

Composition-optimized Hf–Zr–Ti–C–N coatings for exceptional ablation resistance

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ABSTRACT: Multielement carbonitrides have emerged as promising candidates for ultrahigh-temperature thermal protection, yet the influence of compositional variation on their ablation behavior remains insufficiently understood. Here, a series of Hf–Zr–Ti–C–N bulk ceramics with systematically varied metallic atomic ratios are fabricated by spark plasma sintering. A comprehensive evaluation of fracture toughness, flexural strength and oxyacetylene flame ablation performance identifies $\text{Hf}_{4/6}\text{Zr}_{1/6}\text{Ti}_{1/6}\text{CN}$ as the optimal ceramic matrix, which is subsequently applied as a coating on graphite with a SiC-graded functional transition layer. After ablation for 120 s at 3000 °C, the coating exhibits excellent ablation resistance, with mass and linear ablation rates of -1.23 ± 0.25 mg/s and -2.07 ± 0.37 $\mu\text{m/s}$, respectively. Its superior ablation resistance originates from a synergistic interplay of phase transformation into a dense HfO_2 -dominated oxide barrier, the self-healing effect of the SiO_2 -rich phase coupled with stress relaxation by the Si–C–O nanowire network, and interfacial strengthening induced by the Si-enriched diffusion layer. Combined with molecular dynamics simulations, the oxidation evolution pathway during the initial stage of ablation is further elucidated and validated at the atomic scale. This work establishes a composition-optimized carbonitride coating with outstanding ablation resistance and provides a mechanistic framework for the rational design of next-generation thermal protection systems intended for extreme aerospace environments.

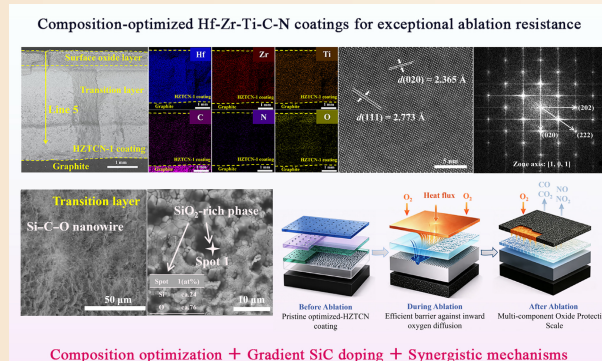
KEYWORDS: ultrahigh-temperature ceramics; Hf–Zr–Ti–C–N; multielement coating; ablation-resistant mechanism

1 Introduction

Hypersonic vehicles experience extreme thermal and chemical environments during high-speed flight and re-entry, with leading edges and combustion chambers subjected to temperatures exceeding 2000 °C accompanied by severe thermochemical ablation [1–3]. Conventional metallic alloys and polymer-matrix composites are incapable of long-term service under such coupled thermomechanical-chemical extremes. Graphite offers excellent thermal shock resistance, high thermal conductivity, good machinability, and retains reasonable mechanical strength at elevated temperatures, making it a widely used material for high-temperature structural components such as rocket nozzle throats. However, graphite suffers from susceptibility to oxidative ablation in high-temperature oxidizing atmospheres, which remains a critical bottleneck limiting its long-term reliability [4]. A proven strategy to overcome this limitation is the application of ultrahigh

temperature ceramic (UHTC) coatings on graphite substrates, constructing a dual-functional system combining load-bearing capacity with surface protection [5,6].

UHTC coatings can be fabricated using various processes, including slurry deposition, thermal spraying, chemical vapor deposition, and spark plasma sintering (SPS) [7–9]. Their density, thickness, interfacial bond strength, thermal stability, and ablation resistance are typically used as key evaluation criteria [10,11]. Transition metal carbonitrides, particularly those of Group IV transition metals, possess extremely high melting points, outstanding mechanical properties, and excellent chemical and phase stability [12,13] and are considered UHTC coating materials with great application potential. HfCN and ZrCN not only possess extremely high melting points (e.g., the theoretically predicted melting point of $\text{HfC}_{0.76}\text{N}_{0.24}$ is as high as 4419 ± 37 K), high hardness, high elastic modulus, and excellent thermochemical stability, but their oxidation products also feature



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high melting points and low vapor pressures (HfO_2 : $\sim 2810^\circ\text{C}$; ZrO_2 : $\sim 2670^\circ\text{C}$) [14–17]. However, the insufficient oxidation resistance of $(\text{Hf,Zr})\text{CN}$ limits its applications [18]. The further introduction of TiCN to form a multicomponent carbonitride solid solution promotes densification and induces lattice distortion, thereby achieving solid solution strengthening. On the other hand, during high-temperature oxidation, the low-melting-point Ti -containing oxides can synergistically combine with high-melting-point oxides such as HfO_2 and ZrO_2 to form a dense, continuous oxidation-resistant protective layer [19,20]. However, there is currently a lack of systematic understanding regarding the influence of the Hf/Zr/Ti ratio on the mechanical properties, ablation resistance, and postablation structural integrity of carbonitrides.

Long-term protection of graphite under extreme oxidative thermal environments requires not only a ceramic matrix with excellent high-temperature stability but also a tailored architecture capable of accommodating the complex thermal, chemical, and mechanical gradients that develop during ablation. The significant coefficient of thermal expansion (CTE) mismatch between refractory carbonitride coatings and graphite substrates can generate substantial thermal stresses during rapid heating and cooling, thereby promoting crack initiation, interfacial damage, and coating spallation [21]. The incorporation of SiC has been regarded as an effective strategy for improving the thermal compatibility and oxidation protection of UHTC/graphite systems. In addition to its excellent high-temperature stability, SiC can form a SiO_2 -rich phase upon oxidation, which fills and seals coating defects, suppresses inward oxygen transport, and consequently enhances oxidation and ablation resistance [18,22–26]. However, a uniformly high SiC content may reduce the volume fraction of the refractory carbonitride continuous phase, thereby compromising the intrinsic high-temperature stability and load-bearing capability of the coating. In contrast, constructing a SiC compositional gradient along the coating thickness provides a more rational approach to progressively regulate thermal expansion, oxidation evolution, and stress transfer. Such a gradient architecture enables the surface region to retain a high fraction of the refractory phase for resistance to extreme heat fluxes, while increasing the SiC content toward the graphite substrate enhances oxidation protection and alleviates thermal mismatch, thereby enabling coordinated protection from the high-temperature exposed surface to the underlying graphite interface. Nevertheless, the synergistic effects of the multicomponent refractory carbonitride matrix and the SiC gradient architecture and their roles in regulating oxidation evolution, elemental migration, and interfacial protection during ablation remain insufficiently understood.

In this study, systematic compositional screening of Hf-Zr-Ti-C-N is integrated with SiC gradient structural design. A series of Hf-Zr-Ti-C-N bulk ceramics with varying Hf/Zr/Ti atomic ratios are fabricated by SPS, and their fracture toughness, flexural strength, oxyacetylene flame ablation resistance, and postablation microstructural evolution are systematically evaluated to identify the multicomponent carbonitride with the most favorable intrinsic properties for subsequent coating design. A SiC -gradient-doped coating with SiC contents of 10, 20, and 30 vol% was constructed on a graphite substrate. Its phase constitution, microstructure, and oxyacetylene flame ablation behavior are systematically investigated. Furthermore, molecular dynamics (MD) simulations are performed to elucidate the initial-stage oxidation mechanism, thereby revealing the relationship among the composition, gradient architecture, and ablation behavior of

the SiC -gradient-doped multicomponent refractory carbonitride coating, providing a new design strategy for the long-term protection of graphite substrates under extreme thermochemical environments.

2 Materials and methods

2.1 Synthesis and sintering

Commercially available HfCN , ZrCN , and TiCN powders (purity > 99.6 wt%, average particle size: 1–3 μm , main impurity: O 0.36 wt%; Beijing HwrkChemical Technology Co., Ltd., China) were used as raw materials. A series of Hf-Zr-Ti-C-N bulk ceramics with Hf:Zr:Ti atomic ratios of 4:1:1, 6:3:1, 3:2:1, 4.5:4.5:1, and 1:1:1 were fabricated and denoted HZTCN-1, HZTCN-2, HZTCN-3, HZTCN-4, and HZTCN-5, corresponding to Hf molar fractions of 66.7%, 60.0%, 50.0%, 45.0%, and 33.3%, respectively. The powder mixtures were subjected to high-energy ball milling in absolute ethanol at 300 r/min for 10 h using ZrO_2 balls as the milling media, with a ball-to-powder ratio of approximately 4:1. After milling, the slurry was dried in an oven at 60°C for 24 h. The resulting powders were then consolidated in a spark plasma sintering furnace (FCT Systeme GmbH) under an argon protective atmosphere. HZTCN bulk ceramics with a diameter of 28 mm were sintered at 2200°C under a uniaxial pressure of 50 MPa, with heating and cooling rates of 200 and 100°C/min , respectively, using graphite foil between the punches and specimens to prevent chemical reactions.

