situ* alloying; oxygen permeability



1 Introduction

Carbon/carbon (C/C) composites are widely used in high-enthalpy thermal-structural components of hypersonic vehicles owing to their low density, high specific strength, and excellent mechanical performance at elevated temperatures [1,2]. However, in oxygen-rich high-temperature environments, carbon-based materials undergo rapid oxidation, leading to structural degradation and a severe loss of load-bearing capability, which fundamentally limits their long-term service reliability [3]. Forming dense and thermally stable ultrahigh-temperature ceramic (UHTC) coatings on carbon-based substrates to block sustained oxygen ingress is therefore regarded as an effective strategy for mitigating oxidation damage and extending service lifetime [4–6].

Among the various candidate systems, HfB₂-SiC-based coatings have attracted considerable attention because of their ultrahigh melting points, relatively low oxygen diffusivity, and stable oxidation products [7,8]. During high-temperature oxidation, these coatings form a Hf-Si-O composite glass layer enriched with Hf oxides within a borosilicate matrix, which effectively suppresses oxidative attack and mechanical spallation under extreme conditions [9]. Zhu *et al.* [10] prepared HfB₂-SiC coatings on C/C composites via slurry impregnation and reported a mass gain of only 1.15 wt% after oxidation at 1500 °C for 460 h. Zhang *et al.* [11] further combined slurry impregnation with vapor silicon infiltration to fabricate a SiC-HfB₂-Si monolayer coating, which exhibited a mass loss below 0.69% after more than 538 h of oxidation in static air at 1500 °C. These performances have been attributed to the formation of Hf-Si-O-based

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composite glass layers with low oxygen permeability during oxidation. Despite the good protection achieved by HfB_2 -SiC-based coatings at 1500 °C, carbon-based thermal protection components are required to withstand increasingly severe thermal environments (~1700 °C) during service due to the rapid development of hypersonic vehicles and high-thrust aerospace engines [12]. At approximately 1700 °C, the oxidation behavior of SiC transitions from passive, protective oxide formation to active oxidation, with accelerated generation of volatile species such as SiO and CO, resulting in continuous material loss and the development of structural relaxation and porosity within the coating [13,14]. As oxidation proceeds, the interconnection of structural defects provides pathways for oxygen penetration, thereby weakening the sustained sealing capability of the glass layer [15]. Maintaining the structural continuity and stable sealing state of the oxide scale at 1700 °C thus remains a central challenge for further improving the service performance of HfB_2 -SiC-based coatings.

To mitigate volatilization-induced structural instability, increasing attention has been directed toward replacing conventional SiC with transition-metal silicides as silicon sources [16]. Compared with SiC, transition-metal silicides can directly supply stable silicon during oxidation and preferentially form continuous silicate glass phases, thereby reducing the formation and volatilization of gaseous species such as SiO and CO. Among them, MoSi_2 has been widely incorporated into UHTC coating systems owing to its favorable high-temperature oxidation resistance and self-generated protective scale [17,18]. Wang *et al.* [19] fabricated HfB_2 -SiC- MoSi_2 composite coatings via *in situ* synthesis, enabling C/C composites to withstand oxidation in air at 1500 °C for up to 408 h. Nevertheless, modification with MoSi_2 alone remains limited by MoO_3 volatilization and insufficient thermal stability of the glassy scale at higher temperatures, restricting its long-term protective effectiveness in more aggressive environments. In contrast, HfSi_2 exhibits higher thermal stability and simultaneously supplies both Hf and Si during oxidation, which is conducive to forming Hf-Si-O-based glass phases with higher viscosity and greater structural compactness [20]. Wu *et al.* [21] demonstrated that introducing HfSi_2 significantly reduced the oxide scale growth rate of MoSi_2 -based coatings at high temperatures, indicating that Hf incorporation enhances oxide scale stability and suppresses sustained oxygen ingress. Taken together, these observations suggest that combining MoSi_2 with HfSi_2 offers a promising route to improving glass-phase regulation and continuous sealing during oxidation. However, the effectiveness of such a dual-silicide strategy depends strongly on how borides and silicides are integrated within the coating system because defect compensation and sustained sealing require not only favorable glass chemistry but also a sufficiently homogeneous microstructural basis.

However, conventional boride-silicon-based coatings are typically fabricated from mechanically mixed powders, which often leads to compositional mismatch across multiple length scales and local phase separation [22]. Such heterogeneities compromise the continuous supply of glass-forming species and weaken effective sealing during high-temperature oxidation. Self-propagating high-temperature synthesis (SHS) enables rapid *in situ* reactions and homogeneous alloying in multicomponent systems, allowing the construction of homogeneous and compact composite structures at the micro- and nano-scale and offering a potential solution to these limitations [23,24]. Shi *et al.* [25] demonstrated that SHS significantly improves phase distribution uniformity and densification in silicide-boride systems, thereby reducing their oxidation reactivity. In our previous work, SHS-

derived alloyed powders, including ZrB_2 - MoSi_2 [26], MoSi_2 - TaSi_2 [27], and HfSi_2 - TaSi_2 [28], were shown to markedly suppress oxidation when used as coating feedstocks. Nevertheless, in binary alloy systems, the glass sealing efficiency remains limited in defect-rich regions. This limitation indicates that the key challenge lies not only in adding silicide components but also in constructing a multicomponent synergistic boride-silicide alloy system capable of further promoting the self-healing and sealing effects of the surface self-generated film on localized damage areas during oxidation. To address this issue, this study employed a one-step SHS method to prepare powders of the HfB_2 - MoSi_2 - HfSi_2 ternary composite system, thereby directly introducing the synergistic effect of the two silicides into the ternary boride-silicide system at the powder stage. This design is expected to further facilitate the transport and repair of locally generated glass phases toward defects by shortening the effective compensation pathway while enhancing the sealing effect through the rapid film-forming capability of the double silicides and the synergistic oxygen barrier effect of the multicomponent oxides. Although this strategy demonstrates significant potential for promoting high-temperature oxygen barrier properties, its effectiveness in enhancing oxidation protection at ultrahigh temperatures has not yet been systematically evaluated, and its underlying mechanism remains unclear.

In this work, HfB_2 - MoSi_2 - HfSi_2 *in situ* alloyed powders with varying HfSi_2 contents were synthesized via a one-step SHS route, and their oxidation response and sealing stability were systematically investigated in an oxygen-containing environment at 1700 °C. To decouple intrinsic material oxidation behavior from coating structural effects, dense ceramic bulks with identical compositions and without carbon substrates were prepared as reference samples.

2 Materials and methods

2.1 Preparation of SHS-derived composite powders

HfB_2 - MoSi_2 - HfSi_2 composite powders were prepared using an SHS route. Elemental powders of Hf, B, Mo, and Si (all purchased from Beijing Licheng Innovation Metal Material Technology Co., Ltd., China; particle size < 100 µm, purity > 95%) were selected as starting materials and proportioned according to theoretical stoichiometry. The volume fraction of HfB_2 was fixed at 60 vol%, while the remaining fraction consisted of $(40 - x)$ vol% MoSi_2 and x vol% HfSi_2 ($x = 0, 2, 4$, and 6) to enable systematic regulation of the dual-silicide content. For convenience, the resulting compositions were designated HMH0, HMH2, HMH4, and HMH6, where “HMH” denotes the HfB_2 - MoSi_2 - HfSi_2 composite system and the numbers 0, 2, 4, and 6 correspond to the nominal HfSi_2 content (vol%). The same naming rule was consistently used for the corresponding powders, coatings, and ceramic bulks throughout this work. Powder mixing was carried out by high-energy ball milling for 12 h using ethanol as a dispersing medium, with agate milling jars and agate balls as the milling media and a ball-to-powder weight ratio of 5 : 1 to ensure homogeneous distribution of all components. After drying, the mixed powders were cold-pressed into green compacts and ignited under an inert atmosphere in an SHS furnace (SGM ZB6-10E, Luoyang Sigma High Temperature Electric Furnace Co., Ltd., China). Before ignition, the reaction chamber was evacuated and refilled with argon three times, and the SHS reaction was initiated by electrically heating a molybdenum wire for 20 s. Upon completion of the reaction, the products were allowed to cool naturally in the chamber to room temperature for approximately 20 min and were

then crushed and sieved, followed by remilling under the same ball-milling conditions (12 h in ethanol, with a ball-to-powder weight ratio of 5 : 1) to obtain SHS-derived composite powders for subsequent sintering.

2.2 SPS fabrication of coating samples

Spark plasma sintering (SPS; Labox-125, Sinter Land Inc., Japan) was employed to densify the SHS-derived powders and fabricate coating samples. To obtain an integrated coating–substrate structure, graphite substrates ($\phi 12 \text{ mm} \times 2.5 \text{ mm}$) with a density of 1.8 g/cm^3 , supplied by Zibo Baoyue Carbon Materials Co., Ltd., China, were embedded into the central region of the powder compacts prior to sintering. The coating thickness was mainly controlled by the annular space between the graphite die ($\phi 15 \text{ mm}$) and the graphite substrate, together with the loaded powder amount. By keeping the die size, substrate size, and powder charge constant, the coating thickness was maintained as uniform as possible among different samples. The SPS process was conducted under a constant uniaxial pressure of 30 MPa, with rapid heating to 1400°C at a rate of $100^\circ\text{C}\cdot\text{min}^{-1}$ and a dwell time of 5 min to achieve densification. During sintering, the temperature was monitored by an infrared pyrometer aligned with the temperature-measurement hole of the graphite die, and the SPS system automatically adjusted the power output in real time according to the measured temperature. To distinguish coating structural effects from intrinsic material oxidation behavior while minimizing interference from graphite substrate consumption during oxidation, bulk ceramics with compositions identical to those of the coating samples and without graphite substrates were prepared as reference samples, using the same sintering parameters as the coating samples and with a thickness of approximately 4 mm, comparable to that of the corresponding coating samples.

2.3 High-temperature oxidation tests at 1700°C

High-temperature oxidation tests were conducted in static air using a high-temperature furnace (SGMM4/19AE, Luoyang Sigma High Temperature Electric Furnace Co., Ltd., China) at 1700°C . Before oxidation, the geometric dimensions of each specimen were measured. To minimize possible material loss during handling, each specimen was then placed into an alumina crucible containing ZrO_2 particles, and the combined mass was

recorded as m_0 . The furnace was subsequently heated to 1700°C at a rate of 7 K/min , after which the samples were placed into the furnace for isothermal oxidation. During oxidation, the samples were removed at 10 min intervals, allowed to cool naturally for approximately 10 min, and then weighed to record the mass values (m_j). Based on a high-temperature oxygen-blocking evaluation model [29,30], the oxidation resistance and oxygen-barrier performance of coatings with different HfSi_2 contents were systematically assessed. The fabrication process and oxidation testing procedure are schematically illustrated in Fig. 1.

$$W = \frac{m_j - m_0}{S} \quad (1)$$

$$N = \frac{m_j - m_{j-1}}{S \times t} \quad (2)$$

$$W_j^2 = \alpha_0 t + b \quad (3)$$

$$\eta = \left[1 - \frac{(W_{s,j} - W_{s,0}) - (W_{c,j} - W_{c,0})}{W_{p,0} - W_{p,j}} \right] \times 100\% \quad (4)$$

$$\alpha_s = \frac{1}{n} \sum_{j=1}^n \frac{(W_{s,j} - W_{s,0}) - (W_{c,j} - W_{c,0})}{W_{p,0} - W_{p,j}} \quad (5)$$

$$\alpha_m = \frac{1}{n-4} \sum_{j=5}^n \frac{W_{s,j} - W_{s,j-1}}{t} \quad (6)$$

$$M = \frac{1}{n-3} \sum_{j=4}^n \frac{N_{c,j} - N_{s,j}}{N_{p,j}} \times 100\% \quad (7)$$

$$V = \frac{1}{n-3} \sum_{j=4}^n \frac{(W_{s,j} - W_{s,0}) - (W_{c,j} - W_{c,0})}{jt} \quad (8)$$

where W denotes mass change, N represents oxidation rate, η is the protection efficiency, α_s and α_m correspond to structural and inert factors, respectively, M is oxygen permeability, and V denotes carbon loss rate. W_j is the mass increment at time j , α_0 is the activation factor, and b is a constant. $W_{p,0}$, $W_{s,0}$, and $W_{c,0}$

