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Research Article

Enhancement mechanism of high temperature stability for *in-situ* oxide scale on high-entropy carbide coatings induced by rare earth

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Abstract: For ultra-high temperature ceramic (UHTC) coatings used in aerospace thermal protection systems, enhancing the oxygen barrier capability and thermal stability of *in-situ* oxide scale during ablation is crucial for stable service. Herein, a high-entropy design strategy is proposed to boost the compactness and phase stability of oxide scales by leveraging multi-component synergistic effects. Three high-entropy carbide coatings, (Hf-Zr-Ti-Sc-Y-Sm)C (HEC-Sm), (Hf-Zr-Ti-Sc-Y-Er)C (HEC-Er) and (Hf-Zr-Ti-Sc-Y-Lu)C (HEC-Lu), with better ablation resistance than ZrC, (Hf-Zr-Ti)C, and (Hf-Zr-Ti-Sc-Y)C coatings,were designed. HEC-Lu delivers optimal ablation resistance, featuring a linear ablation rate of -0.173 ± 0.012 μm·s^{-1}, superior to HEC-Sm (-0.111 ± 0.032 μm·s^{-1}) and HEC-Er (-0.144 ± 0.022 μm·s^{-1}). This superior performance is correlated with higher Ti retention and stronger calculated Ti-O bonding, increasing Ti content in the oxide scale by 53.85 % and 33.33 % compared to HEC-Sm and HEC-Er, thereby inhibiting volatilization. Rare-earth (Sm, Er, Lu) incorporation can reduce the diffusion coefficients of Ti and O atoms in oxide scales by one order of magnitude at 2573 K compared with TiO_2. Notably, Lu introducing yields a higher Mulliken population (0.279) for Ti-O bonds than that of Sm (0.268) and Er (0.274), which strengthens Ti-O bonds inside the oxide scale. This work presents a novel material selection scheme for anti-ablation coatings in extreme environments.

Keywords: High-entropy carbide, Rare earth element, Coating, Ablation resistance.

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1 Introduction

Ultra-high temperature ceramics (UHTCs), represented by HfC, ZrC, HfB_2, and ZrB_2, exhibit high melting points, hardness, modulus and exceptional chemical inertness, rendering them suitable as high-temperature ablation-resistant coatings extensively employed in thermal protection systems (TPS) for heavy-lift launch vehicles [1-3]. The UHTCs coating achieves excellent anti-oxidation and ablation resistance by forming an oxide protective scale to isolate itself from oxidizing media in the service

environment [4, 5]. Consequently, the *in-situ* generated oxide scale on UHTC coatings plays a pivotal role in their high-temperature ablation protection [6]. The oxide scale formed on single-component UHTC coatings typically exhibits a porous and loose microstructure, which makes it difficult to achieve the complete protection from oxidizing media. While such porous oxide scales may afford effective protection during short-term service, prolonged exposure entails its failure risks including cracking and spallation [7]. Enhancing the oxygen barrier capability and high-temperature stability of the *in-situ* oxide scale constitutes a critical challenge for achieving long-life and reliable service of UHTC coatings.

Compositional modification has proven to be an effective strategy for tailoring the performance of *in-situ* oxide scales on UHTC coatings [8]. Incorporating components such as SiC, TiC, TaC, and NbC into UHTC coatings facilitates the formation of low-melting-point glassy phases within the oxide scale [9]. The healing of voids and microcracks in the oxide scale by these glassy phases substantially enhances the structural densification and oxygen barrier capability of the *in-situ* oxide scale [10]. Luo et al. [11] evaluated the ablation resistance of multicomponent UHTC coatings and revealed that the highly viscous (Ti-Si-Ta)O_x glassy phase formed during ablation improves the densification of the oxide layer, thereby imparting superior ablation resistance. Notably, the TiO_2 glassy phase exhibits a low oxygen diffusion rate and excellent self-healing characteristics [12]. Introducing Ti-containing modifiers into UHTC coatings represents an effective route to ameliorate oxygen barrier performance [13]. However, titanium oxides tend to volatilize under ultra-high temperatures (>2400 K), which is detrimental to the stable protection of the oxide scale during ablation [14].