2.2 Coating preparation

Cylindrical graphite blocks (28 mm in diameter, 5 mm in height) were used as the substrate, which were ultrasonically cleaned, sandpapered, and oven-dried prior to coating deposition. A SiC -gradient HZTCN-1 (SG-HZTCN-1) coating was fabricated on the graphite substrate. To alleviate the thermal expansion mismatch between the graphite substrate and the HZTCN-1 coating, a SiC -doped HZTCN-1 gradient transition layer was introduced. Specifically, HZTCN-1 powder was mixed with 10, 20, and 30 vol% SiC by ball milling to prepare three SiC -doped powders. During powder stacking, the powders were sequentially stacked from the graphite substrate toward the coating surface to form 0.3 mm-thick HZTCN-1–30 vol% SiC , 0.3 mm-thick HZTCN-1–20 vol% SiC , and 0.3 mm-thick HZTCN-1–10 vol% SiC layers, followed by a 0.8 mm-thick pure HZTCN-1 top layer. Consequently, the SiC content gradually decreased from the graphite substrate toward the coating surface, forming a SiC -gradient transition layer. The multilayer coating was subsequently consolidated on the graphite substrate by the same SPS process described in Section 2.1.

2.3 Ablation experiment

The ablation experiment was performed in an oxyacetylene torch system based on the GJB 323–96A standard. The flow rates of oxygen and acetylene were 1512 and 1116 L/h, and the pressures of oxygen and acetylene were 0.400 and 0.095 MPa, respectively. After the oxyacetylene flame reached a stable combustion state, the specimen was directly exposed to the flame center for ablation. The distance between the initial sample surface and the nozzle tip was 10 mm, and the sample was exposed to the oxyacetylene flame for 120 s. The ablation results were characterized by the mass ablation rates (MAR) and linear ablation rates (LAR), and the changes in weight and thickness after ablation were measured

by an electronic balance (± 0.0001 g) and calibrator (± 0.01 mm), respectively. The MAR and LAR were calculated using Eqs. (1) and (2) [27]:

$$\text{MAR} = \frac{m_0 - m_1}{t} \quad (1)$$

$$\text{LAR} = \frac{d_0 - d_1}{t} \quad (2)$$

where MAR is the mass ablation rate after ablation; LAR is the linear ablation rate after ablation; t is the ablation time; m_0 and m_1 are the masses of samples before and after ablation, respectively; and d_0 and d_1 are the thicknesses of samples before and after ablation, respectively.

2.4 Mechanical properties

Flexural strength tests were conducted on rectangular bar specimens with dimensions of 25 mm $\times$ 4 mm $\times$ 3 mm using a three-point bending setup mounted on a universal mechanical testing machine. The bending test was performed with a support span of 20 mm and a crosshead loading rate of 0.5 mm/min. Fracture toughness was measured using the single-edge notched beam (SENB) method. The SENB specimens had dimensions of 20 mm $\times$ 4 mm $\times$ 3 mm, with a notch depth of 2 mm. The fracture toughness tests were carried out with a support span of 16 mm and a crosshead loading rate of 0.05 mm/min. To minimize experimental error, the average value of three specimens was taken as the final result. Flexural strength (σ) and fracture toughness (K_{IC}) can be calculated using Eqs. (3)–(5) [28–31]:

$$\sigma = \frac{3FL}{2BW^2} \quad (3)$$

where F is the maximum fracture load, L is the span between two lower supporting points, B is the width of the specimen, and W is the thickness of the specimen.

$$K_{IC} = Y \frac{3FL}{2BW^2} \sqrt{a} \quad (4)$$

$$Y = 1.93 - 3.07 \frac{a}{W} + 14.53 \left(\frac{a}{W} \right)^2 - 25.11 \left(\frac{a}{W} \right)^3 + 25.8 \left(\frac{a}{W} \right)^4 \quad (5)$$

where a is the initial length of a notch, and Y is a factor defined as a/W .

2.5 Characterizations

Phase compositions were identified by X-ray diffraction (XRD; SmartLab SE, Rigaku, Japan) using Cu K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 5 ($^\circ$)/min, with a current of 300 mA and a voltage of 40 kV. Surface and cross-sectional microstructures were examined using scanning electron microscopy (SEM; MIRA 4 LMH, TESCAN, Czech Republic) equipped with energy-dispersive X-ray spectroscopy (EDS; Ultim Max 40, Oxford Instruments, UK) for chemical analysis operated at an accelerating voltage of 5–30 kV. High-angle annular dark-field (HAADF) images were acquired using a 200 kV scanning transmission electron microscope (STEM; FEI Tecnai G2 F30, USA).

2.6 Molecular dynamics simulation

The amorphous Hf–Zr–Ti–C–N/SiC system was constructed using Materials Studio software. The model contains a total of 5352 atoms, including 1640 Hf atoms, 280 Zr atoms, 220 Ti

atoms, 1492 C atoms, 1060 N atoms, 140 Si atoms, and 520 O atoms. Periodic boundary conditions are applied, with lattice parameters of $a = 34.0091$ Å, $b = 27.0909$ Å, and $c = 100.0000$ Å and interaxial angles of $\alpha = \beta = \gamma = 90^\circ$. The COMPASS III force field is employed for all simulations. For nonbonded interactions, van der Waals interactions are treated using the atom-based method, while electrostatic interactions are calculated using the Ewald summation method.

To eliminate unreasonable atomic contacts and internal stresses that might exist in the initial model and to obtain a locally stable configuration with lower potential energy, geometry optimization is first performed using the geometry optimization module in Forcite. The smart minimizer algorithm is employed, with an energy convergence tolerance of 1×10^{-5} kcal/mol. After geometry optimization, high-temperature molecular dynamics relaxation is performed. The system temperature is increased to 3273 K, followed by a 50 ps molecular dynamics simulation in the NPT ensemble. The calculation quality is set to Fine to obtain equilibrated configurations and dynamic trajectories for subsequent structural and performance analyses. The time step for the molecular dynamics simulations is set to 10 fs.

3 Results and discussion

3.1 Microstructural fingerprints of HZTCN ceramics: Phase stability and elemental uniformity

To verify the phase formation and crystal structure of the as-prepared samples, XRD analysis was performed on HZTCN-1 to HZTCN-5 with different elemental ratios, as shown in Fig. 1(a). All samples crystallize in a face centered cubic (FCC) structure with the space group $Fm\bar{3}m$. Additionally, all samples exhibit a very weak diffraction peak at approximately 30° , which can be indexed to tetragonal HfO $_2$ (t-HfO $_2$). Meanwhile, a weak platform-like feature at approximately 50° is observed for HZTCN-5, which is attributed to the overlap of closely spaced diffraction reflections from t-HfO $_2$ and monoclinic HfO $_2$ (m-HfO $_2$). These HfO $_2$ signals likely originate from slight oxidation during the sintering process [32].

The diffraction peaks located at approximately 33° and 40° correspond to the (111) and (200) planes of the FCC structure. Notably, these peak positions are systematically shifted relative to those of the carbonitride standard phases. This shift is attributed to the incorporation of Zr and Ti into the lattice, leading to the formation of (Hf,Zr,Ti)CN solid solutions and indicating sufficient atomic scale mutual diffusion among Hf, Zr, and Ti [33].

SEM coupled with EDS was employed to characterize the surface morphologies and elemental distributions of the samples with different Hf/Zr/Ti atomic ratios, as shown in Fig. 2. HZTCN-1 exhibits a relatively dense and uniform surface morphology, without obvious pores or cracks. EDS elemental mappings show that Hf, Zr, Ti, C, and N are relatively uniformly distributed throughout the samples, indicating the homogeneous incorporation of the constituent elements into the ceramics.

3.2 Linking composition to performance: Mechanical and ablation metric screening

The mechanical properties and ablation resistance of the as-sintered HZTCN ceramics were systematically investigated to establish the underlying composition-microstructure-performance relationships. As shown in Fig. 3(a), the mechanical properties exhibit pronounced compositional dependence. HZTCN-1 exhibits the highest room-temperature fracture toughness of

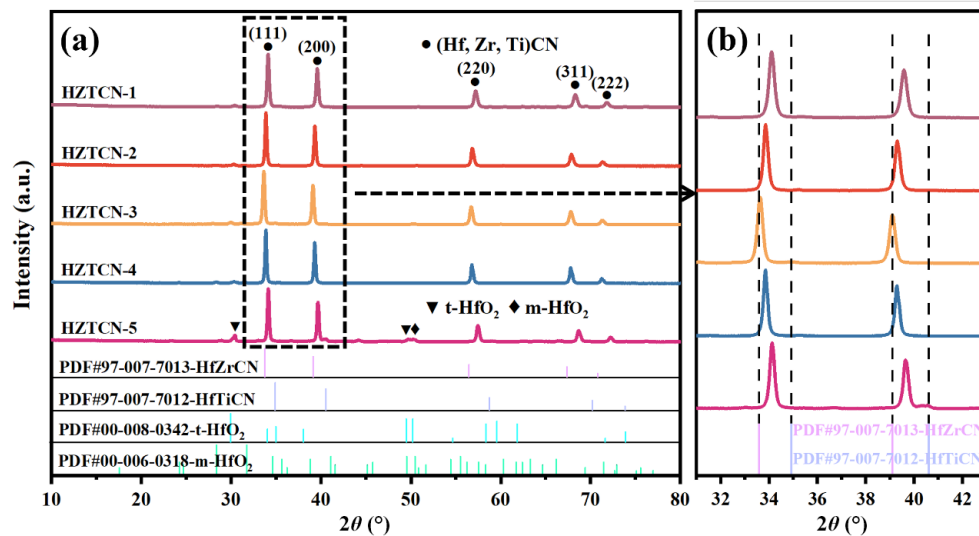


Fig. 1 (a) XRD patterns of the as-prepared HZTCN-1 to HZTCN-5 samples; (b) enlarged view of the XRD patterns in the 2θ range of 31° – 43° .