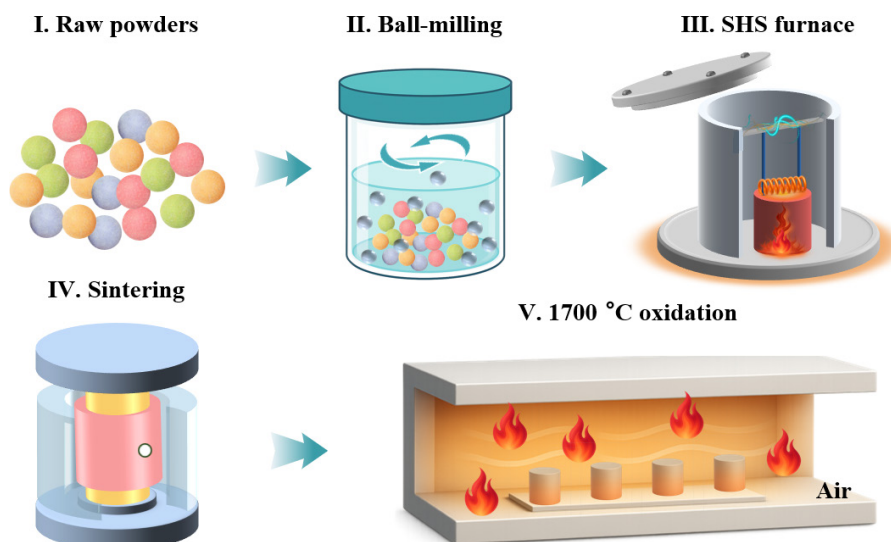


Fig. 1 Schematic of coating preparation and oxidation process at 1700°C .

represent the initial mass per unit area of the graphite substrate, bulk ceramic, and coating samples, respectively. W_{pj} , W_{sj} and W_{cj} are the corresponding mass changes per unit area at the j -th measurement, while N_{pj} , N_{sj} and N_{cj} denote the associated oxidation rates. t is the oxidation time, S is the initial surface area of the specimen, and j ranges from 1 to 10.

2.4 Characterizations

Phase identification of the SHS-derived powders and oxidation products was performed using an X-ray diffractometer (XRD; Bruker D8, Bruker, Germany). Surface and cross-sectional morphologies before and after oxidation were examined by a scanning electron microscope (SEM; Gemini SEM 360, Oberkochen, Germany) equipped with an energy-dispersive spectrometer (EDS; UltimMax 65, Oxford Instruments, UK) to analyze the phase constitution and elemental distribution. An electron probe microanalyzer (EPMA; JXA-8530F, JEOL, Japan) was further employed to analyze the elemental compositions of the sintered samples and oxide scales. A transmission electron microscope (TEM; Tecnai G2 F20, FEI, USA) operated at an accelerating voltage of 150 kV was used to investigate the crystal structure and microstructural features of SHS-derived powders and oxidation-induced glassy phases. For TEM observation of the oxide scale, surface oxide fragments were gently scraped from the oxidized samples, ground and dispersed in alcohol for 30 min, and then allowed to stand for 30 min. The supernatant containing fine fragments was subsequently collected, dropped onto a carbon-supported copper grid, and dried naturally before TEM examination. The bulk density and open porosity of the as-sintered coatings before oxidation were determined according to the Archimedes drainage method. Thermogravimetric (TG) measurements were carried out using a TG analyzer (STA449F5, Netzsch, Germany). Approximately 10 mg of each HfB_2 - MoSi_2 - HfSi_2 powder sample was tested in dry air from room temperature to 1200 °C. Before heating, each sample was held at room temperature for 20–30 min, heated at 10 °C/min, and finally cooled to room temperature at approximately 15–20 °C/min. The three-dimensional surface topography of the coatings after oxidation was examined using a 3D surface profiler (ST400, NANOVEA, USA). Thermodynamic calculations of possible oxidation reactions were conducted using HSC Chemistry software.

2.5 Computational models and methods

To examine the effect of Hf incorporation on the structural stability of SiO_2 , periodic supercell models were constructed based on the β -quartz SiO_2 crystal structure reported by Wang *et al.* [31], which was used therein as a structural model for amorphous SiO_2 because β -quartz and amorphous SiO_2 possess very similar local structures and densities. Hf atoms were introduced into the SiO_2 lattice at interstitial ($\text{SiO}_2 + \text{inHf}$ structure) and substitutional sites ($\text{SiO}_2 + \text{suHf}$ structure), followed by atomic relaxation and lattice optimization, and the formation energies of different configurations were calculated. First-principles calculations were performed using the CASTEP package. The exchange–correlation interaction was described by the generalized gradient approximation (GGA) with the PW91 functional. A plane-wave cutoff energy of 400 eV was employed, and the total energy convergence criterion was set to 1×10^{-5} eV/atom. The formation energies of the $\text{SiO}_2 + \text{suHf}$ and $\text{SiO}_2 + \text{inHf}$ structures were calculated as Eqs. (9) and (10):

$$E_{\text{suHf}}^f = E_{\text{SiO}_2 + \text{suHf}} - E_{\text{SiO}_2} - E_{\text{Hf}} + E_{\text{Si}} \quad (9)$$

$$E_{\text{inHf}}^f = E_{\text{SiO}_2 + \text{inHf}} - E_{\text{SiO}_2} - E_{\text{Hf}} \quad (10)$$

where E_{suHf}^f and E_{inHf}^f denote the formation energies of $\text{SiO}_2 + \text{suHf}$ and $\text{SiO}_2 + \text{inHf}$ structures, respectively. $E_{\text{SiO}_2 + \text{suHf}}$, $E_{\text{SiO}_2 + \text{inHf}}$, and E_{SiO_2} correspond to the total energies of SiO_2 containing substitutional Hf, interstitial Hf, and pristine SiO_2 , respectively. E_{Si} and E_{Hf} represent the chemical potentials of Si and Hf, respectively.

To further investigate the influence of Hf doping on SiO_2 interface binding behavior, interface models were constructed using $\text{SiO}_2(001)$ and Hf-doped $\text{SiO}_2(110)$ surfaces, which were selected because this interface combination gives a small lattice mismatch of 1.34%. The top vacuum layer was 10 Å, and the interface spacing was approximately 2 Å. Structural optimization of the interfaces was also carried out within the CASTEP framework, employing the CA-PZ functional under the local density approximation (LDA), while all other computational parameters were kept identical to those used in the bulk SiO_2 supercell calculations. The ideal interface binding energy (E_{adh}) was calculated as Eq. (11):

$$E_{\text{adh}} = E_{\text{int}} - (E_{\text{sub}} + E_{\text{coat}}) / (2S) \quad (11)$$

where E_{int} denotes the total energy of the interface at equilibrium, E_{sub} represents the energy of the pristine $\text{SiO}_2(001)$ surface, E_{coat} corresponds to the energy of the pristine or Hf-doped SiO_2 (110) surface, and S is the interfacial area.

3 Results and discussion

3.1 Morphology and structure of SHS-derived powders and coatings

The one-step SHS route enabled rapid synthesis of HfB_2 - MoSi_2 - HfSi_2 composite powders. XRD (Fig. 2) indicates that all samples with different HfSi_2 contents consist exclusively of HfB_2 (PDF#38-1398), MoSi_2 (PDF#41-0612), and HfSi_2 (PDF#38-1373), with no discernible secondary phases detected. This demonstrates that within the selected compositional range, the SHS pathway yields a stable and well-controlled phase assemblage. Such phase selectivity is consistent with the transient ultrahigh temperatures and intense exothermic nature of SHS reactions, which favor rapid transformation along thermodynamically stable routes toward the target products [32].

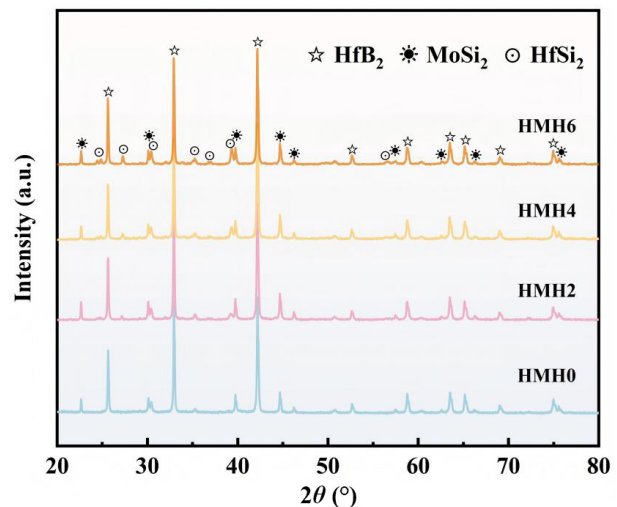


Fig. 2 XRD pattern of HfB_2 - MoSi_2 - HfSi_2 alloy powders synthesized via a one-step SHS process.

SEM observations and particle size statistics of SHS-derived composite powders after ball milling (Fig. 3) reveal a systematic reduction in average particle size from 712.76 nm for HMH0 to 497.60 nm for HMH6 as the HfSi_2 content increases, accompanied by a pronounced narrowing of the size distribution. The concurrent particle refinement and improved size uniformity indicate that HfSi_2 introduction effectively suppresses excessive grain growth during the SHS process [28], which is expected to favor subsequent sintering by increasing interparticle contact and shortening diffusion distances during densification. Elemental mapping further confirms a homogeneous distribution of Hf, B,

Mo, and Si within the composite powders with no evident compositional segregation (Figs. 3(a2)–3(d2)), suggesting a uniformly coupled microstructural feature characteristic of SHS-derived multiphase powders, consistent with the intergrowth behavior commonly reported in SHS-derived boride-silicide composite systems [25], and providing a chemically uniform starting structure for subsequent densification and oxidation processes.

TEM analysis further verifies the multiphase coexistence and elemental uniformity of the powders (Fig. 4). High-resolution transmission electron microscopy (HRTEM) images clearly

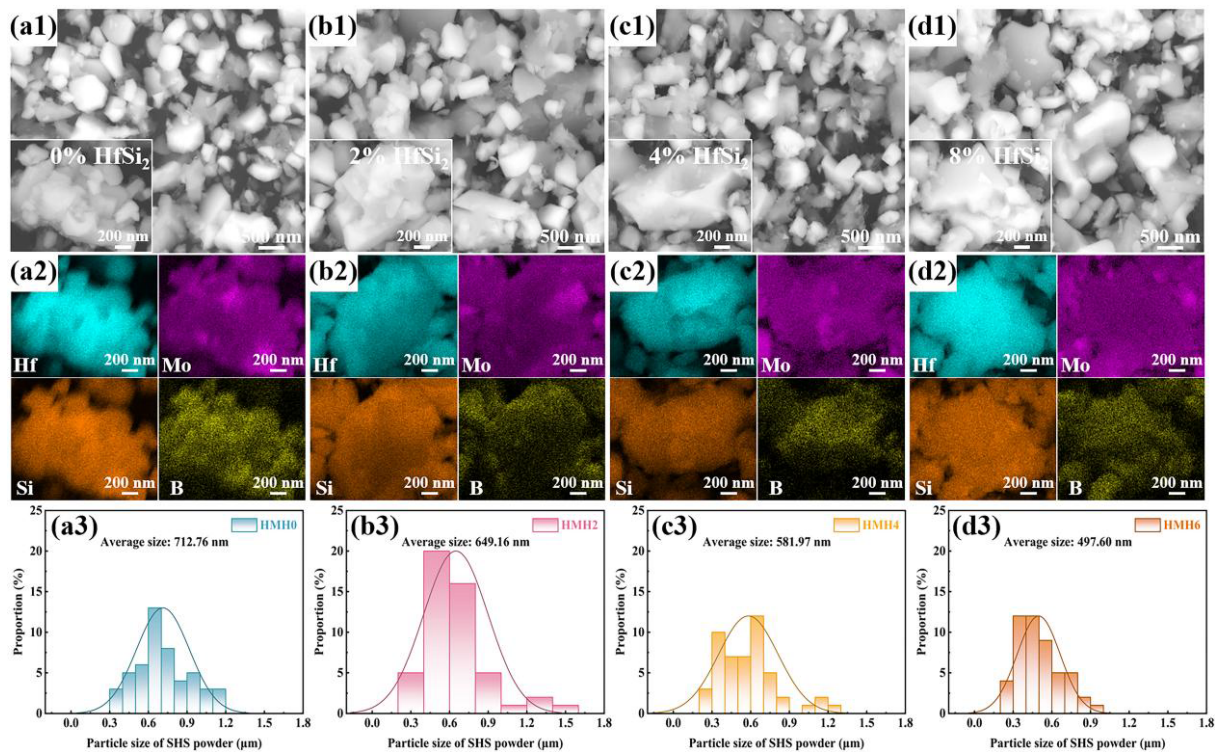


Fig. 3 SEM images and corresponding EDS element mappings of SHS-derived composite powders after ball milling: (a1) HMH0, (b1) HMH2, (c1) HMH4, (d1) HMH6; (a2–d2) corresponding EDS element maps of the enlarged regions in (a1–d1); (a3–d3) particle size distribution.