Incorporating rare-earth components, such as Y, Yb and Sc, as phase stabilizers into UHTC coatings can suppress phase transformations of HfO_2 and ZrO_2 in the oxide scale, thereby circumventing stress-induced cracking associated with phase transitions [15, 16]. In recent years, the selection of rare-earth components has gradually expanded to the lanthanide elements. Brenner et al. [17] reported that Sm-doped ZrB_2/SiC coatings exhibited exceptional ablation resistance by forming a

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Sm-stabilized *t*-ZrO_2 layer at 1700 °C. Meanwhile, heavy rare-earth elements with small atomic radii have also been introduced into UHTC coatings to enhance the ablation resistance. In a study focusing on the Sm and Er co-modified ZrB_2/SiC ceramics, Angel et al. [18] reported that the oxide scale with $(Sm, Er)_{0.2}Zr_{0.8}O_{1.9}$ as the dominant phase was formed during ablation, which enabled stable 300-s ablation resistance at 2000 °C. Among lanthanide elements, Lu possesses the smallest atomic radius, and its oxide possesses the highest melting point. Modifying UHTCs by introducing Lu may yield superior performance compared to Sm and Er reported in existing studies. However, relevant research has rarely been reported so far. Meanwhile, the stabilizing effect of rare-earth elements Sm, Er and Lu on TiO_2 remains unclear.

In recent years, the concept of high entropy has extended from the metallic domain to the ceramic field [19]. High-entropy UHTCs represent a class of multicomponent solid solutions, typically comprising at least five metallic elements in equimolar proportions or more than six metallic elements [20]. Benefiting from the synergistic effects of multiple components, high-entropy UHTCs exhibit superior thermal protection properties [21], and integrate structural-functional characteristics [22, 23]. However, current research on high-entropy UHTC coatings has predominantly concentrated on transition metal carbides from groups IVB, VB, and VIB. The inherent high-entropy effect of high-entropy ceramics provides an opportunity to incorporate rare earth elements with significantly different atomic radii into the lattice. However, there are no high-entropy carbides containing Sm, Er and Lu, and their ablation resistance remains unknown.

In this work, Hf and Zr (totaling 60 mol.%) were selected as the principal components of the rare-earth-containing high-entropy carbide to guarantee superior high-temperature resistance of its *in-situ* oxide scale. Ti (10 mol.%) and rare-earth elements (30 mol.%) serve as the self-healing and phase-stabilizing components, respectively. The phase-stabilizing component consists of three equimolar rare-earth species, which are Sc, Y, and one chosen from Sm, Er and Lu. Following this compositional strategy, a highly stable high-entropy oxide scale forms in situ on the high-entropy carbide coating

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during ablation, improving the ablation resistance of coatings. Three high-entropy carbide coatings were deposited on C/C composites via supersonic atmospheric plasma spraying, and their ablation resistance was comparatively evaluated. To assess the ablation resistance, a high-enthalpy Ar-H_2 plasma ablation system was employed to simulate the ultra-high temperature environment encountered by the TPS during spacecraft atmospheric re-entry. Through detailed characterization of phase composition and microstructure, the stabilization mechanism of the oxide scale during ablation and its intrinsic correlation with ablation resistance were elucidated. This investigation elucidates the ablation behavior of rare-earth-containing high-entropy carbide coatings and provides a theoretical foundation for the optimization of oxide scale stability design.

2 Methods

2.1 Synthesis of high-entropy carbide powders

The commercially available HfO_2, ZrO_2, TiO_2, Sc_2O_3, Y_2O_3, Sm_2O_3, Er_2O_3 and Lu_2O_3 powders (grain size: 1-3 μm, purity: 99.9 %, Beijing Huawei Ruike Chemical Technology Co., Ltd.) and graphite powders (5000 mesh, purity 99.99 %, Shandong Guanzhi New Materials Technology Co., Ltd.) were used to synthesize the rare-earth-containing high-entropy carbide powders according to the following chemical equations:

$$0.36HfO_2+0.24ZrO_2+0.1TiO_2+0.05Sc_2O_3+0.05Y_2O_3+0.05Sm_2O_3+1.925C = (Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Sm_{0.1})C+0.925CO_2\ (g) \quad (1)$$

$$0.36HfO_2+0.24ZrO_2+0.1TiO_2+0.05Sc_2O_3+0.05Y_2O_3+0.05Er_2O_3+1.925C = (Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Er_{0.1})C+0.925CO_2\ (g) \quad (2)$$

$$0.36HfO_2+0.24ZrO_2+0.1TiO_2+0.05Sc_2O_3+0.05Y_2O_3+0.05Lu_2O_3+1.925C = (Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Lu_{0.1})C+0.925CO_2\ (g) \quad (3)$$

The weighed oxide and carbon powders with stoichiometric ratios were mixed by planetary ball milling at 400 rpm for 8-12 h. The mixed powders were placed in a graphite crucible for heat treatment

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under an Ar atmosphere. The temperature was programmatically increased slowly to 2100 °C at a heating rate of 2-4 °C·min^{-1}, followed by a 2 h holding period, and then cooled naturally. Thus, high-entropy carbide powders were synthesized.