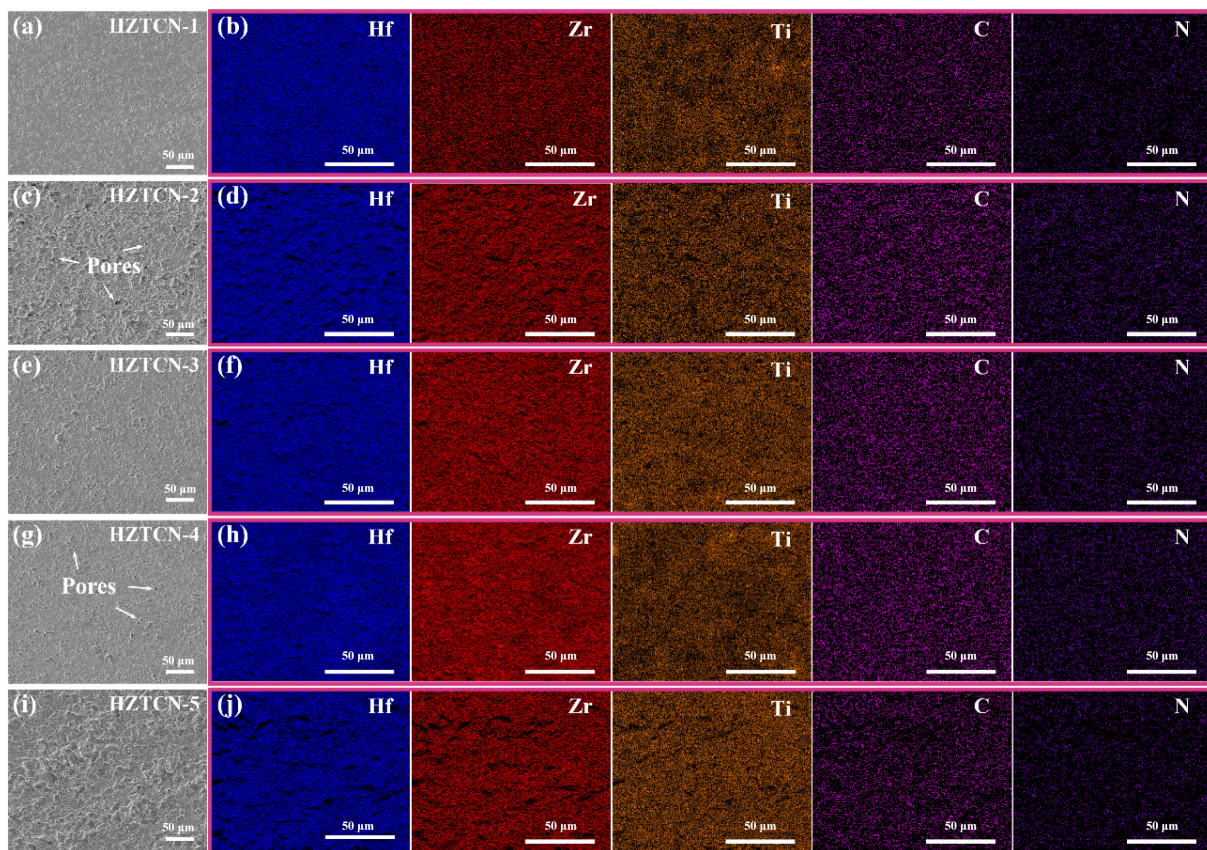


Fig. 2 Surface SEM images and corresponding EDS mappings of (a, b) HZTCN-1, (c, d) HZTCN-2, (e, f) HZTCN-3, (g, h) HZTCN-4, and (i, j) HZTCN-5.

$5.98 \pm 0.34 \text{ MPa} \cdot \text{m}^{1/2}$ along with a high flexural strength of $416.70 \pm 44.12 \text{ MPa}$. The superior fracture toughness and flexural strength of HZTCN-1 can be attributed to the synergistic effects of the following factors: The high Hf content effectively suppresses grain coarsening during sintering, thereby maintaining a fine-grained microstructure [34]; the lattice parameter mismatch among Hf, Zr, and Ti atoms inhibits rapid grain growth during the sintering process [35].

The ablation resistance of the five ceramics was evaluated via

oxyacetylene flame testing at 3000°C for 120 s (Figs. 3(b) and 3(c)). Quantitative measurements demonstrate that HZTCN-1 exhibits the optimal overall ablation resistance, featuring a low MAR of $-0.78 \pm 0.53 \text{ mg/s}$ and a moderate LAR of $-2.83 \pm 1.50 \text{ } \mu\text{m/s}$. Although HZTCN-2 displays the lowest LAR value ($-1.99 \pm 0.09 \text{ } \mu\text{m/s}$), its MAR is substantially higher ($-1.66 \pm 0.88 \text{ mg/s}$). Moreover, Fig. 3(d) presents the XRD patterns of the postablation surfaces, revealing complex oxide phase assemblages, suggesting the formation of multielement oxide scales.

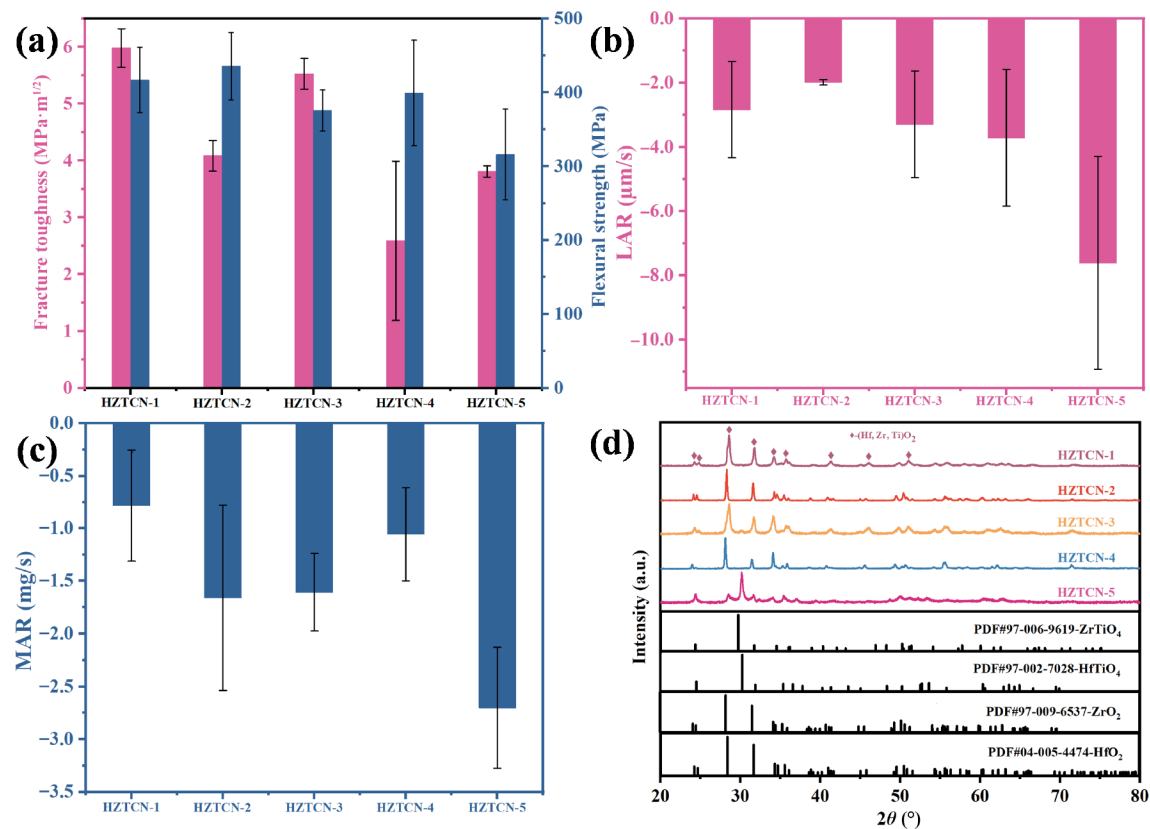


Fig. 3 (a) Fracture toughness and flexural strength of HZTCN ceramic samples, (b) LAR after ablation for 120 s, (c) MAR after ablation for 120 s, and (d) XRD patterns of ablated samples.