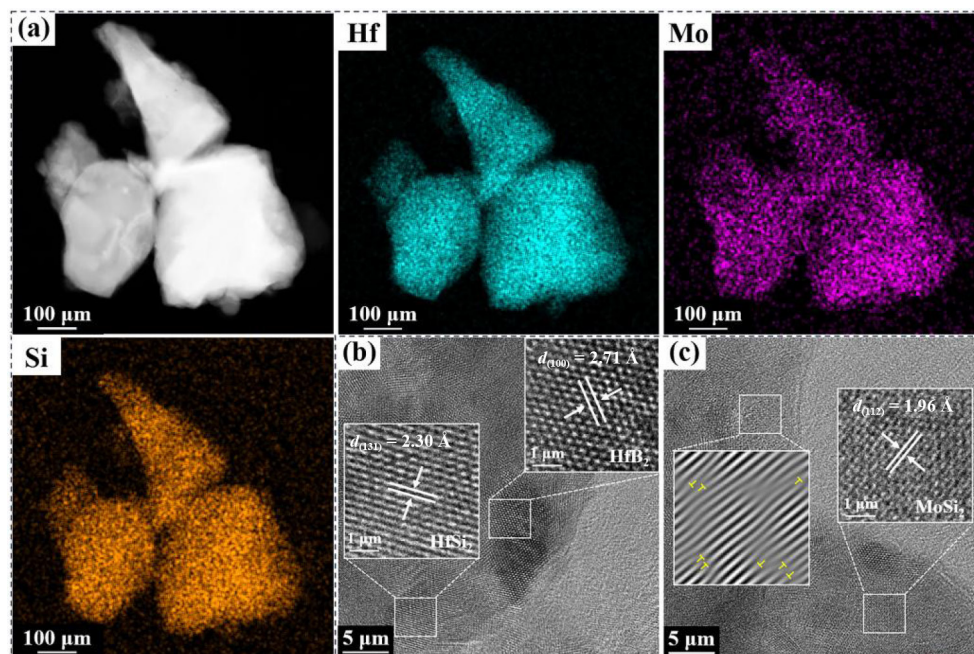


Fig. 4 (a) TEM image and corresponding EDS mappings of HfB_2 - MoSi_2 - HfSi_2 powders; (b, c) HRTEM images.

resolve lattice fringes corresponding to HfB_2 , MoSi_2 , and HfSi_2 , in agreement with the XRD results. Localized dislocations are observed in certain regions (Fig. 4(c)), which are likely associated with defect structures introduced by the rapid heating and cooling inherent to SHSs. These defects can provide a driving force for particle rearrangement and densification during subsequent sintering [33].

3.2 Densification behavior of SPS-fabricated coatings

After SPS treatment at 1400 °C under 30 MPa, all HfB_2 - MoSi_2 - HfSi_2 coatings with different HfSi_2 contents exhibit crack-free cross-sections and continuous, well-bonded interfaces with the graphite substrate (Fig. 5), indicating that this processing route enables robust coating-substrate integration. The surface morphologies (Fig. 6) show that coatings with low HfSi_2 contents (HMH0 and HMH2) retain a considerable number of irregular

pores. To further evaluate the densification state, the density and open porosity of the as-sintered coatings were measured by the Archimedes drainage method. The measured densities of HMH0, HMH2, HMH4, and HMH6 are 8.594, 8.709, 8.814, and 8.878 g/cm³, respectively, while their corresponding open porosities are 0.31%, 0.28%, 0.08%, and 0.21%, respectively. When the HfSi_2 content reaches 4 vol%, the surface of the HMH4 coating becomes markedly more continuous, with pores between the HfB_2 skeletal framework effectively filled by silicide phases (Fig. 6(c1)). Together with the low open porosity of HMH4, this suggests that an appropriate amount of HfSi_2 promotes particle rearrangement and pore elimination during SPS, possibly through softening or localized liquid-phase effects [34]. In contrast, further increasing the HfSi_2 content to 6 vol% leads to an increase in surface defects and interparticle gaps (Fig. 6(d1)), with the open porosity increasing again to 0.21%. Although HMH6 exhibits the

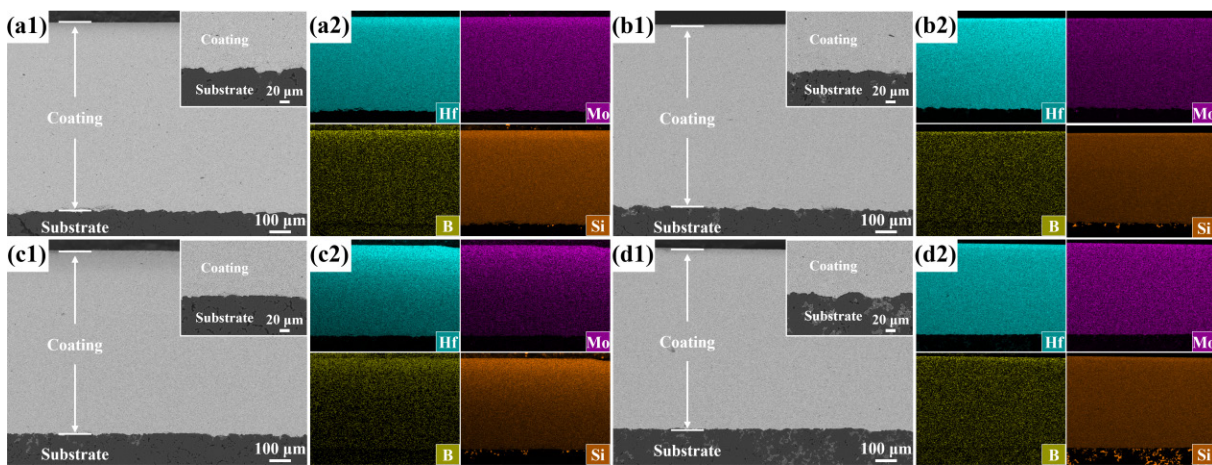


Fig. 5 Cross-sectional morphology of coatings after SPS sintering: (a1) HMH0, (b1) HMH2, (c1) HMH4, (d1) HMH6; (a2)–(d2) corresponding EDS element mappings of (a1)–(d1).

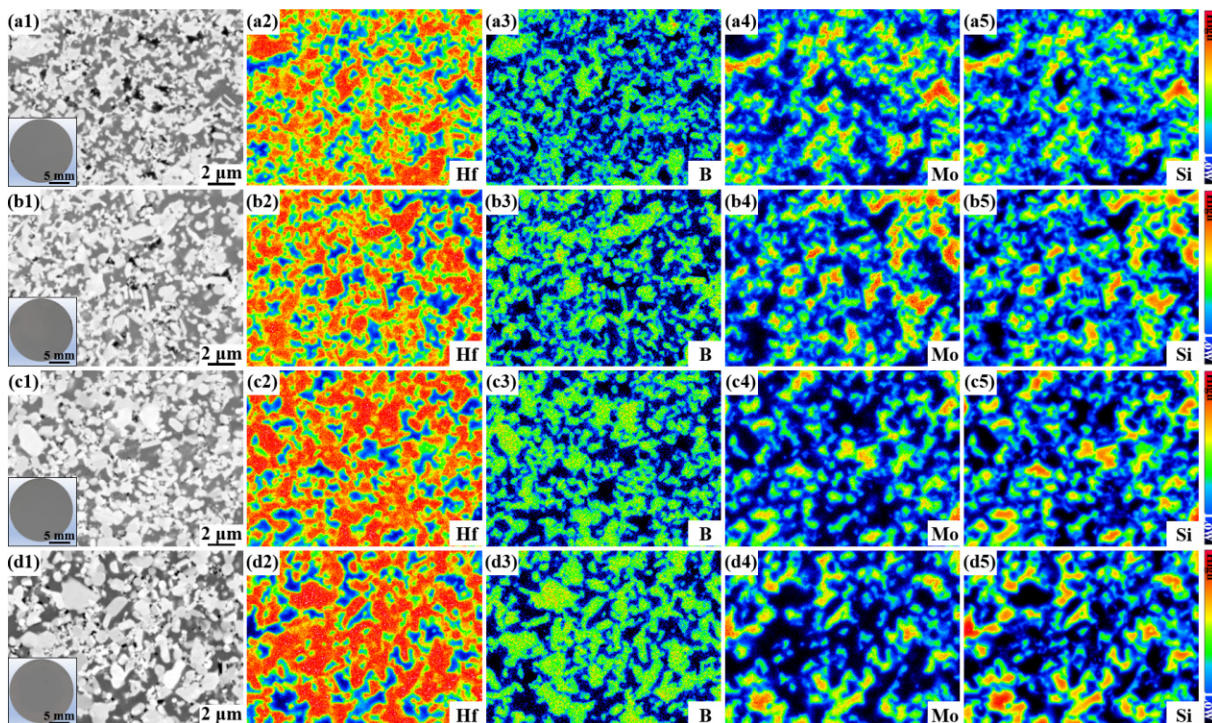


Fig. 6 Surface morphology and EPMA spectra of samples after sintering: (a1–a5) HMH0, (b1–b5) HMH2, (c1–c5) HMH4, and (d1–d5) HMH6.

highest measured density, the increased open porosity indicates that excessive HfSi₂ does not further improve local densification but instead introduces additional pore defects. This indicates that excessive filler phases destabilize structural rearrangement and reduce overall densification [35].

EPMA results show that all functional phases are uniformly distributed within the coatings, with MoSi₂ and HfSi₂ exhibiting an interwoven and interconnected spatial configuration (Figs. 6(a2)–6(d5)). Such connectivity facilitates the formation of a continuous initial structural barrier and provides favorable pathways for glass formation, migration, and sealing during subsequent oxidation. Cross-sectional backscattered electron (BSE) and EDS analyses further reveal a pronounced reduction in the number of internal pores with increasing HfSi₂ content (Fig. 5), confirming that moderate HfSi₂ incorporation effectively optimizes the coating microstructure during SPS.

3.3 High-temperature oxidation behavior of HfB₂-MoSi₂-HfSi₂

3.3.1 Oxidation behavior of SHS powders

TG-differential scanning calorimetry (DSC) analyses were performed to evaluate the influence of HfSi₂ on the oxidation behavior of the SHS powders (Fig. 7). All samples exhibit a characteristic oxidation sequence typical of boride-silicide systems, including an initial plateau, multiple successive mass-gain stages, and a mass-loss stage at elevated temperatures. Compared with the undoped powder, HfSi₂-containing samples show a delayed onset of oxygen uptake and reduced mass loss at high temperatures, indicating a moderated oxidation process. The DSC curves reveal that oxidation is predominantly exothermic throughout the investigated temperature range (Fig. 7(b)),

consistent with the thermodynamic characteristics of the reactions.

Thermodynamic calculations (Fig. 7(d)) indicate that HfSi₂ possesses a high reaction driving force at the early stages of oxidation, allowing it to participate preferentially while simultaneously supplying Si and Hf species. This promotes the early formation of high-melting-point HfO₂ and facilitates the development of Hf-rich borosilicate composite oxide films. Owing to their higher viscosity and thermal stability, these films effectively suppress volatilization of low-melting oxides such as B₂O₃ and MoO₃. This behavior is consistent with the smoother mass-change trends observed in the TG curves, demonstrating that HfSi₂ regulates oxidation pathways and mitigates high-temperature volatilization at the powder scale.