2.2 Preparation of high-entropy carbide coatings

The supersonic atmospheric plasma spraying (SAPS) technology (HEPJ-II type, The Academy of Armored Forces Engineering, China) was used to prepare HEC-Sm, HEC-Er, and HEC-Lu coatings on SiC-coated C/C composites. The 2.5D needled C/C composites (Research Institute of Carbon/Carbon Composites, Northwestern Polytechnical University, China) with a density of approximately 1.70 g cm^{-3} were machined into cylindrical plates (Φ25 mm × 7 mm). Before preparation of high-entropy carbide coatings, a SiC coating with a coefficient of thermal expansion (CTE) intermediate between the C/C substrate and carbides was prefabricated on the surface of C/C composites to mitigate thermal mismatch between the coating and substrate and enhance the bonding strength of the SAPS coating to the substrate. [24]. The machined C/C composite was placed into a graphite crucible, which was filled with a powder mixture consisting of Si, C and Al_2O_3 at a mass ratio of 5-7:1:0.5 to achieve sufficient contact between the C/C composite and the mixed powders. The graphite crucible was then transferred into a graphite furnace (VHSF303, Shenyang Vacuum Technology Institute, China) for high-temperature heat treatment. The detailed heat-treatment parameters were identical to those adopted for synthesizing high-entropy carbide powders. The SiC coating with a thickness of 200-250 μm was formed on the C/C composite surface via the high-temperature reaction with the powder mixture. The detailed SAPS parameters are as follows: (I) spraying voltage and current: 105~115 V and 400 A; (II) primary Ar gas flux: 70~75 L·min^{-1} (III) second H_2 gas flux: 3~4 L·min^{-1}; (IV) spraying distance: 100 mm; (V) powder feeding rate and Ar gas flux: 1.5 rpm and 5~10 L·min^{-1}. The as-fabricated HEC-Sm, HEC-Er, and HEC-Lu coatings were ultrasonically cleaned in ethanol and dried prior to ablation tests.

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2.3 Ablation test

An Ar-H_2 plasma torch (HEPJ-II type, The Academy of Armored Forces Engineering, China) with a heat flux density of approximately 10 MW·m^{-2} was used to evaluate the ablation resistance of the high-entropy carbide coatings [25]. The ablation duration and distance were set to 300 s and 40 mm, respectively. A dual-color infrared thermometer (PYROVIEW 768 N, Dresden, Germany) was used to measure the maximum surface temperature of the coatings during ablation.

After ablation, the mass ablation rate (R_m) and linear ablation rate (R_l) were calculated using the following equations to evaluate the ablation resistance:

$$R_m = (m_0 - m_1)/t \quad (4)$$

$$R_l = (l_0 - l_1)/t \quad (5)$$

where m_0 and m_1 represent the mass of samples before and after ablation, l_0 and l_1 represent the average thickness before ablation and the minimum thickness after ablation, respectively, and t is the ablation duration.

2.4 First-principles calculation

First-principles calculations based on density functional theory (DFT) were performed using the Cambridge Serial Total Energy Package (CASTEP) within Materials Studio 19.0. For the structural calculations of HEC-Sm, HEC-Er, and HEC-Lu, a 3 × 1 × 1 supercell containing 24 atoms was constructed. To ensure accuracy, three random structures with disordered distributions of Hf, Zr, Ti, Sc, Y, and RE (RE = Sm, Er, Lu) atoms were generated for each composition using the Shuffle function. The crystal structure with the lowest energy after DFT relaxation was selected for lattice constant determination.

The same approach was applied to model the crystal structures and electronic properties of the oxide scales formed after ablation of the HEC-Sm, HEC-Er, and HEC-Lu coatings. For the *in-situ* oxide scales, 2 × 2 × 2 fluorite supercells containing 96 atoms were built. The generalized gradient

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approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) was selected as the exchange-correlation functional. On-the-fly generated (OTFG) ultrasoft pseudopotentials and the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm were used for geometry optimization. Fig. S1 displays the convergence test results of the calculation parameters. After conducting the convergence test, the cutoff energy, self-consistent field (SCF) tolerance, and maximum *k*-point spacing were set to 650 eV, 10^{-5} eV, and 0.05 $Å^{-1}$, respectively, for all DFT calculations.