Based on the integrated evaluation of fracture toughness, flexural strength, and ablation behaviors, representative samples (HZTCN-1, HZTCN-3, and HZTCN-5) were selected for detailed microstructural characterization of their ablated cross-sections, aiming to elucidate the underlying composition-structure-performance relationships.

The microstructure and compositional uniformity of the ablated sample cross-sections were investigated by SEM and EDS for HZTCN-1, HZTCN-3, and HZTCN-5, as shown in Figs. 4–6. Figure 4(a) presents the overall cross-sectional morphology and corresponding EDS elemental maps of ablated HZTCN-1. A distinct multilayer architecture is observed from the surface to the interior, sequentially composed of a continuous oxide layer (~219 μm thick), a dense transition layer, and the unaffected matrix. The transition layer and the underlying matrix remain highly dense and free of cracks or voids, whereas the surface oxide layer (Fig. 4(b)) features a fine, submicron-grained morphology interspersed with small pores. These micropores are attributed to the evolution channels formed by gaseous CO/CO₂ during high-temperature oxidation of the carbonitride [36]. From the EDS maps and line-scan profiles, uniform distributions of Hf, Zr, and Ti are revealed, whereas oxygen is substantially enriched in the oxide layer and then decreases sharply across the transition layer, indicating that the dense transition layer effectively blocks inward oxygen diffusion. A high-magnification micrograph of the oxide layer confirms the structural continuity of the oxide layer. The interfacial transition behavior between the oxide layer and the substrate is further elucidated in Figs. 4(c) and 4(d). Figure 4(c) displays the high-magnification SEM morphology of the boundary region between the oxide layer and transition layer. EDS spot scanning results confirm the existence of a distinct two-phase

microstructure within the transition layer, in which the off-white phase exhibits a nearly zero Ti atomic fraction, while the gray phase possesses a Ti content of up to 12 at%. This compositional difference is attributed to the formation and partial melting of low-melting-point TiO₂ under extreme ablation conditions, which induces the migration of the Ti-containing liquid phase. The migrated liquid phase fills internal micropores and defects within the transition layer, effectively blocking the rapid diffusion pathways of oxygen and promoting microstructural densification of the transition zone, thereby restraining the deep penetration of oxygen into the ceramic matrix [37,38]. The EDS mapping results of the transition region (Fig. 4(e)) further verify evident Ti enrichment within the low-porosity transition zone.

The high porosity of the surface oxide layer may deteriorate the mechanical erosion resistance under oxyacetylene flame ablation, whereas the densified transition layer can effectively inhibit the inward diffusion of oxygen, endowing HZTCN-1 with excellent overall ablation resistance.

The cross-sectional microstructures and elemental distribution of HZTCN-3 after ablation are shown in Fig. 5. Pronounced transverse cracks are observed in the surface oxide layer, mainly induced by stresses during cross-sectional polishing. EDS line-scan profiles reveal that the oxygen signal decays slowly and remains dispersedly distributed across the transition layer, indicating that oxygen has penetrated through the transition layer into the deep matrix [39]. In contrast, HZTCN-3 forms a relatively thin oxide layer with a thickness of approximately 41 μm. This can be attributed to the relatively low porosity of its surface oxide scale. The EDS spot analysis in Fig. 5(c) identifies low-melting-point Ti-rich phases within the surface oxide layer. The pore-sealing effect of these Ti-rich phases hinders inward

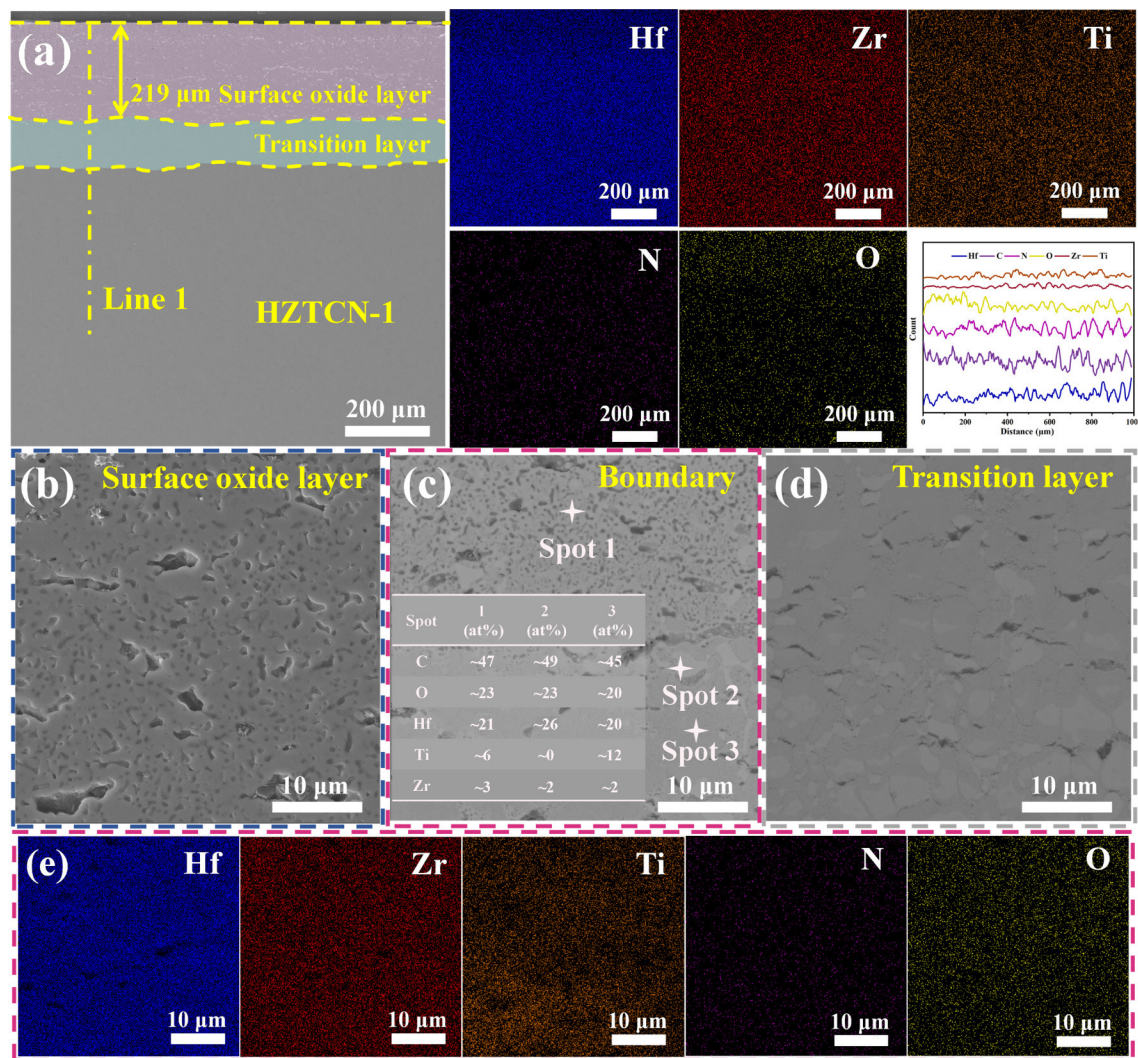


Fig. 4 Cross-sectional microstructure and elemental distribution of HZTCN-1 after oxyacetylene ablation: (a) cross-sectional SEM image and corresponding EDS elemental analysis, (b) enlarged SEM image of the surface oxide layer, (c) enlarged SEM image and EDS analysis of the boundary region between the surface oxide layer and transition layer, (d) enlarged SEM image of the transition layer, and (e) corresponding EDS mappings in (c).

oxygen transport and suppresses the overall oxidation reaction, which reduces the yield of oxide products and ultimately results in a thin oxide scale.

The cross-sectional microstructure and elemental distribution of HZTCN-5 after ablation are characterized in Fig. 6. The ablated sample is free of visible cracks. A marked drop in oxygen content from the oxide layer to the transition layer suggests that the oxide layer offers partial resistance to oxygen ingress. Nevertheless, as shown in Figs. 6(b)–6(d), the surface oxide layer is highly loose and porous, containing numerous voids left by the evolution of CO/CO₂ gases. The transition layer (Fig. 6(d)) exhibits well-defined grain boundaries and structurally intact polygonal grains, with a grain size of approximately 10–20 μm. Notably, EDS point analysis reveals a relatively high oxygen content at the grain boundaries, suggesting that these boundaries may serve as preferential pathways for oxygen diffusion and reaction under the high-temperature oxidizing environment, thereby promoting localized oxidation along the grain boundaries.

In summary, HZTCN-1 exhibits the most favorable overall performance, featuring the highest fracture toughness ($5.98 \pm 0.34 \text{ MPa}\cdot\text{m}^{1/2}$), relatively high flexural strength, and low ablation rate. Its excellent ablation resistance is closely associated with the

layered oxide structure formed after ablation: The relatively thick surface oxide layer can withstand and buffer the mechanical erosion caused by the flame and ablation products during ablation, while the underlying densified transition layer effectively suppresses inward oxygen diffusion, thereby retarding further oxidation and maintaining the structural integrity of the matrix. This layered structure provides both mechanical protection and oxygen diffusion resistance, establishing a synergistic protective system that enables HZTCN-1 to maintain good structural stability under extreme ablation conditions.