3.3.2 Isothermal oxidation at 1700 °C

Figure 8 shows the XRD patterns of the HfB₂-MoSi₂-HfSi₂ coatings after isothermal oxidation at 1700 °C. Diffraction peaks from the original constituents disappear completely, and the oxide scales consist mainly of HfSiO₄ (PDF#77-1759), HfO₂ (PDF#78-0050), and MoB (PDF#51-0940). No distinct SiO₂ peaks are observed, indicating that silica is predominantly present in an amorphous glassy state [36]. HfSiO₄ forms through solid-state diffusion reactions between HfO₂ and SiO₂ at high temperatures and, together with HfO₂, provides a high-melting-point framework that enhances oxide-scale stability under high-temperature conditions [37].

To eliminate interference from graphite oxidation, dense ceramic bulks with identical compositions were first subjected to isothermal oxidation at 1700 °C (Fig. 9). As calculated using Eqs. (1) and (2), all samples exhibit rapid mass gain during the initial 0–30 min, followed by a marked decrease and stabilization

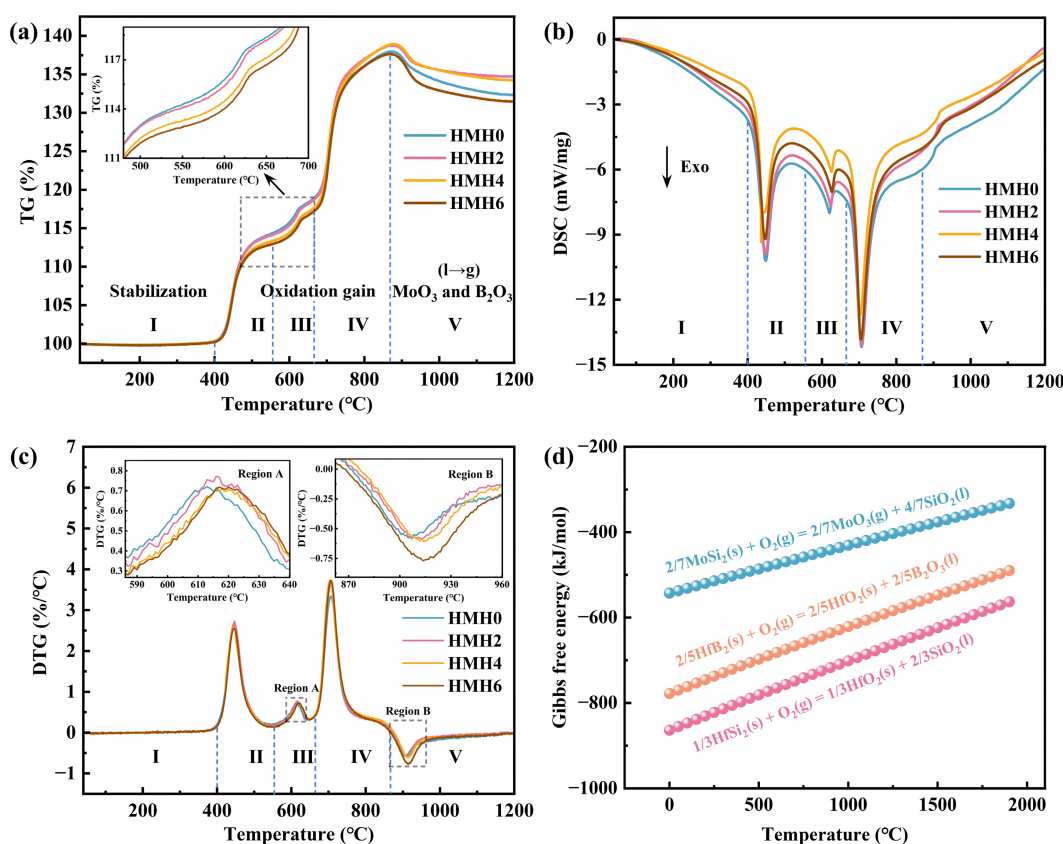


Fig. 7 TG oxidation of SHS powders: (a) TG curves, (b) DSC curves, and (c) DTG curves. (d) Gibbs free energy change curve based on 1 mol O₂ reaction.

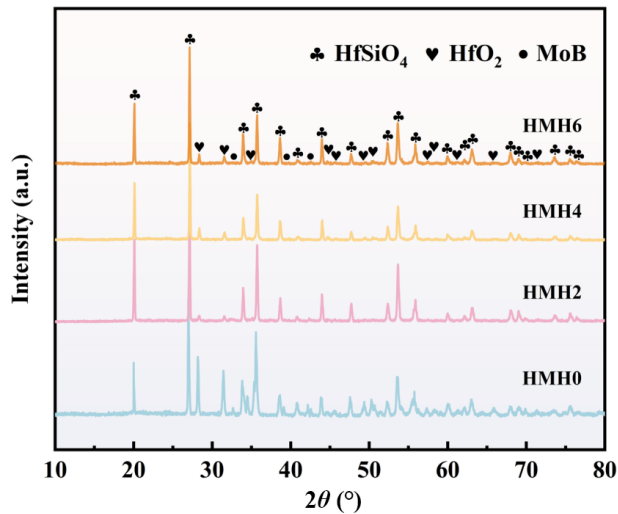


Fig. 8 XRD patterns of coating after oxidation at 1700 °C.

of the mass-gain rate as the oxide scale densifies. Among the samples, HMH4 shows the lowest total mass gain of $0.22 \times 10^{-2} \text{ g}\cdot\text{cm}^{-2}$, representing a 55.10% reduction relative to HMH0. Oxidation rate analyses (Figs. 9(c) and 9(d)) reveal a nonmonotonic dependence on HfSi_2 content, with both peak and average rates decreasing initially and then increasing. HMH4 exhibits the lowest oxidation rate, whereas HMH6 shows a pronounced rebound, indicating the existence of an optimal HfSi_2 content. By fitting the mass-gain curves (Fig. 10(a)) and extracting the corresponding activation factors using Eq. (3) (Fig. 10(b)), it is found that all HfSi_2 -containing samples exhibit lower oxidation sensitivity than the

undoped system, with HMH4 showing the minimum value. This behavior is consistent with the oxidation trends observed in the powder TG analyses, further indicating that HfSi_2 effectively regulates oxidation reaction kinetics across different scales.

In coating systems, simultaneous mass loss from graphite oxidation and mass gain from ceramic oxidation complicate the direct interpretation of mass-change curves. To decouple these effects, structural and inert factors calculated using Eqs. (5) and (6) were introduced to separately evaluate the intrinsic structural barrier of the coating and the oxygen-blocking capability of the oxide glass, respectively. Lower structural factors correspond to denser and more continuous initial barriers, whereas lower inert factors indicate stronger suppression of oxygen diffusion by the glass layer [38]. As shown in Fig. 10(c), the protection efficiency calculated using Eq. (4) during the early oxidation stage is dominated by the intrinsic structural barrier. The HMH4 coating exhibits the lowest structural factor (0.051%), which is 63.57% lower than the value reported by Zhu *et al.* [13], indicating a substantially improved structural oxygen-blocking capability of the HfB_2 -based coating.

As oxidation proceeds, the protection efficiency increases and stabilizes, becoming governed primarily by the glass sealing layer formed during oxidation. The inert factors of HMH0, HMH2, HMH4, and HMH6 are 0.43×10^{-6} , 0.36×10^{-6} , 0.19×10^{-6} , and $0.46 \times 10^{-6} \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, respectively, with HMH4 showing the strongest suppression of oxygen diffusion. For this sample, the inert factor is 77.04% and 74.32% lower than those reported by Ji *et al.* [27] and Kan *et al.* [30], respectively, suggesting that the glass sealing layer formed in HMH4 provides a more effective barrier to oxygen diffusion. Owing to the optimal synergy

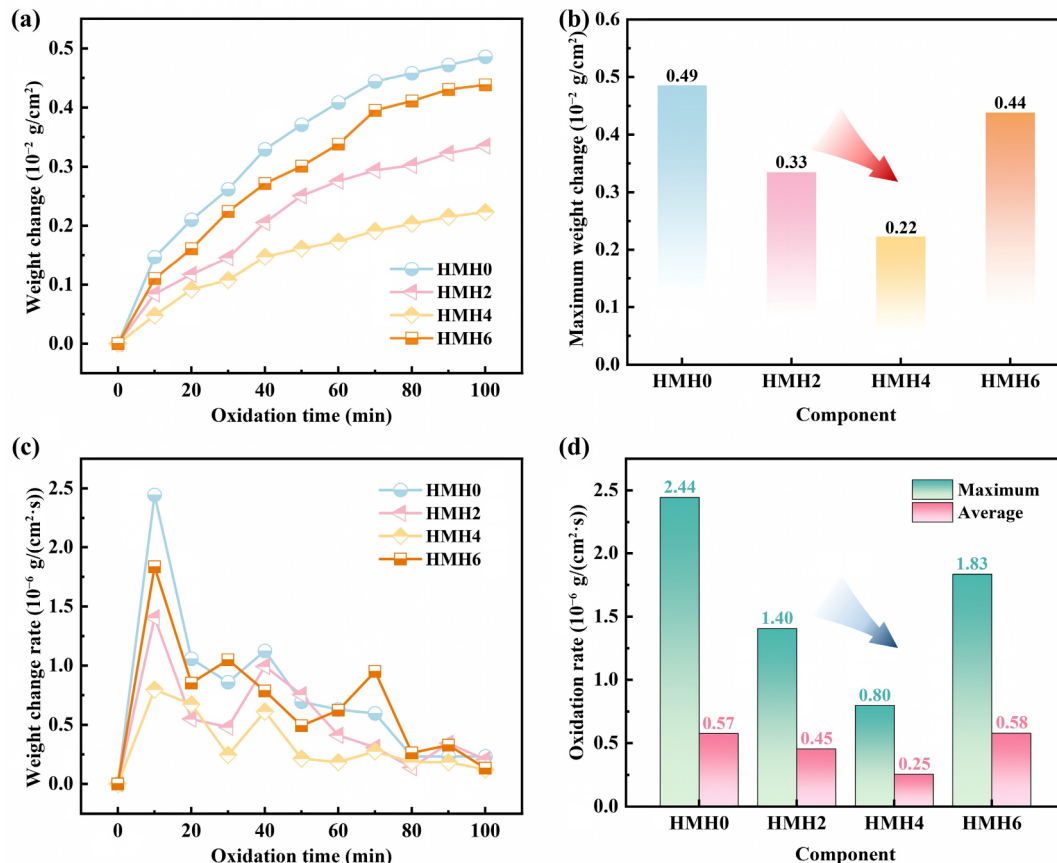


Fig. 9 Oxidation of HfB_2 - MoSi_2 - HfSi_2 ceramic bulk at 1700 °C: (a) mass change curves, (b) histogram of maximum mass increase, (c) oxidation rate curves, and (d) histogram of oxidation rate.