2.5 Molecular dynamics simulation

To investigate the atomic motion behavior and volatility tendency of TiO_2 and the *in-situ* oxide scales of high-entropy carbide coatings in the high-temperatrure environments, ab initio molecular dynamics (AIMD) simulations were conducted. A 2×2×3 TiO_2 supercell and 2×2×2 (Hf-Zr-Ti-Sc-Y-Sm)$O_{2-\delta}$, (Hf-Zr-Ti-Sc-Y-Er)$O_{2-\delta}$, (Hf-Zr-Ti-Sc-Y-Lu)$O_{2-\delta}$ supercells were constructed. The NPT ensemble were first performed to obtain fully relaxed crystal configurations. The AIMD simulation parameters for the NPT stage were set as 2573 K, 0 GPa and 50 fs, corresponding to temperature, pressure and total simulation time, respectively. After structural relaxation, subsequent AIMD simulations were carried out under the NVT ensemble at 2573 K for 1000 fs to track the high-temperature migration trajectories of individual atoms [26].

2.6 High-temperature volatilization experiment

Commercially available HfO_2, ZrO_2, TiO_2, Sc_2O_3, Y_2O_3, and Lu_2O_3 powders (grain size: 1-3 μm, purity: 99.9 %, Beijing Huawei Ruike Chemical Technology Co., Ltd.) were selected as raw materials. Firstly, high-entropy oxide powders were prepared via ball milling mixing and solid-state reaction [27]. The as-synthesized high-entropy oxide powders were ground to reduce particle size and sieved through a 300-mesh screen. Subsequently, the sieved powders were uniaxially pressed in a stainless-steel mold

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at 20 MPa into disk-shaped blocks with a diameter of 10 mm. Finally, the green bodies were placed in Al_2O_3 crucibles and sintered at 1500 °C for 5 h in a muffle furnace to obtain dense oxide blocks.

The rapid Joule heating systems (Xi'an Jiasuo Equipment Co., Ltd. and Guizhou Shangli Experimental Equipment Co., Ltd.) were employed to conduct heat treatment on the as-sintered high-entropy oxide blocks. The ultrahigh heating rate generated by the Joule heating effect enables effective reproduction of the extreme thermal conditions encountered during ablation [28]. First, the synthesized bulk high-entropy oxide ceramics were subjected to vacuum heat treatment at 1700 °C for 100 s to verify the high-temperature volatilization behavior of TiO_2 [29]. Subsequently, the high-entropy oxide powders were thermally treated in vacuum at 2300 °C for 30 s, a temperature close to the actual ablation temperature, to simulate the TiO_2 volatilization process of the oxide scale during the ablation reaction.

2.7 Characterization

The phase compositions of the high-entropy carbide powders, coatings, and ablated coatings were characterized by X-ray diffraction (XRD, X'Pert Pro, PANalytical, Netherlands) using Cu Kα radiation (λ = 1.54056 Å). Inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP PRO, Thermo Fisher, USZ) and thermogravimetric analysis (TGA, STA449F5 Jupiter, NETZSCH, Germany) were carried out to determine the actual composition of the high-entropy carbides. The morphologies of the coatings before and after ablation were observed using scanning electron microscopy (SEM, EVO10 ZEISS, Germany). Elemental analysis was conducted using energy-dispersive spectroscopy (EDS) attached to the SEM. The morphology, phase structure, and elemental distribution of the high-entropy carbide powders and ablated coatings were further characterized by field-emission transmission electron microscopy (TEM, FEI Themis Z, USA).

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3 Results and discussion

3.1 Phase structure of high-entropy carbide

Three types of high-entropy carbide powders, namely $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Sm_{0.1})C$ (HEC-Sm), $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Er_{0.1})C$ (HEC-Er) and $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Lu_{0.1})C$ (HEC-Lu), were synthesized via a carbothermal reduction method. A series of characterization techniques were employed to analyze their phase structures, as illustrated in Fig. 1. Fig. 1(a) presents the XRD patterns of HEC-Sm, HEC-Er, and HEC-Lu powders, where single-phase solid solutions with a rock salt structure ($Fm\bar{3}m$) are evident. Figs. S2(a-c) present the XRD refinement patterns corresponding to Fig. 1(a), with no obvious diffraction peaks of secondary phases detected. This indicates that the various oxides fully reacted with carbon at 2100 °C. Fig. 1(b) displays the locally magnified view of the XRD patterns from the area marked by a red dashed box in Fig. 1(a). Minor differences in the positions of the (111) diffraction peaks among the three HEC powders are observed, suggesting variations in their lattice constants. Based on the refined XRD patterns, the lattice constants of HEC-Sm, HEC-Er, and HEC-Lu were calculated to be 4.621 Å, 4.618 Å, and 4.627 Å, respectively. These values are close to the DFT-calculated lattice constants of 4.62 Å, 4.61 Å, and 4.62 Å, respectively, as shown in Fig. 1(c). Fig. S3 shows the ideal crystal structures of HEC-Sm, HEC-Er, and HEC-Lu obtained from DFT calculations. Lattice distortions are clearly observed in the high-entropy carbide models, primarily arising from the incorporation of atoms with different atomic radii within the same lattice (Table S1). Such distortions are expected to contribute to enhanced thermophysical and mechanical properties [30].