3.3 Ablation-induced evolution of the optimized coating: From oxide scale to transition layer

Based on the excellent combination of fracture toughness, flexural strength, and ablation resistance of HZTCN-1 bulk ceramic, HZTCN-1 is selected as the primary ceramic constituent for the SPS-fabricated SG-HZTCN-1 coating, with a SiC gradient transition layer introduced to mitigate the CTE between the coating and graphite substrate [40]. The as-fabricated coating sample is shown in Fig. 7(a). After ablation at 3000 °C for 120 s, the MAR and LAR of the SG-HZTCN-1 coating are $-1.23 \pm 0.25 \text{ mg/s}$ and $-2.07 \pm 0.37 \text{ μm/s}$, respectively. Figure 7(b)

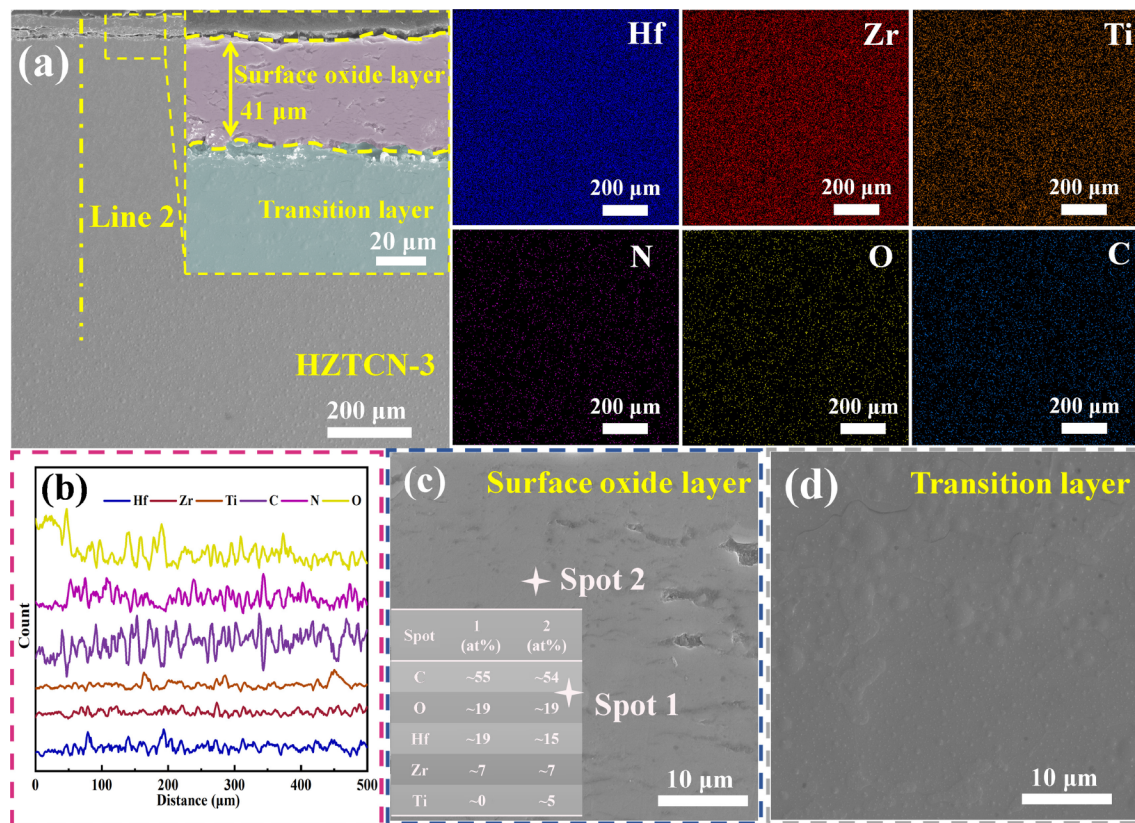


Fig. 5 Cross-sectional microstructure and elemental distribution of HZTCN-3 after oxyacetylene ablation: (a) cross-sectional SEM image and corresponding EDS elemental analysis, (b) line-scan elemental distribution profiles, (c) enlarged SEM image and EDS analysis of the surface oxide layer, and (d) enlarged SEM image of the transition layer.

compares the LAR and MAR values of SG-HZTCN-1 with those of other reported related coatings [39, 41–49], revealing that SG-HZTCN-1 possesses superior ablation resistance. Prior to ablation, the coating exhibits a dense structure without visible cracks. After ablation, no cracks or spallation are observed on the coating surface, which is attributed to the effective mitigation of thermal stress concentration at the coating/substrate interface by the SiC gradient transition layer. Following oxyacetylene flame ablation, a white oxide scale forms on the sample surface and distinctly separates into two regions: the central ablation zone (region I) and the peripheral edge region (region II). Specifically, region I displays obvious oxide protuberances originating from the evolution channels created by gaseous oxides during the ablation process. Meanwhile, low-melting-point oxides are swept by the thermal flow into cooler region II, producing a splashed morphology [50].

The phase composition of the ablated coating is determined by XRD (Fig. 7(c)), revealing complex oxide phases dominated by HfO_2 . The formation of these high-melting-point oxides indicates that a protective oxide scale composed of multicomponent oxides develops during high-temperature ablation, effectively dissipating heat and hindering further oxidation. Furthermore, SEM images of the ablated coating surface (Fig. 7(d)) reveal a pronounced radial structural gradient across the surface oxide layer from the ablation center to the edge: the microstructure becomes progressively denser toward the center, whereas the region away from the center exhibits a porous morphology.

The microstructure of the oxide layer is further characterized by TEM analysis (Fig. 7(e)). The corresponding FFT pattern along the $[\bar{1}, 0, 1]$ zone axis corroborates the monoclinic structure of the

oxide phase, consistent with the XRD results. The measured (111) and (020) interplanar spacings are 2.7733 and 2.365 Å [51], respectively, both slightly lower than the reference values for monoclinic HfO_2 (2.8253 and 2.5861 Å, PDF#04-005-4474), which can be attributed to the dissolution of smaller Ti atoms into the HfO_2 lattice [52]. The strain distribution map further reveals the deformation characteristics of the SG-HZTCN-1 coating prior to ablation. The surface strain exhibits a relatively uniform distribution, with strain fluctuations mainly ranging from -0.1 to 0.1 , indicating low residual stress and good structural integrity of the as-prepared coating. Although localized alternating tensile and compressive strain bands can be observed, no severe strain concentration or penetrating cracks are detected, suggesting that the coating maintains a dense and stable microstructure. STEM-EDS elemental mapping of the oxide layer (Fig. 7(f)) presents the nanoscale distribution of Hf, Zr, Ti, C, and N. The uniform distribution of Hf, Zr, and Ti within the oxide layer confirms the formation of a multicomponent oxide solid solution.

The initial structural state of the SG-HZTCN-1 coating prior to ablation was systematically characterized on the cross-section, as shown in Fig. 8. The cross-sectional SEM image and corresponding EDS elemental mappings in Fig. 8(a) reveal that the coating exhibits a relatively dense and continuous structure before ablation. No obvious pores, cracks, or delamination defects are observed at the interface between the coating and the graphite substrate, indicating that the preparation process achieves satisfactory coating deposition and favorable interfacial bonding. The EDS elemental mapping results further show that Hf, Zr, and Ti are uniformly distributed within the coating. The Si content increases gradually with increasing depth and diffuses into the