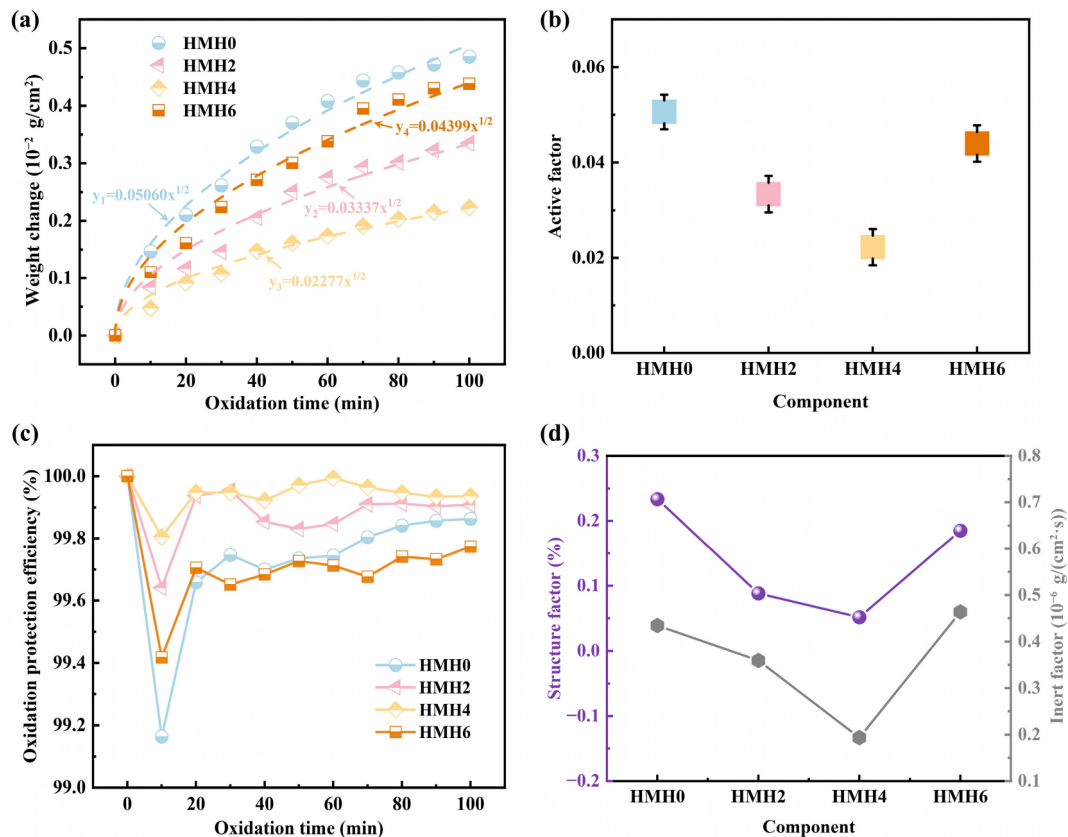


Fig. 10 Oxidation of samples at 1700 °C: (a) fitted mass change curve, (b) activation factor, (c) protection efficiency curve, and (d) structure-inert factor curve.

between structural integrity and glass sealing, HfSi₄ achieves a steady-state protection efficiency of 99.94%, significantly outperforming the other samples.

The post-oxidation surface morphologies provide direct structural evidence supporting the above analysis (Fig. 11). For the HfSi₀ coating without HfSi₂ addition, the surface is characterized by abundant blocky Hf oxide particles accompanied by pronounced cavities (Figs. 11(a1) and 11(a2)), indicating that the glass film formed during oxidation fails to achieve continuous sealing. At higher magnification, residual pores and microcracks are still visible within the surface oxide scale (Fig. 11(a3)), further confirming the incomplete sealing of oxidation-induced defects. A high fraction of rigid Hf oxides locally increases the viscosity of the glass phase, thereby restricting its flow and reconstruction at elevated temperatures and reducing its ability to heal defects [39]. After introducing HfSi₂, the amount of surface Hf oxides decreases markedly, and overall oxidation consumption is suppressed. However, in the HfSi₂ sample, localized cavity enrichment is still observed, suggesting that sealing behavior remains spatially nonuniform at this stage.

When the HfSi₂ content is increased to 4 vol%, the Hf oxides in the oxidation products become further refined and are uniformly dispersed within the glass matrix. The coating surface appears smooth and continuous, without obvious open cracks or large cavities (Figs. 11(c1) and 11(c2)). At higher magnification, refined oxide particles are embedded in a continuous glassy matrix (Fig. 11(c3)), indicating that defect filling and surface sealing are effectively promoted during oxidation. EDS point analysis of the gray glassy matrix shows that this continuous phase is mainly composed of Si and O, with a small amount of Hf detected, whereas the bright oxide particles are Hf-rich (Fig. 11(e)). The XRD results in Fig. 8 further confirm that the Hf-rich crystalline phases in the oxide scale are mainly HfO₂ and HfSiO₄. As

reported by Zhuang *et al.* [40], hard ceramic oxides embedded in glass films can act as crack-pinning sites and provide skeletal support, while hardness mismatch with SiO₂ enhances energy dissipation during crack propagation, thereby retarding crack initiation and growth. Meanwhile, SiO₂ exhibits a certain degree of flowability at high temperatures, enabling microcracks to be filled during self-healing. Compared with the stepwise formation and reconstruction of oxidation products in the HfB₂-MoSi₂ system, HfSi₂ incorporation promotes the early *in situ* formation of an Hf-Si-O multiphase sealing layer, shortening the transitional stage dominated by discrete phases [41]. In addition, the presence of MoB within the oxide scale enhances the chemical stability of the glass film, further improving high-temperature oxidation resistance [42].

In contrast, when the HfSi₂ content is further increased to 6 vol%, the surface oxide scale becomes rough and uneven (Fig. 11(d)). Excessive HfSi₂ leads to volume expansion, which damages the continuity of the seal and weakens the adaptive reconstruction ability of the glass phase at high temperature [43], resulting in a reduction in the stability of the oxygen-blocking structure and ultimately a reduction in the oxidation resistance (Fig. 10(c)).

Three-dimensional surface profilometry yields results consistent with the morphological evolution described above (Fig. 12). The HfSi₀ sample without HfSi₂ exhibits the highest surface roughness ($S_a = 74.45 \mu\text{m}$) and a broad particle size distribution, reflecting a highly nonuniform accumulation of coarse oxidation products. Such features readily promote local agglomeration and compositional segregation within the glass film, creating potential oxygen diffusion pathways [44]. In contrast, the surface roughness of HfSi₄ is significantly reduced ($S_a = 41.04 \mu\text{m}$), and the particle size distribution becomes markedly narrower. This indicates that an appropriate HfSi₂

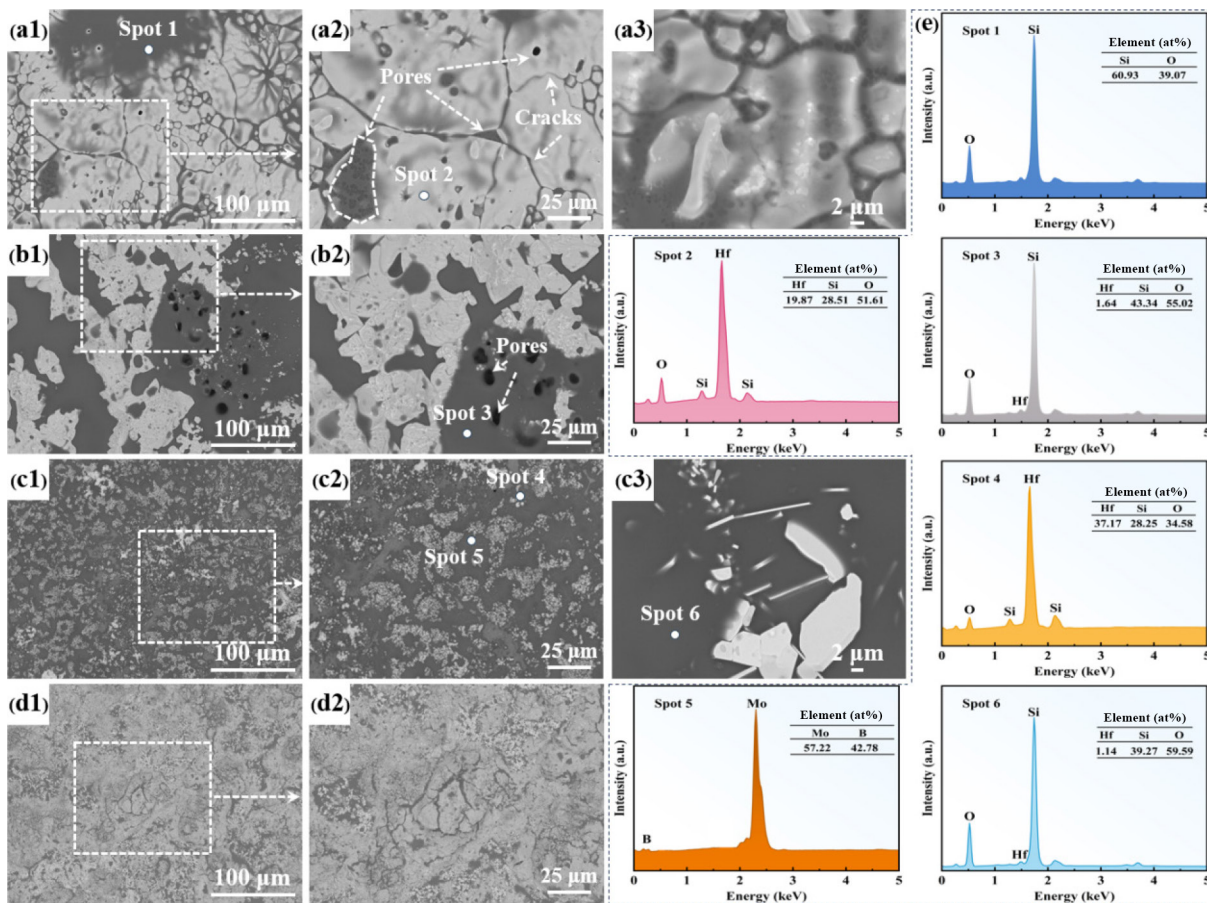


Fig. 11 BSE images of coating surface after oxidation: (a1) HMH0, (b1) HMH2, (c1) HMH4, and (d1) HMH6; (a2–d2) enlarged views of (a1–d1); high-magnification BSE images of (a3) HMH0 and (c3) HMH4; (e) EDS point analysis.

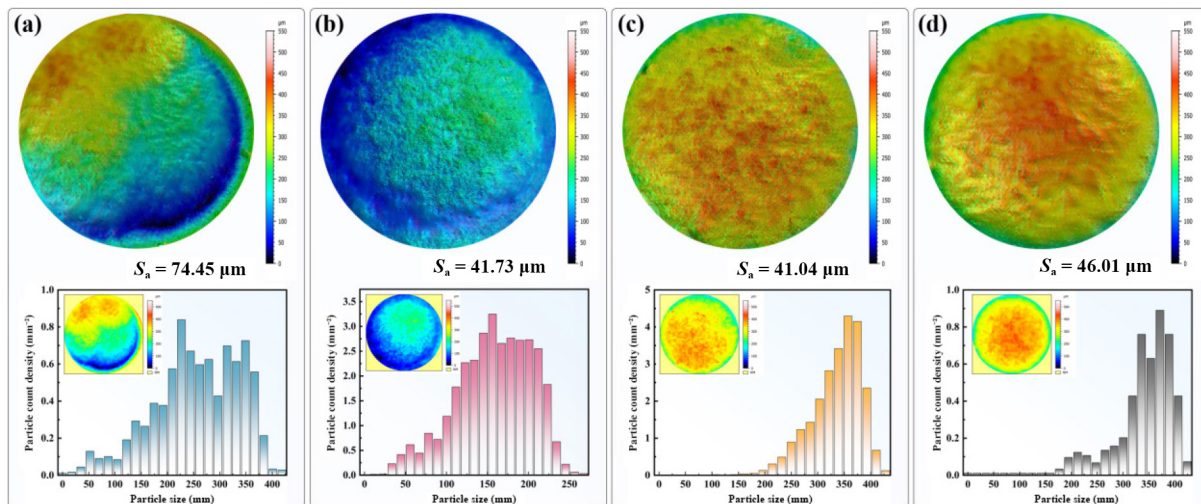


Fig. 12 3D surface topography and particle size distribution of coating after oxidation: (a) HMH0, (b) HMH2, (c) HMH4, and (d) HMH6.

content promotes uniform precipitation of oxidation products and facilitates the formation of a dense, continuous sealing structure during oxidation, thereby enhancing both the local defect-healing capability and overall oxygen-blocking efficiency.

To further elucidate the compositional characteristics of the oxide scales, EPMA results for the HMH0 and HMH4 coatings are presented in Fig. 13. After oxidation, the HMH0 coating exhibits a typical island-like accumulation of Hf oxides, with strong spatial overlap between Hf and O signals, indicating that

the scale is dominated by discontinuous HfO₂ aggregates. In contrast, Si is sparsely and unevenly distributed, preventing the formation of a continuous silicate barrier layer. By comparison, the HMH4 coating displays a uniform interwoven distribution of Hf, Si, and O, forming a dense and continuous Hf–Si–O-based glass sealing layer. The introduction of HfSi₂ promotes the cooperative formation of Hf oxides and borosilicate glass, driving a structural transition of the oxide scale from discrete oxide-particle domination to a continuous glass-phase-dominated

network barrier, thereby significantly enhancing scale integrity and oxygen-blocking performance [45]. Local enrichment of Mo in the HMH4 sample further indicates that, in addition to forming volatile MoO_3 , part of the Mo remains as solid MoB incorporated into the glass structure (Figs. 8 and 11), which contributes to improved chemical stability of the oxide scale.