To further confirm the formation of a single-phase high-entropy structure, the TEM analysis was performed. Figs. 1(d, g, j) show high-resolution TEM (HRTEM) images of the HEC-Sm, HEC-Er, and HEC-Lu powders, respectively. The arrangement of lattice fringes is consistent with that of the carbide ceramics with a rock salt structure. In Fig. 1(d), the lattice spacings of the (020) planes in HEC-Sm are measured as 2.316 Å and 2.321 Å, confirming the presence of lattice distortion, which is in good

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agreement with DFT results (Fig. 1(c)). Similar differences in identical lattice planes are observed in HEC-Er (2.705 Å and 2.677 Å for the (111) planes) and HEC-Lu (2.671 Å and 2.674 Å for the (111) planes), as shown in Figs. 1(g, j). The fast Fourier transform (FFT) patterns of HRTEM images are presented in Figs. 1(e, h, k), all confirming a single-phase rock-salt structure.

To reveal the atomic-scale distribution characteristics of each element, high-angle annular dark-field (HAADF) images of the three high-entropy carbides and the corresponding EDS elemental mappings were acquired, as shown in Figs. 1(f, i, l). In contrast to Hf and Zr, the other rare-earth elements exhibit a non-uniform distribution at the nanoscale. Given the feature of homogeneous elemental distribution at the nanoscale in high-entropy carbides [31], rare-earth containing high-entropy carbide was further investigated (Fig. S4 and Fig. S5). This segregation phenomenon of rare-earth elements can be observed within the nanometer scale of 25-100 nm. HRTEM images and their corresponding FFT patterns demonstrate that the areas with segregated components maintain the same crystal structure. Fig. S6 shows the mixing enthalpies (ΔH_{mix}) between each constituent single component in high-entropy carbides. Binary pairs with a high ΔH_{mix} tend to exhibit segregation behavior within the solid solution. The ΔH_{mix} values among transition metal carbides (HfC, ZrC and TiC) are less than 0.75 $eV \cdot atom^{-1}$, which are markedly lower than those between transition metal carbides and rare-earth carbides (> 9 $eV \cdot atom^{-1}$), as well as between different rare-earth carbides (> 20 $eV \cdot atom^{-1}$). This constitutes the fundamental origin of the fluctuated distribution of rare-earth elements in the lattice of high-entropy carbides.

To determine the actual compositions of the three high-entropy carbide powders, ICP-OES and TGA were performed for the quantitative analysis of metal and carbon elements, respectively (Table S3 and Fig. S7). The actual chemical formulas of the high-entropy carbides were determined to be $(Hf_{0.33}Zr_{0.27}Ti_{0.12}Sc_{0.10}Y_{0.09}Sm_{0.09})C_{0.95}$, $(Hf_{0.33}Zr_{0.27}Ti_{0.12}Sc_{0.11}Y_{0.09}Er_{0.08})C_{0.93}$ and $(Hf_{0.33}Zr_{0.28}Ti_{0.12}Sc_{0.10}Y_{0.09}Lu_{0.08})C_{0.96}$, which are close to the theoretically designed stoichiometries. Combining XRD, TEM, and quantitative compositional analysis, it can be concluded that despite the

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presence of nanoscale compositional fluctuations, all three high-entropy carbides form a single-phase rock-salt structure. Thus, three rare-earth-containing high-entropy carbide powders were successfully synthesized.

3.2 Microstructure and phase analysis of high-entropy carbide coatings

SAPS system was applied to prepare the high-entropy carbide coatings, and the microscopic morphology analysis of the high-entropy carbide coatings is shown in Fig. 2. Prior to the SAPS process, the high-entropy carbide powders with a spherical morphology were prepared via spray drying technology. The microstructures of HEC-Sm, HEC-Er, and HEC-Lu particles are shown in Figs. 2(a-c). At the micrometer scale, the high-entropy carbide powders are interconnected via polyvinyl alcohol (PVA), forming spherical structures [32]. The particle size of the high-entropy carbide powders is approximately 30-50 μm. Fig. 2(d) presents the actual composition of high-entropy carbide powders obtained by ICP-OES. Compared to the theoretical composition of the high-entropy carbides, slight differences are observed in the actual compositions of HEC-Sm, HEC-Er, and HEC-Lu powders.