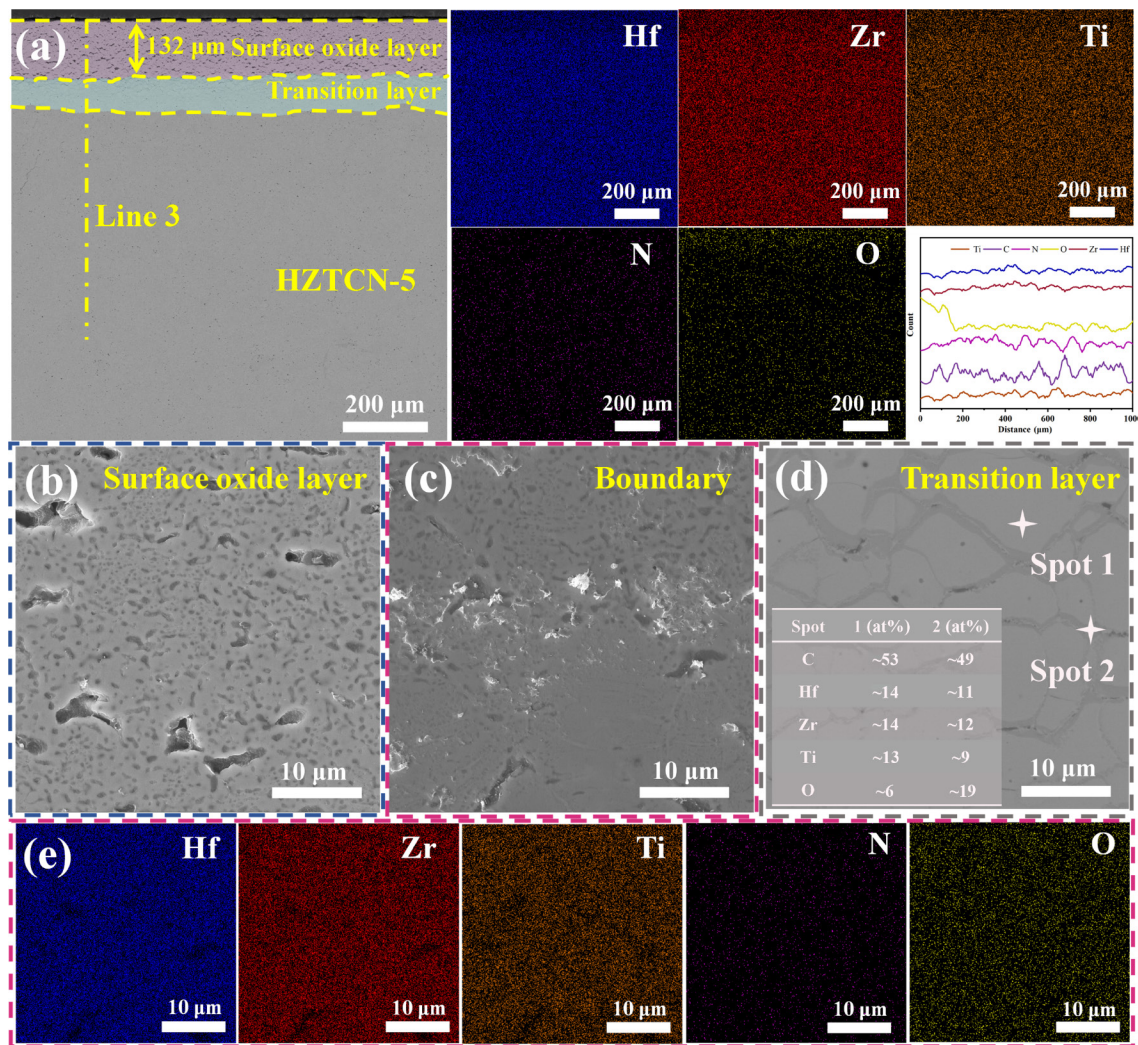


Fig. 6 Cross-sectional microstructure and elemental distribution of HZTCN-5 after oxyacetylene ablation: (a) cross-sectional SEM image and corresponding EDS elemental analysis, (b) enlarged SEM image of the surface oxide layer, (c) enlarged SEM image of the boundary region between the surface oxide layer and transition layer, (d) enlarged SEM image and EDS analysis of the transition layer, and (e) corresponding EDS mappings in (c).

graphite substrate. The line-scan results in Fig. 8(b) further verify the gradient variation of composition at the coating-substrate interface.

Figure 8(c) presents a high-magnification SEM image of the coating surface region, revealing a continuous microstructure with good structural uniformity. In addition, the SEM image of the coating-graphite boundary in Fig. 8(d) further confirms the close contact between the coating and the graphite substrate without apparent interfacial separation. The localized EDS mappings at the interface region in Fig. 8(e) reveal that Hf, Zr, Ti, C, N, and Si are continuously distributed across the coating-substrate interface. In particular, significant penetration of Hf and Si into the graphite substrate can be observed, while Si is enriched at the coating-substrate interface. These results indicate the formation of a chemically bonded transition region [53,54], which is beneficial for improving the interfacial adhesion and structural stability of the HZTCN-1 coating [55].

The cross-sectional SEM image and corresponding EDS mappings of the SG-HZTCN-1 coating after 120 s of oxyacetylene flame ablation are presented in Fig. 9(a). A continuous oxide layer approximately 460 μm in thickness forms on the coating surface after ablation. The coating-graphite interface remained intact, with no obvious through-thickness cracks or extensive delamination

observed. The EDS elemental mappings indicate that O is mainly enriched in the surface region of the coating and decreases markedly within the transition layer, which is consistent with the elemental line-scan results shown in Fig. 9(b). Figures 9(c)–9(e) show the high-magnification SEM morphology and corresponding EDS analysis of the transition layer. The amorphous region exhibits pronounced co-enrichment of Si and O, which can be assigned to a SiO₂-rich oxide phase. Under high-temperature ablation conditions, the oxidation of SiC incorporated in the coating promotes the generation of Si-rich oxide phases. Owing to its favorable fluidity at elevated temperatures, this phase facilitates the filling of local pores and microdefects, increases the local compactness of the transition layer, and provides a barrier against further oxygen penetration into the coating [18,54,56,57]. Figure 9(d) further reveals numerous nanowire structures within the transition layer. The local high-magnification morphology and EDS analysis in Fig. 9(e) demonstrate that these nanowire regions are primarily composed of C, Si, and O and can thus be assigned to Si–C–O nanowires. Their formation is related to the oxidation of coating-incorporated SiC during ablation, which produces volatile SiO species. These gaseous SiO species undergo vapor-phase transport driven by the temperature gradient and subsequently participate

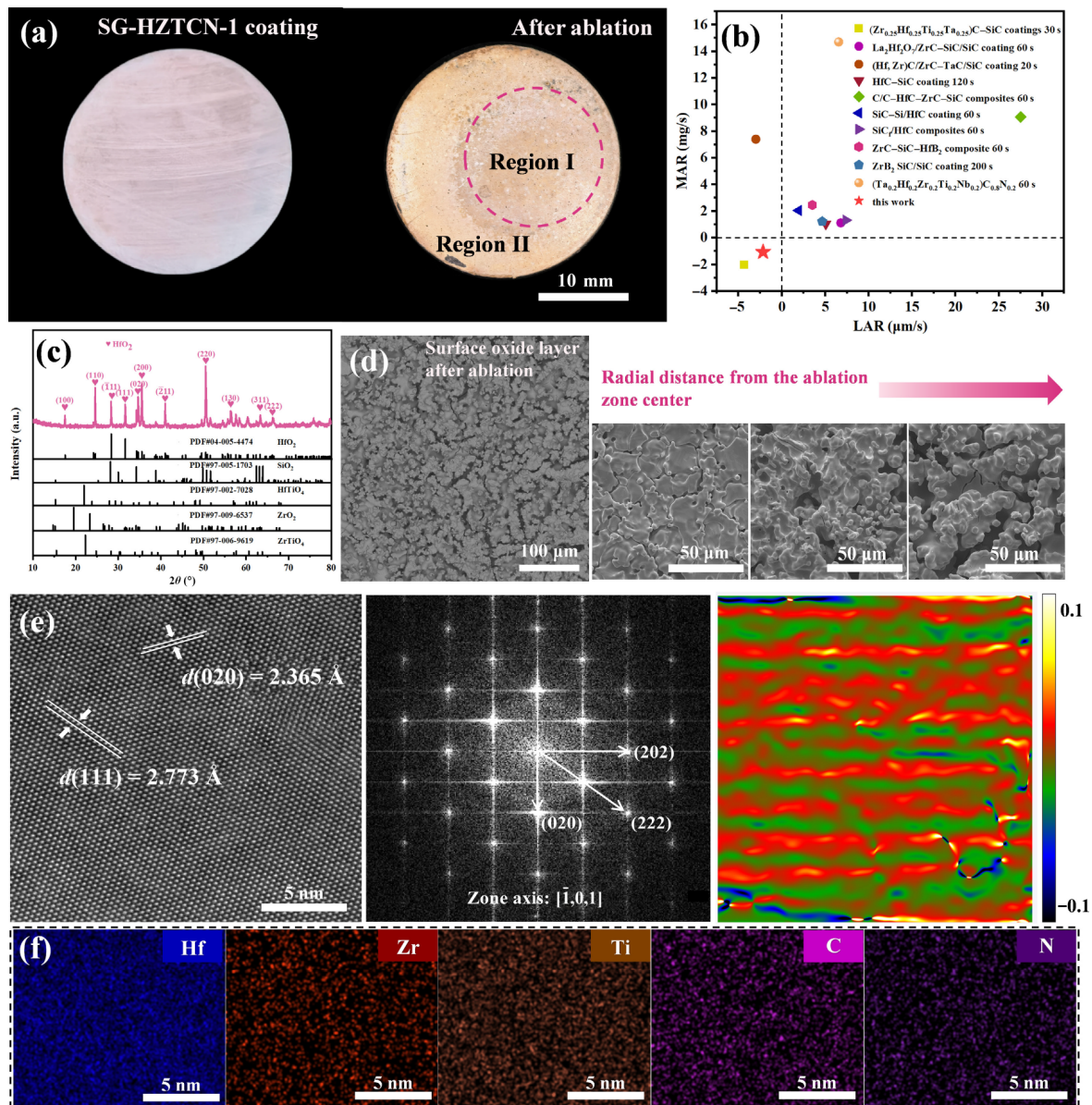


Fig. 7 (a) Macroscopic morphologies of the SG-HZTCN-1 coating before and after ablation, (b) comparison of the ablation properties of the SG-HZTCN-1 coating from the present work with other related coatings reported in recent years, (c) XRD pattern of the SG-HZTCN-1 coating after ablation, (d) SEM images of the radial evolution of the surface oxide layer from the central ablation zone to the edge, and (e) HRTEM image of the oxide scale, the corresponding FFT pattern along the $[1,0,1]$ zone axis, and the GPA ε_{yy} stress-strain map. (f) Corresponding STEM-EDS mappings of Hf, Zr, Ti, C, and N.

in gas-solid reactions at high temperatures [58,59], leading to the *in situ* growth of Si–C–O nanowires. The Si–C–O nanowires fill local pores and increase the tortuosity of oxygen diffusion pathways, thus preserving the structural integrity and improving the oxygen-blocking capability of the coating [60,61]. Figure 9(f) presents the SEM morphology and corresponding EDS elemental mappings of the coating-graphite interface after ablation. Noticeable cross-interface elemental redistribution of Hf and Si is detected, with pronounced Si enrichment near the interface region. This behavior is consistent with the interfacial element diffusion behavior observed before ablation.