TEM analysis provides further insight into the microstructure of the oxide scales (Fig. 14). Transmission observations reveal pronounced overlap of Hf and O in localized regions, while more extensive overlap of Hf, Si, and O is observed across broader areas. High-resolution TEM images clearly resolve lattice fringes corresponding to HfSiO_4 and HfO_2 , consistent with the XRD

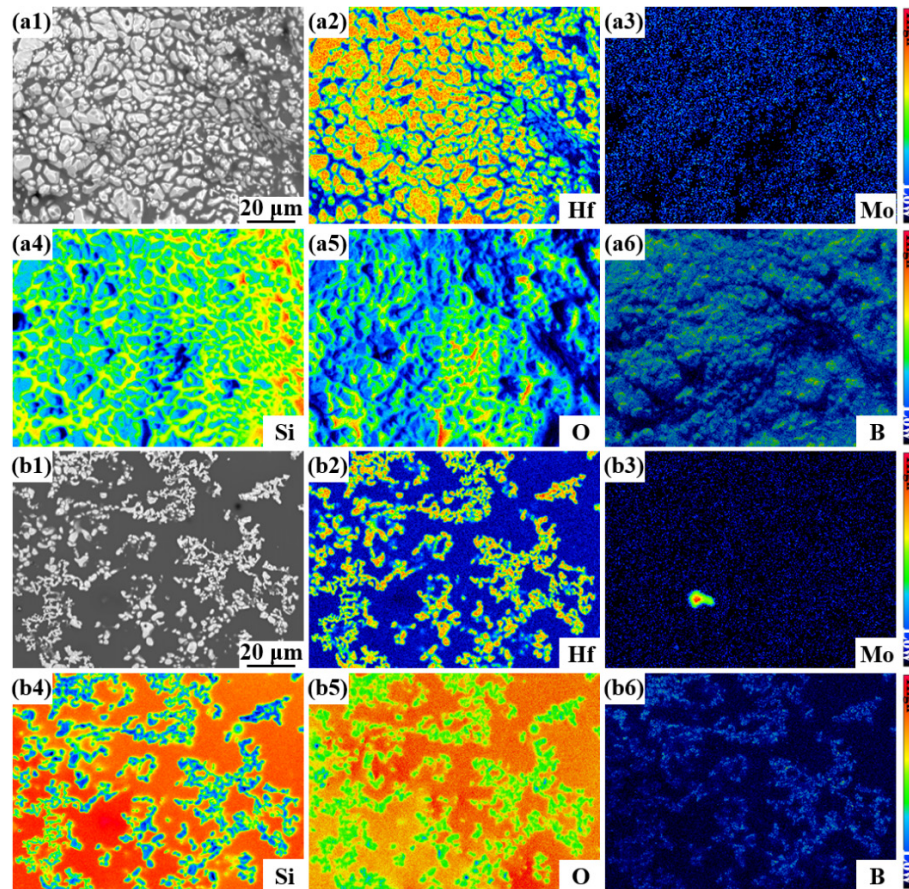


Fig. 13 Surface morphology and EPMA elemental mappings of coatings after oxidation at 1700 °C: (a1–a6) HMH0, (b1–b6) HMH4.

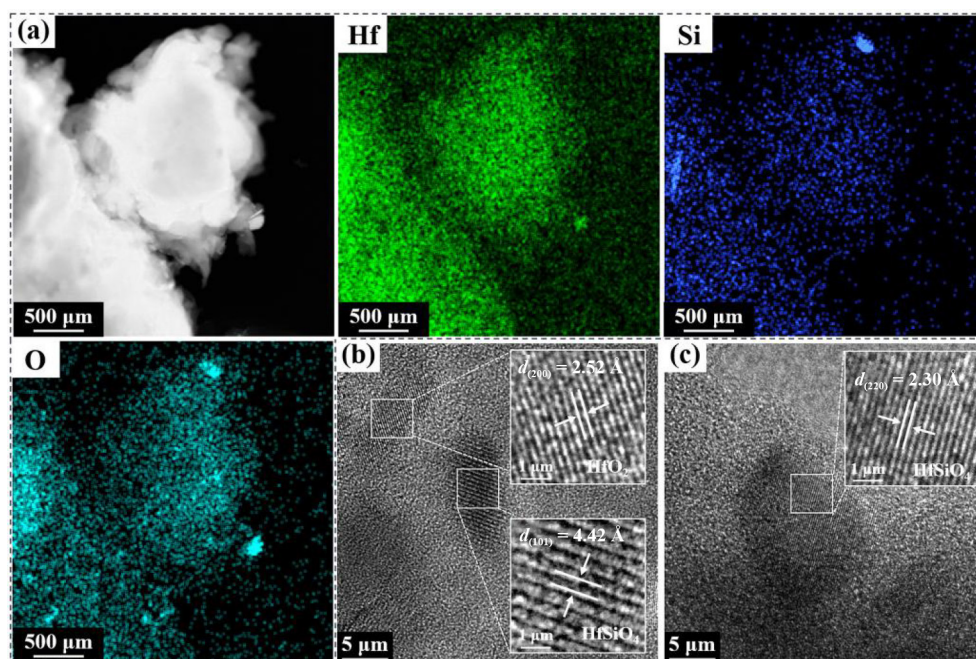


Fig. 14 (a) TEM images of oxide scale with corresponding EDS elemental maps; (b, c) HRTEM images of nanocrystalline HfSiO_4 and HfO_2 .

results and confirming the structural stability of the high-melting-point compounds formed during oxidation.

To further clarify the influence of HfSi_2 content on oxidation protection mechanisms, cross-sectional BSE images and corresponding oxide-scale thickness statistics after oxidation at 1700 °C are shown in Fig. 15. All samples exhibit a typical layered architecture, consisting of an outer glass sealing layer formed during oxidation and an inner region retaining the original coating structure. The tight bonding between these layers, without apparent interfacial delamination, indicates good structural integrity under high-temperature oxidation.

Significant differences in oxide-scale thickness are observed among coatings with different HfSi_2 contents. The median oxide-scale thicknesses for HMH0, HMH2, HMH4, and HMH6 are 44.48, 42.39, 29.97, and 39.89 μm , respectively, showing a nonmonotonic dependence on the HfSi_2 content. The HMH0 coating exhibits the largest and most dispersed thickness distribution, with pronounced cavities visible in localized regions (Fig. 15(a2)). Such porous features are commonly associated with the hindered escape of volatile species such as B_2O_3 and MoO_3 during oxidation, whose sustained release induces pore accumulation within the scale and compromises sealing compactness [46].

With HfSi_2 incorporation, the oxide-scale thickness decreases, and its distribution becomes progressively narrower for HMH2 and HMH4. Notably, HMH4 exhibits the lowest median thickness and a dense, continuous near-surface structure without observable

cavities. This behavior is consistent with the lowest mass gain and oxidation rate observed for HMH4 (Fig. 9), indicating more effective suppression of oxidation reactions. However, when the HfSi_2 content is further increased to 6 vol%, the oxide-scale thickness increases again, and its distribution broadens, reflecting reduced growth uniformity. This behavior is likely associated with oxide-scale expansion and localized growth imbalance induced by excessive HfSi_2 [47].

To quantify the effectiveness of the coating in suppressing oxygen permeation and protecting the substrate, the oxygen permeability and carbon loss rate were calculated based on Eqs. (7) and (8), as shown in Fig. 16(a). The HMH0 coating exhibits the highest values for both parameters, indicating limited suppression of oxygen diffusion. With increasing HfSi_2 content, oxygen transport toward the substrate is effectively impeded, leading to a concomitant reduction in substrate oxidation consumption. At an HfSi_2 content of 4 vol%, the oxygen permeability and carbon loss rate of the HMH4 coating decrease to 0.023% and $0.047 \times 10^{-6} \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, respectively, corresponding to reductions of 61.67% and 75.26% relative to the undoped system. As a result, the average protection efficiency reaches 99.94%.

In contrast, further increasing the HfSi_2 content to 6 vol% leads to a pronounced rebound in oxygen permeability and carbon loss rate, reaching 0.19% and $0.28 \times 10^{-6} \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, respectively, with the corresponding average protection efficiency decreasing to 99.71%. Combined with the surface morphology observations (Fig. 11(d1)), these results suggest that excessive HfSi_2 weakens the

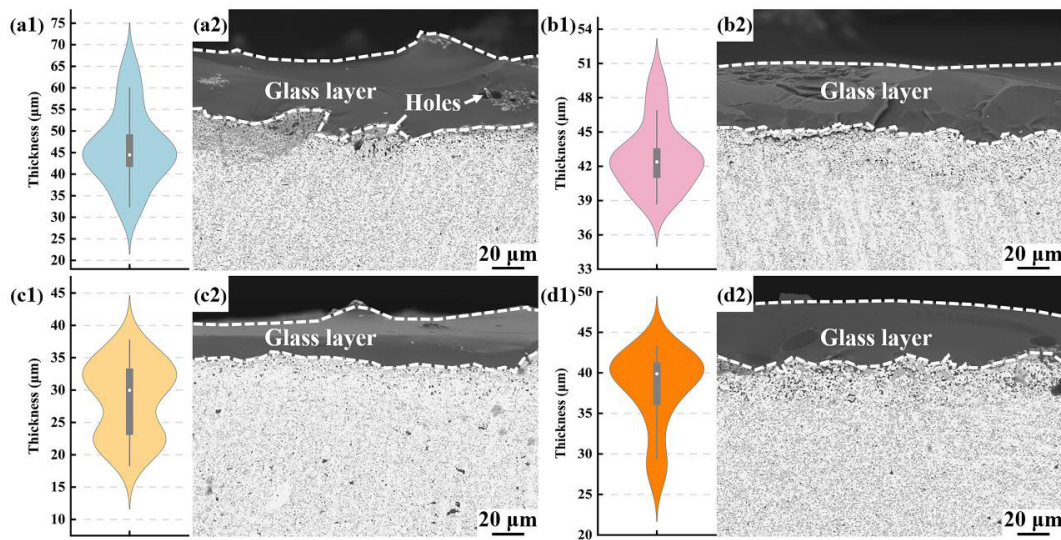


Fig. 15 Oxide scale thickness and BSE images of near-surface region in the cross-section of coatings after oxidation at 1700 °C: (a1, a2) HMH0, (b1, b2) HMH2, (c1, c2) HMH4, and (d1, d2) HMH6.

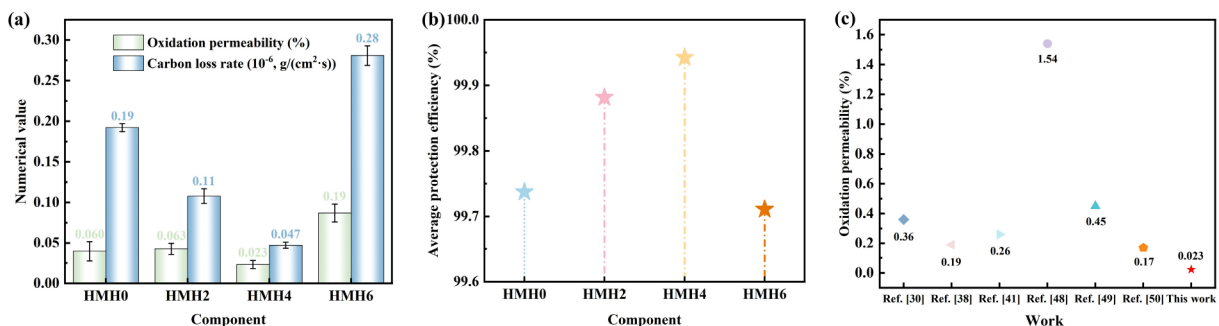


Fig. 16 Oxidation resistance of coatings after oxidation at 1700 °C: (a) oxygen permeability and carbon loss rate and (b) average protection efficiency. (c) Comparison of oxygen permeability with similar coatings reported in Refs. [30,38,41,48–50].

stable sealing capability of the glass phase at high temperatures and introduces greater structural fluctuations, thereby diminishing the overall oxygen-blocking performance. Collectively, these findings demonstrate the existence of an optimal HfSi₂ content window beyond which further addition becomes detrimental to oxidation protection. Furthermore, as shown in Fig. 16(c), the optimized HMM4 coating developed in this work exhibits lower oxygen permeability than most similar coatings reported in Refs. [30,38,41,48–50], indicating that the present coating system compares favorably in oxygen-barrier performance. This favorable performance can be attributed to the integrated design of one-step SHS-enabled *in situ* alloying and dual-silicide synergy, which promotes the formation of a stable glass-phase sealing layer and improves resistance to oxygen diffusion under high-temperature oxidation at 1700 °C.