A schematic diagram of the SAPS process is presented in Fig. 2(e). The spherical high-entropy carbide powders were transported to the spray gun by Ar gas. The Ar-H_2 plasma flame, generated by exciting the Ar-H_2 mixture gas with high-voltage power, melted the high-entropy carbide powders into molten droplets. These droplets then impacted the SiC-coated carbon/carbon (C/C) substrates to form the high-entropy carbide coatings. Figs. 2(f-h) show the cross-section microstructure of HEC-Sm, HEC-Er, and HEC-Lu coatings. The thickness of each of the three high-entropy carbide coatings is approximately 150 μm. The as-prepared high-entropy carbide coatings with a layered structure exhibit good interface bonding with the C/C substrates, with no obvious interface cracks or delamination observed.

Fig. S8 show the EDS elemental mappings of the HEC-Sm, HEC-Er, and HEC-Lu coatings. All elements exhibit a uniform distribution, indicating no significant elemental segregation occurred during the SAPS process. However, the evolution behavior of the microstructure, phase composition,

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and elemental distribution of high-entropy carbides after heating and melting by high-temperature plasma flames remains unclear. The SAPS-treated high-entropy carbide powders were collected in water for phase and compositional characterization, as shown in Fig. S9(a). Figs. S9(b-f) display the micro-morphologies and EDS elemental mappings of the three high-entropy carbide powders after the SAPS process. All three high-entropy carbide powders melted into smooth microspheres with particle sizes of 10-20 μm. At the micrometer scale, all elements are uniformly distributed within the microspheres. Fig. S10 and Fig. S11 present the TEM analyses of the three high-entropy carbide powders after the SAPS process. The high-entropy carbides retain their original cubic rock-salt structure, and the elements are also homogeneously distributed at the nanoscale. This indicates that the transient high-temperature treatment in the plasma gun further promotes elemental diffusion and homogenization [33], which accounts for the uniform elemental distribution in the coating (Fig. S8). Meanwhile, EDS elemental analysis reveals that the composition of the high entropy carbide powder before and after SAPS treatment is very similar.

3.3 Ablation resistance of high-entropy carbide coatings

To evaluate the ablation resistance of three kinds of rare-earth-containing high-entropy carbide coatings, an ultra-high-temperature plasma ablation system was employed. The macroscopic morphologies of HEC-Sm, HEC-Er, and HEC-Lu coatings before and after ablation are shown in Fig. 3(a). It can be clearly observed that a white or pink oxide scale formed on the surface of the coating after ablation. Except for slight cracking and lifting of the oxide scale at the edges of the HEC-Sm and HEC-Er coatings, the oxide scales on all three high-entropy carbide coatings are dense and intact, demonstrating excellent ablation resistance.

Fig. 3(b) shows the surface temperature curves at the center area of HEC-Sm, HEC-Er, and HEC-Lu coatings during ablation. The surface temperatures of three kinds of high-entropy carbide coatings increased rapidly and reached their highest values within the first 10 seconds. Subsequently, the surface

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temperatures remained stable until the end of the ablation process. The maximum ablation temperatures of HEC-Er and HEC-Lu coatings are similar, ranging between 2312 °C and 2362 °C. In contrast, the highest ablation temperatures of the HEC-Sm coatings are lower, ranging from 2250 °C to 2300 °C. Differences in ablation temperature are attributed to Sm incorporation, which tunes the emissivity of thermally grown oxide scales (Fig. S12). In the 2.5-5.0 μm short-to-medium wavelength range, the oxide scale formed on HEC-Sm coatings exhibits remarkably higher emissivity values of 0.24-0.26, in sharp contrast to HEC-Er (0.04-0.10) and HEC-Lu (0.06-0.12). Such elevated emissivity grants HEC-Sm excellent radiative cooling capability. Consistent with earlier reports, Sm modification of UHTC coatings facilitates radiative heat dissipation and mitigates surface overheating during ablation [34, 35].