Overall, the ablated SG-HZTCN-1 coating develops a continuous surface oxide layer as well as a transition layer containing SiO₂-rich oxide phases and Si–C–O nanowire structures. These multiscale features, coupled with interfacial elemental redistribution, help maintain the structural integrity of

the coating upon ablation and impede further oxygen penetration into the coating and graphite substrate, consequently improving the ablation resistance of the SG-HZTCN-1 coating.

3.4 Deciphering the ablation-resistance mechanism of the SG-HZTCN-1 coating

The outstanding ablation resistance of the SG-HZTCN-1 coating arises from the synergistic interplay of several key mechanisms, which can be categorized into three aspects: phase stability and oxide barrier formation, self-healing and nanowire, and interfacial strengthening, as illustrated in Fig. 10.

1) Phase stability and oxide barrier formation. MD simulations are employed to elucidate the atomic-scale evolution of the initial oxidation stage of the SG-HZTCN-1 coating. As shown in Fig. 10(a), oxygen atoms initially distributed on the coating surface gradually migrate into the Hf–Zr–Ti–C–N matrix under the high-

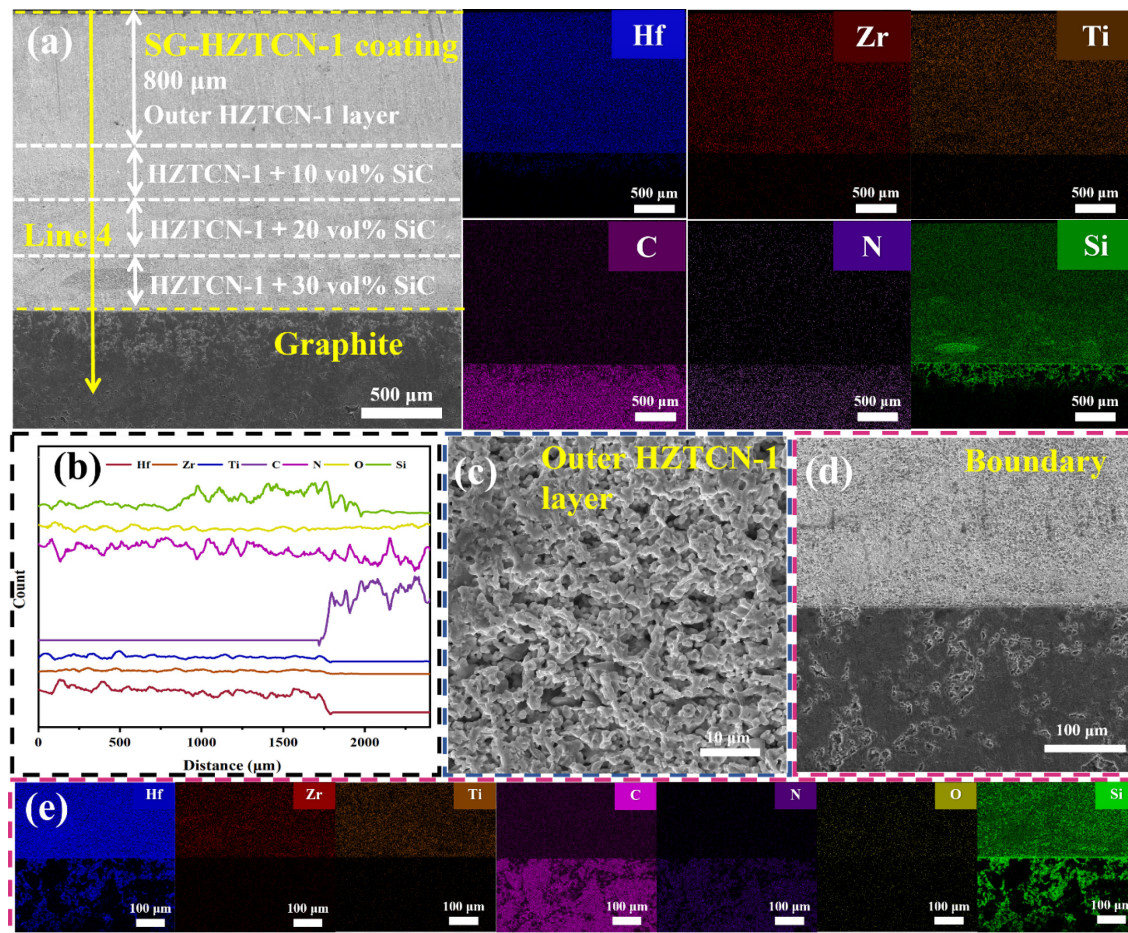


Fig. 8 Cross-sectional microstructure and elemental distribution of the SG-HZTCN-1 coating before ablation: (a) cross-sectional SEM image and corresponding EDS elemental analysis, (b) line-scan elemental distribution profiles, (c) enlarged SEM image of the outer HZTCN-1 layer, (d) enlarged SEM image of the boundary between the coating and substrate, and (e) corresponding EDS mappings in (d).

temperature environment and interact with Hf, Zr, and Ti atoms, promoting the development of metal-oxygen coordination structures near the surface. As oxidation proceeds, oxygen is enriched within the superficial layer of the coating, while its concentration decreases sharply with increasing depth from the surface, indicating that further inward oxygen transport is increasingly restricted by the oxidized surface region. The resulting Hf-, Zr-, and Ti-containing oxide layer can thus serve as an effective barrier to oxygen diffusion, suppressing further oxygen penetration into the coating and thereby protecting the underlying graphite substrate. This atomic-scale oxygen migration and enrichment behavior is consistent with the experimentally observed dense, oxygen-rich surface oxide layer and the pronounced decrease in oxygen content toward the underlying transition layer, providing further insight into the initial oxidation mechanism of the SG-HZTCN-1 coating, in which the formation of a surface oxide layer effectively impedes inward oxygen diffusion. XRD and HRTEM analyses reveal that the as-prepared FCC carbonitride solid solution transforms into HfO_2 -dominated multicomponent oxides after ablation. Cross-sectional observations confirm an oxygen-rich dense oxide layer on the top surface, whereas the oxygen content in the underlying transition layer decreases sharply, establishing a distinct oxygen concentration gradient. This oxide layer acts as an efficient barrier against inward oxygen diffusion, thus inhibiting further oxidation of the substrate and substantially enhancing ablation resistance [62,63].

2) Self-healing and nanowire synergistic effects. Silicon,

originating from the SiC-doped transition layer, oxidizes to form a SiO_2 -rich oxide phase at high temperatures [54]. This oxide phase flows into defects and pores, sealing them and increasing the compactness of the transition layer [64]. Additionally, a Si-C-O nanowire network forms within the transition layer, as shown in Fig. 9(e). These nanowires help relieve thermal stress, increase the tortuosity of oxygen diffusion pathways, hinder oxygen inward diffusion, and consequently improve the ablation resistance of the coating [58,65].

3) Interfacial strengthening and thermal expansion accommodation. An elemental diffusion transition layer forms between the coating and the graphite substrate, characterized by the interpenetration of Hf and Si into the graphite. This gradient layer effectively alleviates the thermal expansion mismatch between the ceramic coating and the carbon substrate, preventing interfacial cracking and delamination [54,66].

In summary, the exceptional ablation resistance of the SG-HZTCN-1 coating is the result of a multifactor synergy: (i) the structural stability of the multielement carbonitride solid solution and its transformation into a HfO_2 -dominated multicomponent oxide scale, which effectively isolates the invasion of external oxygen, significantly reduces the oxygen content in the transition layer, and thus provides reliable protection for the graphite substrate; (ii) the self-healing effect of the SiO_2 -rich oxide phase and the stress-relieving function of the Si-C-O nanowire network; (iii) the strong interfacial bonding and thermal mismatch accommodation provided by the Si-enriched diffusion layer.