3.3.3 Effect of Hf incorporation on SiO₂ structure and interfaces

Given that phase analysis after oxidation indicates the formation of a continuous Hf–Si–O glass phase accompanied by HfSiO₄/HfO₂-rich structural units on the oxide scale, atomic-scale calculations were further carried out to evaluate the compatibility of Hf with the Si–O network and its influence on interfacial binding. To capture bonding tendencies and energetic stability induced by Hf incorporation, the local Si–O coordination environment in crystalline SiO₂ was selected as a representative model. Substitutional (SiO₂ + suHf) and interstitial (SiO₂ + inHf) doping configurations were constructed as shown in Figs. 17(a1) and 17(b1) and subjected to geometry optimization (Table 1).

After optimization, the lattice parameters (*a*, *b*, and *c*) of the SiO₂ + suHf model change by −0.31%, −0.31%, and +0.72% relative to pristine SiO₂, whereas those of the SiO₂ + inHf model

change by −0.88%, −1.37%, and −0.49%, respectively. In both cases, only minor lattice responses are observed, indicating that the impact on the overall SiO₂ framework can be considered negligible. The formation energies of the SiO₂ + suHf and SiO₂ + inHf structures calculated using Eqs. (9) and (10) are −0.23 and −1.31 eV, respectively, indicating that both incorporation modes are thermodynamically feasible, with interstitial doping being more favorable. Local structural analysis (Figs. 17(a2) and 17(b2)) shows that substitutional Hf forms fourfold-coordinated Hf–O bonds with neighboring oxygen atoms, with a bond length of 2.032 Å. Correspondingly, the Mulliken population value increases to approximately 0.60, compared with 0.53 for the intrinsic Si–O bond, indicating strengthened local bonding. In contrast, interstitial Hf tends to disrupt adjacent Si–O rings and form new Hf–Si and Hf–O bonds with bond lengths of 2.602 and 2.088 Å, respectively.

To further explore the influence of Hf-doped SiO₂ lattice structure on SiO₂ stability, the interface structure models of Hf atom substitutionally doped SiO₂ (110)/(001) and Hf interstitially doped SiO₂ (110)/(001) were designed as shown in Figs. 18(a) and 18(b). Based on Eq. (11), the calculated interface binding energies of Hf atom substitutional and interstitial doped SiO₂(110)/(001) structures are −0.2061 and −0.2341 eV/Å², respectively, both lower than that of the undoped interface (−0.2017 eV/Å²), indicating that Hf doping in SiO₂ is favorable for enhancing the interfacial bonding strength between different SiO₂ interfaces. This trend provides atomic-scale support for the formation of dense and continuous Hf–Si–O sealing layers in HMM4, as well as for the experimentally observed reduction in permeability.

3.3.4 Oxidation protection mechanism

Figure 19 schematically illustrates the evolution of oxide-scale structures and their impact on oxygen-blocking performance as a function of HfSi₂ content. In the absence of HfSi₂ (HMH0), the surface sealing layer mainly consists of Hf oxide particles dispersed within a B₂O₃–SiO₂ glass matrix. Although high-melting-point oxides can locally deflect cracks and provide skeletal support, the continuous volatilization of MoO₃ and B₂O₃ weakens the ability of the glass phase to immediately fill reaction-induced pores. As a result, initially loose regions progressively evolve into interconnected pore networks, shortening oxygen diffusion pathways and leading to a decline in protection efficiency [51].

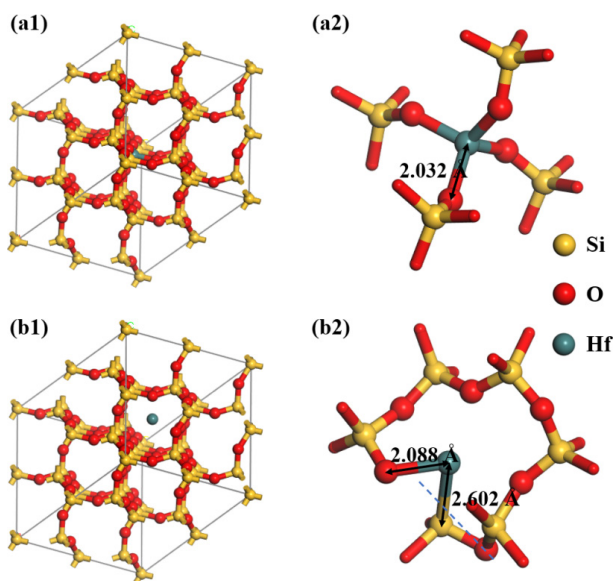


Fig. 17 Lattice models before geometry optimization: (a1) SiO₂ + suHf and (b1) SiO₂ + inHf. Shortest closed paths after geometry optimization: (a2) SiO₂ + suHf and (b2) SiO₂ + inHf.

Table 1 Crystal lattice parameters of pure SiO₂ and Hf-doped SiO₂ structures following geometric optimization (Unit: Å)

Lattice constant	<i>a</i>	<i>b</i>	<i>c</i>
SiO ₂	10.26343	10.26343	14.74647
SiO ₂ + suHf	10.23211	10.23211	14.85289
SiO ₂ + inHf	10.17277	10.12306	14.67462

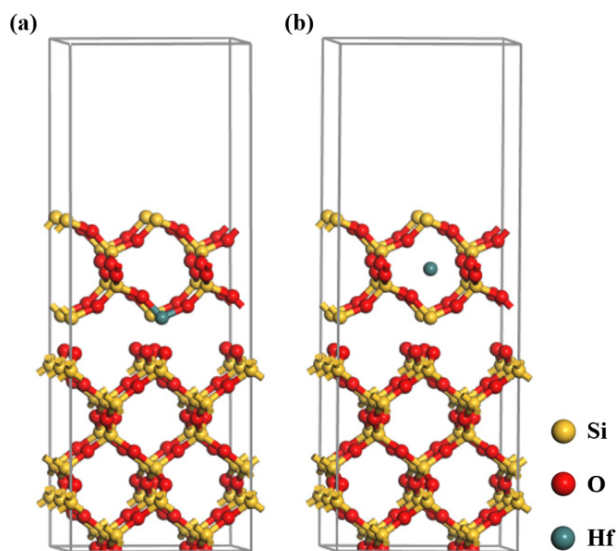


Fig. 18 (a) Hf substitutionally doped SiO₂(110)/(001) interfaces and (b) Hf interstitially doped SiO₂(110)/(001) interfaces.

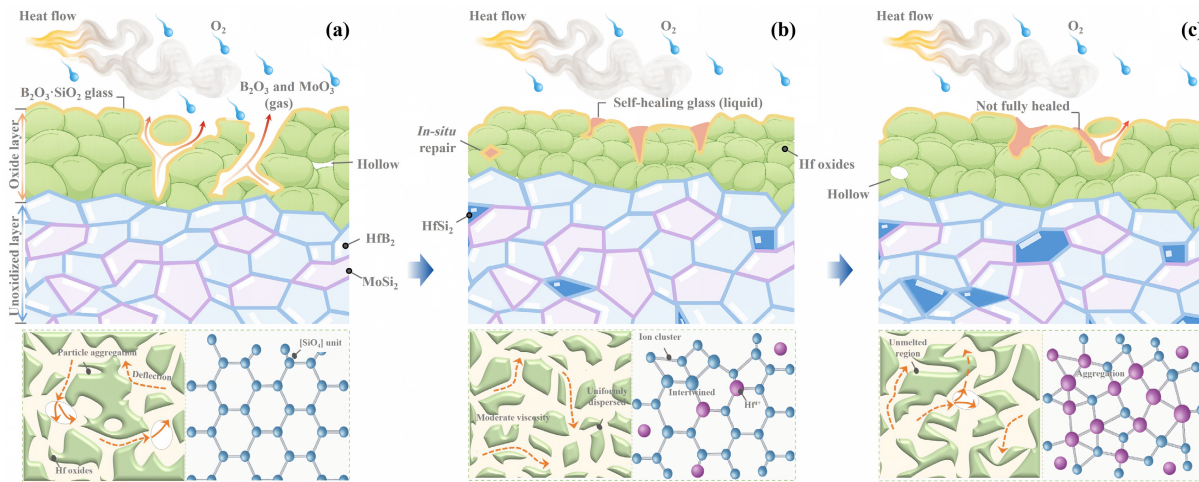


Fig. 19 Schematic illustration of coating oxidation: (a) HMF0, (b) HMF4, and (c) HMF6.

In contrast, the introduction of HfSi_2 enables the simultaneous supply of Hf and Si film-forming precursors during the early stages of oxidation, promoting earlier and more continuous *in situ* formation of a highly sealing Hf–Si–O multiphase layer. This effectively shortens the transitional time window in the HfB_2 – MoSi_2 system that is otherwise dominated by the separate formation and subsequent reconfiguration of discrete oxides and glass phases. Meanwhile, incorporation of Hf optimizes the silicate network structure, rendering the glass film more compact and significantly enhancing resistance to oxygen diffusion while reducing inward oxygen flux [52], consistent with the lower oxygen permeability and higher protection efficiency observed experimentally (Fig. 16). When the HfSi_2 content is further increased to 6 vol%, the elevated viscosity of the glass phase restricts its high-temperature flowability and weakens its adaptive healing capability for cracks and pores [21], leading to compromised sealing continuity and a consequent decline in oxygen-blocking performance.

4 Conclusions

In this work, a high-temperature oxidation-protective HfB_2 – MoSi_2 – HfSi_2 coating was developed through powder-stage *in situ* alloying to regulate the formation and evolution of self-sealing glassy phases during oxidation. The main conclusions are as follows.

(1) As the HfSi_2 content increased, the oxidation protection of the coatings first improved and then declined. The HMF4 coating exhibited the best performance at 1700 °C, achieving an average protection efficiency of 99.94%.

(2) Compared with the HfSi_2 -free coating, HMF4 reduced the oxygen permeability and carbon loss rate by 61.67% and 75.26%, respectively. This improvement is mainly attributed to the formation of a dense and continuous Hf–Si–O glass sealing layer and Hf doping in SiO_2 , which strengthens bonding across SiO_2 interfaces and improves the stability of the glassy sealing layer.

(3) Excessive HfSi_2 addition increases glass viscosity and restricts high-temperature reconstruction of the sealing layer, leading to reduced sealing continuity and oxidation resistance.

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Author contributions

Yuxing Chen: Writing—original draft, Writing—review & editing, Methodology, Investigation, Data curation. Dalin Shi: Investigation, Data curation, Validation. Xiang Ji: Writing—review & editing, Methodology, Funding acquisition, Project administration. Peipei Wang: Conceptualization, Investigation, Methodology. Zhichao Shang: Validation, Project administration. Chengshan Ji: Investigation, Resources. Xueqin Kang: Methodology, Resources. Baojing Zhang: Supervision, Resources. Yi Sun: Resources. Xuanru Ren: Writing—review & editing, Conceptualization, Methodology, Project administration, Supervision, Funding acquisition. Peizhong Feng: Supervision, Resources, Conceptualization.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

References

- [1] Wang JX, Zhong ML, Li JX, et al. Mitigating hypersonic heat barrier via direct cooling enhanced by Leidenfrost inhibition. *Nat Commun* 2025, **16**: 6931.
- [2] Liao MD, Hu XB, Zhong CH, et al. Controlling the Si/C ratio in SiC matrix based on the modified polymethylsilane for C/C–SiC composites with enhanced mechanical properties. *J Adv Ceram* 2024, **13**: 220–236.
- [3] Gao Q, Hu P, Xun LC, et al. A scalable method allows for the rapid fabrication of C/SiC composites with excellent mechanical properties and ablation resistance. *J Adv Ceram* 2025, **14**: 9221162.