R_m and R_l of the high-entropy carbide coatings after ablation are shown in Fig. 3(c). Note that negative values of R_m and R_l indicate weight gain and thickening of the coatings, reflecting excellent ablation resistance. Conversely, positive values indicate severe ablation, resulting in weight loss and thinning of the coatings. It should be noted that TGA analysis of the three high-entropy carbide powders (Fig. S13 and Table S4) reveals that their high-temperature oxidation is generally accompanied by mass gain. Compared to the single-component ZrC, the high-entropy carbides have a higher onset oxidation temperature (T_o), indicating that they possess superior oxidation resistance properties. The R_m and R_l values of HEC-Lu coatings are -0.089 ± 0.017 mg·s^{-1} and -0.178 ± 0.012 μm·s^{-1}, respectively, which are lower than those of the HEC-Sm and HEC-Er coatings, demonstrating superior ablation resistance. The R_m values of the HEC-Sm and HEC-Er coatings are positive, which can be attributed to cracking and partial ablation at the edge areas (Fig. 3(a)). Compared to the HEC-Sm coatings (-0.111 ± 0.032 μm·s^{-1}) and HEC-Er coatings (-0.144 ± 0.022 μm·s^{-1}), the R_l of the HEC-Lu coatings is reduced by 60.36 % and 23.61 %, respectively.

In conclusion, the ablation resistance of three kinds of rare-earth-containing high-entropy carbide coatings follows the order: HEC-Lu > HEC-Er > HEC-Sm. Fig. 3(d) compares the ablation resistance

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of HEC-Sm, HEC-Er, and HEC-Lu coatings on C/C composites with other UHTC coatings, ceramics, and composites [36-48]. At similar ablation temperature levels, the rare-earth-containing high-entropy carbide coatings in this work exhibit the lowest ablation rates (as listed in Table S5) and the most excellent ablation resistance.

3.4 Ablation mechanism

The microstructure and phase analysis of the high-entropy carbide coatings is shown in Fig. 4. Pores and cracks can be clearly observed in the cross-sectional microstructures of the coatings, as illustrated in Figs. 4(a, f, k). During ablation, the high-entropy carbides are oxidized to form CO and CO_2 gases, resulting in a porous oxide scale [49]. Simultaneously, the porous oxide scale tends to crack under the combined effects of thermal and mechanical stress [50]. The thicknesses of the HEC-Sm, HEC-Er, and HEC-Lu coatings are ~173 μm, ~188 μm, and ~196 μm, respectively. Compared to the pre-ablation thicknesses (HEC-Sm: ~161 μm, HEC-Er: ~169 μm, HEC-Lu: ~180 μm), all coatings show an increase in thickness, which is consistent with the R_l results shown in Fig. 3(c). EDS line scan was employed to determine the thickness of the *in-situ* formed oxide scale on the three ablated coatings, as shown in Fig. S14. The oxide scale, unoxidized coating, and SiC transition layer can be distinguished via the linear distribution profiles of O, C, and Si elements (Figs. S14(b, d, f)). Through measurements, it was determined that the HEC-Sm, HEC-Er, and HEC-Lu coatings formed oxide scales with thicknesses of 98-106 μm, 109-119 μm, and 118-125 μm, respectively, after ablation.

To identify the phase composition and crystal structure of oxide scales on the coatings, XRD measurements and corresponding Rietveld refinements were conducted, with the results displayed in Fig. S15. Only a single crystalline phase with a fluorite structure was detected, and no secondary crystalline phase precipitated in the *in-situ* oxide scale of three rare-earth-containing high-entropy carbide coatings. This demonstrates that the single crystalline phases in the oxide scales may be high-entropy solid solutions (Hf-Zr-Ti-Sc-Y-Sm)$O_{2-\delta}$ (HEO-Sm), (Hf-Zr-Ti-Sc-Y-Er)$O_{2-\delta}$ (HEO-Er), and

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$(Hf\text{-}Zr\text{-}Ti\text{-}Sc\text{-}Y\text{-}Lu)O_{2\text{-}\delta}$ (HEO-Lu), which inherit all six constituent elements from the pristine coatings. This observation aligns with our previous studies [51, 52], in which high-entropy oxides were also found to form on the surface of rare-earth-containing UHTC coatings after ablation.

To further confirm the formation of high-entropy oxide scales, TEM analysis was conducted. The oxide scale was mechanically removed from the coating and ground into powders for TEM analysis. According to the HAADF images (Figs. 4(d, i, n)) and corresponding EDS elemental mappings (Figs. 4(e, j, o)), all elements are uniformly distributed within individual oxide particles at the nanoscale for the *in-situ* oxide scales of HEC-Sm, HEC-Er, and HEC-Lu coatings. This homogeneous distribution confirms the formation of high-entropy solid solutions, corroborating the XRD results (Fig. S15). Figs. 4(b, g, l) show HRTEM images of the oxide scales, where atomic arrangements and lattice fringes are visible. The measured lattice fringes are 0.291 nm, 0.183 nm, and 0.292 nm, corresponding to the (111), (022), and (111) planes of the fluorite oxides, respectively. Figs. 4(c, h, m) show the FFT patterns of the oxide scale, all exhibiting diffraction characteristics of a face-centered cubic structure, consistent with the spacings measured from the HRTEM images (Figs. 4(b, g, l)). Fig. S16 present GPA images of the oxide scale in different directions, where red areas indicate positive strain (tensile stress) and blue areas indicate negative strain (compressive stress). No abrupt strain boundaries are detected in the GPA mappings, confirming that the HRTEM field of view corresponds to a single crystalline phase. The GPA strain mappings of the three oxide scales display randomly distributed positive-negative strain pairs, which originate from lattice distortion induced by multi-element solid solution [53]. Based on XRD, HRTEM, FFT, EDS and GPA characterizations, the single crystalline phase within the oxide scale generated on the three high-entropy carbide coatings under ablation conditions can be identified as a high-entropy oxide.