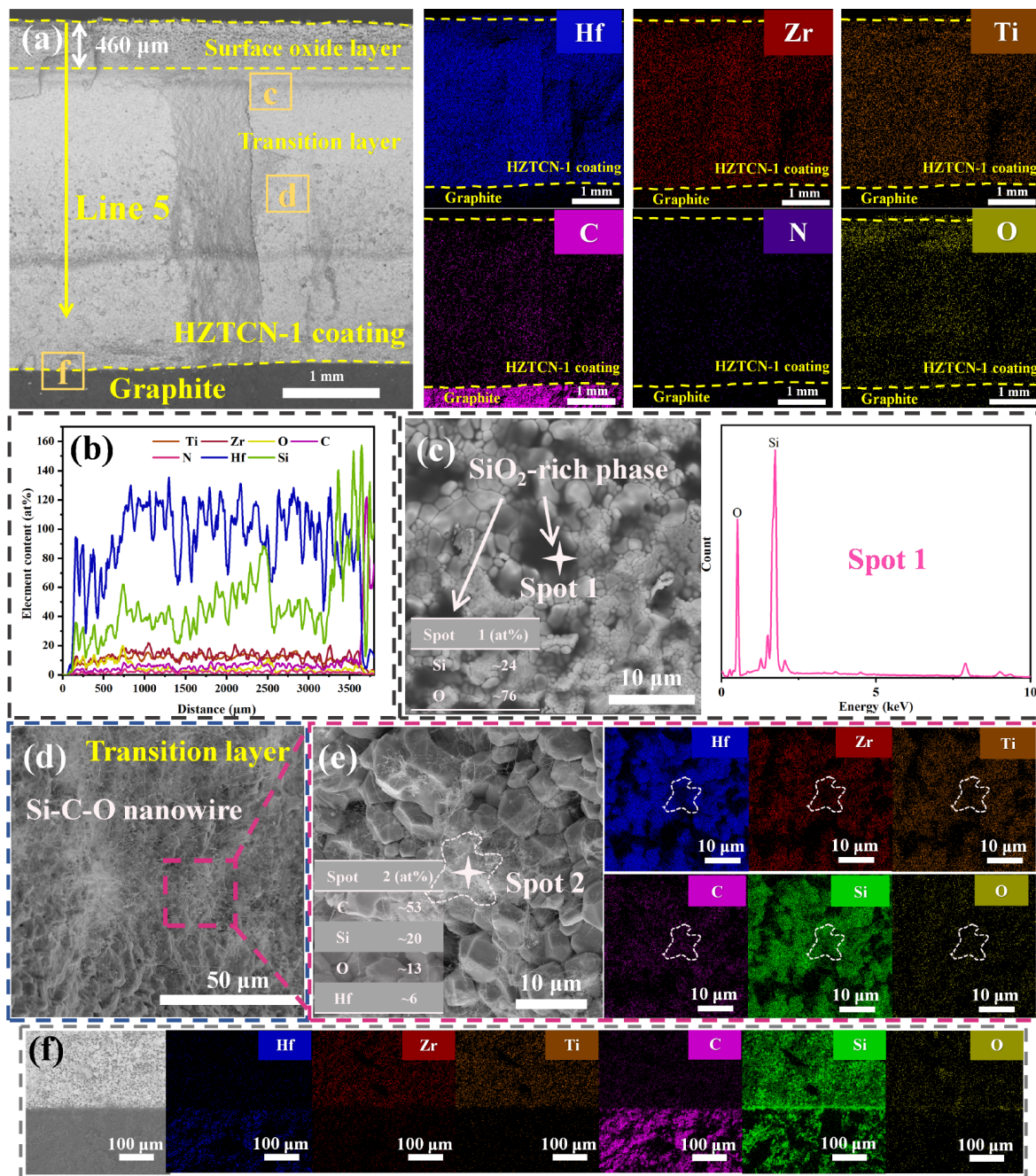


Fig. 9 (a) Cross-sectional SEM image and corresponding EDS elemental mappings of the SG-HZTCN-1 coating after ablation, (b) line-scan elemental distribution profiles, (c–e) high-magnification SEM image and corresponding EDS analysis of the transition layer, and (f) high-magnification SEM image and corresponding EDS elemental mappings of the interfacial region.

4 Conclusions

Hf-Zr-Ti-C-N bulk ceramics with varied Hf/Zr/Ti atomic ratios are fabricated by SPS, all forming FCC carbonitride solid solutions with homogeneous elemental distributions. Based on the highest fracture toughness and excellent ablation resistance, HZTCN-1 is selected as the primary ceramic component. When deposited as a coating on graphite with a SiC-graded transition layer, the SG-HZTCN-1 coating maintained structural integrity after 120 s of oxyacetylene flame ablation, preserving dense interfacial bonding and multilayered structure. The excellent ablation resistance arises from three synergistic mechanisms: (i) MD simulations of the initial oxidation stage reveal oxygen migration and enrichment near the coating surface, consistent with the

experimentally observed HfO₂-dominated oxide scale, which effectively impedes inward oxygen diffusion; (ii) the formation of a SiO₂-rich phase and Si-C-O nanowire network that seal defects, mitigate thermal stress, and extend oxygen diffusion pathways; and (iii) the formation of a Si-enriched diffusion layer at the coating-substrate interface, which strengthens interfacial adhesion. Collectively, this work establishes a composition-optimized Hf-Zr-Ti-C-N coating with outstanding ablation resistance and provides a mechanistic blueprint for designing multielement carbonitride thermal protection systems for extreme aerospace environments. Future studies may further focus on the long-term reliability of the coating under complex service environments and optimize the graded structure for practical applications.

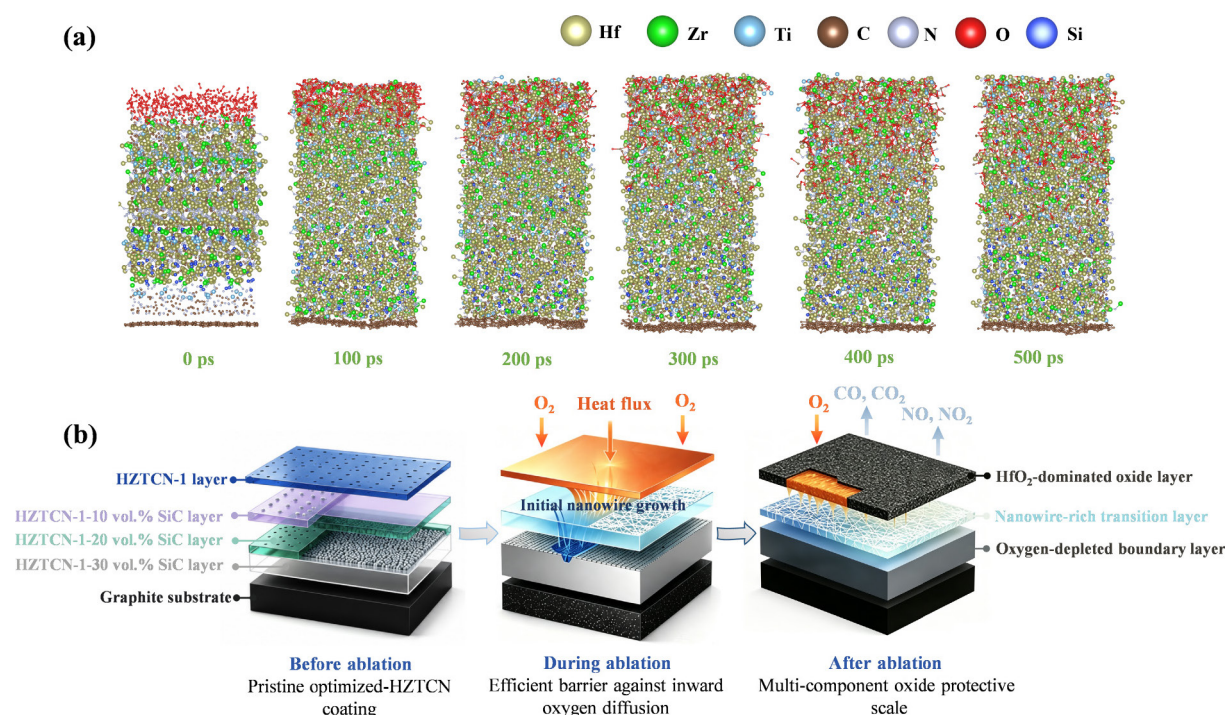


Fig. 10 (a) Atomic-scale evolution of SG-HZTCN-1 at different stages of oxidation; (b) ablation resistance mechanism of the SG-HZTCN-1 coating.

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Author contributions

All authors contributed to the study conception and design. Zheng Peng: Conceptualization, project administration, investigation, methodology. Lu Yu: Writing – original draft, visualization, validation, methodology, investigation, formal analysis, data curation. Junping Li: Funding acquisition, supervision, validation, writing – review & editing. Jianbo Song: Software, Resources, Data curation, Validation. Weide Wang: Supervision, methodology, conceptualization. Lei Guo: Validation, Data curation. Qingsong Ma: Investigation, Formal analysis. Jiecai Han: supervision, writing – review & editing. Zheng Peng and Lu Yu contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

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.

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