- [4] Chen H, Xiang HM, Dai FZ, *et al.* Porous high entropy (Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})B₂: A novel strategy towards making ultrahigh temperature ceramics thermal insulating. *J Mater Sci Technol* 2019, **35**: 2404–2408.
- [5] Zhu ZJ, Liu YW, Qin YB, *et al.* Tough and strong bioinspired high-entropy all-ceramics with a contiguous network structure. *Nat Commun* 2025, **16**: 4587.
- [6] Chen H, Zhao ZF, Xiang HM, *et al.* High entropy (Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})₃Al₂O₁₂: A novel high temperature stable thermal barrier material. *J Mater Sci Technol* 2020, **48**: 57–62.
- [7] Simonenko EP, Simonenko NP, Kolesnikov AF, *et al.* Oxidation of graphene-modified HfB₂-SiC ceramics by supersonic dissociated air flow. *J Eur Ceram Soc* 2022, **42**: 30–42.
- [8] Xu YX, Yu L, Zhao T, *et al.* Composition design of oxidation-resistant non-equimolar high-entropy ceramic materials: An example of (Zr-Hf-Ta-Ti)B₂ ultra-high temperature ceramics. *J Adv Ceram* 2024, **13**: 2087–2100.
- [9] Lv JS, Li W, Li T, *et al.* Ablation behavior of high-entropy boride (Hf-Zr-Ta-Ti)B₂ coating fabricated via supersonic atmospheric plasma spraying for carbon/carbon composites. *Compos Part B-Eng* 2024, **270**: 111137.
- [10] Zhu XF, Zhang YL, Zhang J, *et al.* Microstructure evolution and oxidation mechanism of HfB₂-SiC coating on SiC-coated C/C composites at 1173 and 1773 K. *Ceram Int* 2022, **48**: 30807–30816.
- [11] Zhang P, Fu QG, Hu D, *et al.* Oxidation behavior of SiC-HfB₂-Si coating on C/C composites prepared by slurry dipping combined with gaseous Si infiltration. *Surf Coat Tech* 2020, **385**: 125335.
- [12] Xie W, Fu QG, Cheng CY, *et al.* Experimental and first-principles simulation study on oxidation behavior at 1700 °C of Lu₂O₃-SiC-HfB₂ ternary coating for SiC coated carbon/carbon composites. *Ceram Int* 2022, **48**: 8088–8096.
- [13] Zhu CZ, Ji X, Chen YX, *et al.* Enhanced oxidation resistance of LaB₆-modified HfB₂-SiC coating at 1700 °C by low-loss film-forming treatment. *Appl Surf Sci* 2025, **688**: 162397.
- [14] Xiang Y, Li W, Wang S, *et al.* ZrB₂/SiC as a protective coating for C/SiC composites: Effect of high temperature oxidation on mechanical properties and anti-ablation property. *Compos Part B-Eng* 2013, **45**: 1391–1396.
- [15] Chen H, Zhang YL, Fu YQ, *et al.* Novel Hf_xTa_{1-x}C solid solution nanowire toughened HfC coating: An effective strategy for synchronous enhanced mechanical and anti-ablation performance. *J Adv Ceram* 2024, **13**: 590–601.
- [16] Zhang YF, Xiao LR, Zeng DL, *et al.* A novel niobium based oxidation protective coating with three lines of defense at ultra-high temperature. *Corros Sci* 2022, **206**: 110515.
- [17] Zhu L, Zhang SP, Ye F, *et al.* Recycling of MoSi₂-based industrial solid wastes for the fabrication and high-temperature oxidation behavior of MoSi₂-ZrSi₂-SiC composite coating. *Compos Part B-Eng* 2024, **274**: 111281.
- [18] Silvestroni L, Liu HT, Sciti D, *et al.* Rare earth-doped ZrB₂-MoSi₂ ceramics: Densification and oxidation behavior. *J Eur Ceram Soc* 2025, **45**: 116992.
- [19] Wang PP, Li HJ, Ren XR, *et al.* HfB₂-SiC-MoSi₂ oxidation resistance coating fabricated through *in-situ* synthesis for SiC coated C/C composites. *J Alloys Compd* 2017, **722**: 69–76.
- [20] Zhu XF, Ou CY, Li T, *et al.* HfSi₂-HfB₂-SiC coating prepared at low temperature to protect SiC-coated C/C composites against oxidation at 1473–1973 K. *Ceram Int* 2024, **50**: 13490–13499.
- [21] Wu JH, Wu WX, Sun AY, *et al.* Study on high temperature oxidation resistance of HfSi₂ modified MoSi₂ coating. *J Mater Res Technol* 2025, **37**: 242–251.
- [22] Zhang MC, Wang LY, Ren XR, *et al.* Oxygen barrier resistance of HfB₂-MoSi₂-TaB₂ coatings in a wide temperature region. *Ceram Int* 2023, **49**: 25504–25515.
- [23] Kurbatkina VV, Patsera EI, Loginov PA, *et al.* Structure and properties of (Ta_{1-x}Zr_x)C and (Ta_{1-x}Hf_x)C solid solutions produced by SHS and hot pressing. *Ceram Int* 2021, **47**: 26205–26214.
- [24] Zhu NN, Zhu L, Zhang BJ, *et al.* Microstructural evolution and 1500 °C oxidation resistance of Mo(Al, Si)₂ fabricated via an innovative two-step SHS-SPS technique. *Mater Design* 2024, **247**: 113397.
- [25] Shi HL, Zhang ML, Zhou L, *et al.* Improved oxidation protective ability of SHS powder-synthesized ZrB₂-MoSi₂-SiC-Si coating on carbon/carbon composites. *Surf Coat Tech* 2022, **447**: 128838.
- [26] Zhang ML, Ren XR, Zhang MC, *et al.* Preparation of ZrB₂-MoSi₂ high oxygen resistant coating using nonequilibrium state powders by self-propagating high-temperature synthesis. *J Adv Ceram* 2021, **10**: 1011–1024.
- [27] Ji X, Chen YX, Yao L, *et al.* Enhanced oxidation resistance of ZrB₂-MoSi₂ coating through MoSi₂-TaSi₂ double-silicide alloying modifying. *Corros Sci* 2024, **233**: 112070.
- [28] Chen YX, Ji X, Wang PP, *et al.* A promising high-temperature oxygen barrier of ZrB₂-HfSi₂-TaSi₂ coating for 1500 °C based on HfSi₂-TaSi₂ dual-transition-metal silicide alloying enhancement. *Compos Part B-Eng* 2025, **298**: 112384.
- [29] Chen YX, Wang PP, Ren XR, *et al.* Oxidation of TaB₂-SiC coatings prepared by spark plasma sintering and effect of pre-oxidation treatments. *J Eur Ceram Soc* 2022, **42**: 5238–5248.
- [30] Kan TF, Wang PP, Ren XR, *et al.* Oxygen barrier capability of ZrB₂-SiC coating at 1700 °C strengthened by film-forming treatment. *Corros Sci* 2022, **205**: 110456.
- [31] Wang PP, Ji X, Sun WC, *et al.* Oxidation protection of ZrB₂-SiC-LaB₆ ceramics coating in a wide temperature range. *Ceram Int* 2025, **51**: 6916–6925.
- [32] Licheri R, Orrù R, Musa C, *et al.* Combination of SHS and SPS Techniques for fabrication of fully dense ZrB₂-ZrC-SiC composites. *Mater Lett* 2008, **62**: 432–435.
- [33] Li XN, Wang XM, Bai X, *et al.* Densification mechanism during hot-pressing of single-phase zirconium boride powders with different dislocation density. *Ceram Int* 2022, **48**: 19305–19313.
- [34] Liao N, Ji ZX, Yang ZH, *et al.* Improved oxidation resistance of SPS sintered Si₂BC₃N ceramics with disilicides (MoSi₂, HfSi₂, TaSi₂) addition. *Ceram Int* 2020, **46**: 18079–18088.
- [35] Chen C, Zhen Q, Li R, *et al.* Pressureless sintering of HfC-HfB₂-SiC-HfSi₂ ceramics and their ultra high-temperature ablation resistance. *Ceram Int* 2024, **50**: 37525–37532.
- [36] Sun CH, Zhou XG, Yu JS, *et al.* Preparation and anti-oxidation performance of TaC-SiC nanocomposites by precursor-derived ceramic method. *Ceram Int* 2024, **50**: 45675–45682.
- [37] Peng KX, Qiao Y, Li Q, *et al.* Gradient tri-layered TGOs in MoSi₂/HfO₂ duplex EBCs for effective protection of SiC substrate against steam corrosion at 1500 °C for 200 h. *J Adv Ceram* 2025, **14**: 9221101.
- [38] Jiang C, Ji X, Chen YX, *et al.* Oxidation resistance and protective mechanism of ZrB₂-SiC coating modified by Y₂O₃ at 1700 °C. *J Eur Ceram Soc* 2025, **45**: 117293.
- [39] Lv JS, Zhang YL, Li W, *et al.* Microstructure evolution of HfB₂-SiC/SiC coating for C/C composites during long-term oxidation at 1700 °C. *Corros Sci* 2022, **206**: 110524.
- [40] Zhuang L, Fu QG. Bonding strength, thermal shock and oxidation resistance of interlocking (Zr,Hf)C-SiC/SiC double-layer coating for C/C composites. *Surf Coat Tech* 2017, **315**: 436–442.
- [41] Shi DL, Ji X, Wu BB, *et al.* Oxygen blocking enhancement of HfB₂-SiC coating using HfB₂-HfSi₂ alloyed composite powders by self-propagating high-temperature synthesis. *Ceram Int* 2023, **49**: 36679–36690.
- [42] Yang Y, Li MS, Xu L, *et al.* Oxidation behaviours of ZrB₂-SiC-MoSi₂ composites at 1800 °C in air with different pressures. *Corros Sci* 2019, **157**: 87–97.

- [43] Tsunoura T, Okubo Y, Yoshida K, *et al.* Oxidation behavior of monolithic HfSi₂ and SiC fiber-reinforced composites fabricated by melt infiltration using Si-8.5 at% Hf alloy at 800–1200 °C in dry air. *J Ceram Soc Jpn* 2018, **126**: 27–33.
- [44] Wang YF, Liu YB, Ma Z, *et al.* Oxidation ablation resistance of ZrB₂-HfB₂-SiC-TaSi₂ coating prepared on C/C composite surface. *Surf Coat Tech* 2023, **466**: 129615.
- [45] Hu KY, Deng JL, Mao YH, *et al.* Feasibility and ablation behavior of on-site HfSi₂ and HfSi₂-HfO₂ repair coatings on C/C-SiC-ZrC composites. *Ceram Int* 2025, **51**: 65537–65550.
- [46] Ye ZY, Wang SQ, Zou YC, *et al.* Plasma-assisted particle deposition manufacturing: Multi-functional integrated superhigh temperature thermal protection coating on niobium alloy. *Compos Part B-Eng* 2025, **288**: 111905.
- [47] Liu ZQ, Zhang SB, Zhang JP, *et al.* Effect of gaseous silicon infiltration process on mechanical and ablation properties of C/C-HfC-iC composites with HfSi₂/HfC coating prepared by reactive melt infiltration. *Compos Commun* 2025, **56**: 102358.
- [48] Qian DY, Chen YX, Ren XR, *et al.* Effect of La₂O₃ content on the oxygen barrier ability of the HfB₂-SiC coating at 1973 K. *J Am Ceram Soc* 2023, **106**: 2155–2168.
- [49] Wu BB, Wang PP, Ren XR, *et al.* Effect of film-forming regulation of the self-formed compound layer on the oxidation inhibition capacity of HfB₂-SiC coating. *Ceram Int* 2022, **48**: 22039–22052.
- [50] Zhang S, Ji X, Chen YX, *et al.* Enhancing oxygen-blocking properties of HfB₂-MoSi₂-SiC coating by CeO₂ modification. *J Am Ceram Soc* 2025, **108**: 20266.
- [51] Tang ZY, Wen ZH, Zhuang L, *et al.* Enhanced oxidation resistance of high-entropy diborides by multi-component synergistic effects. *Sci China Mater* 2024, **67**: 3392–3400.
- [52] Zafirah Zulfikri NI, Mustaffa NA, Mohamed R, *et al.* Electrospun light-emitting Tm³⁺-doped SiO₂-HfO₂ nanofiber for photonic applications. *J Lumin* 2023, **257**: 119723.