The high-entropy oxides formed on the surface of HEC-Sm, HEC-Er, and HEC-Lu coatings are labelled as HEO-Sm, HEO-Er, and HEO-Lu, respectively. The melting point (T_m) and CTE of oxide scales exert crucial influences on their ablation resistance [54]. High-melting-point oxide scales

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maintain enhanced strength at high temperatures and exhibit strong resistance to flame erosion. A high-CTE oxide scale aggravates thermal mismatch between the coating and the oxide layer, which readily triggers spalling failure of the oxide scale during ablation. Table S6 summarizes the T_m of the oxide components in the high-entropy oxides. Since the three high-entropy oxides differ only in rare-earth components (Sm, Er, and Lu), their overall T_m can be reasonably evaluated based on the intrinsic melting characteristics of the distinct rare-earth oxides. Among the three rare-earth oxides, Lu_2O_3 possesses the highest T_m of 2490 °C, while Er_2O_3 (2344 °C) exhibits a slightly higher melting point than Sm_2O_3 (2325 °C). The maximum T_m discrepancy is less than 165 °C, indicating similar melting temperatures for the three high-entropy oxides formed during ablation. To measure the CTE values, bulk high-entropy oxides with dimensions of 4 × 4 × 20 mm were fabricated, as shown in Fig. S17. The specimens were slowly heated from room temperature to 1600 °C, and their dimensional variations upon heating were recorded (Figs. S17(b-d)). The CTE values of the three high-entropy oxides were subsequently calculated and displayed in Fig. S17(e). The maximum CTE values of HEO-Sm, HEO-Er and HEO-Lu are 7.860×10^{-6} K^{-1}, 8.071×10^{-6} K^{-1} and 8.078×10^{-6} K^{-1}, respectively. A 2.7% difference indicates that the CTE of the three oxide scales has a very insignificant impact on the ablation resistance.

Fig. 5 presents the surface microstructure of high-entropy carbide coatings after ablation. Fig. 5(a) presents a schematic diagram of the coating ablation process. During ablation, the surface temperature of the coating samples exhibits a distribution that gradually decreases from the center to the edge areas, as illustrated in Figs. 5(b, c). The surface temperature of the coating exhibits the Gaussian distribution [55]. To distinguish regions with different temperatures, the sample surface was divided into four areas, which are labeled as A1, A2, A3, and A4. Fig. 5(d) shows the surface microstructure of HEC-Sm coatings after ablation. In the A1 area, large hexagonal particles are closely bonded, forming a dense oxide scale. From A1 to A4, the oxide grain size decreases from 18.53 μm to 0.42 μm, indicating a gradual reduction in the degree of sintering toward the edge area. A porous and loose oxide scale is

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observed in the A4 area, resulting from oxidation reactions of the carbides at relatively low temperatures [54]. A similar trend is observed in the oxide scales of HEC-Er coatings (Fig. 5(e)) and HEC-Lu coatings (Fig. 5(f)). The oxide grain sizes in the A1 area are 18.53 μm, 20.16 μm, and 29.24 μm for HEC-Sm, HEC-Er and HEC-Lu coatings, respectively. Fig. 5(h) presents a statistical analysis of grain size, showing that the oxide grain size in each area follows the trend HEC-Lu > HEC-Er > HEC-Sm. This phenomenon can be attributed i) to differences in surface temperatures during ablation, as shown in Fig. 3(b), and ii) to the influence of different rare-earth elements on the sintering behavior of the oxide scale [56]. The oxide scales formed after the ablation of the three high-entropy carbide coatings exhibit highly consistent sintering behavior. Therefore, the sintering of the oxide scales is not the key factor causing the differences in the ablation resistance.

In order to identify the source of the differences in the ablation resistance of coatings, the elemental composition of the oxide scale was obtained through EDS. It should be noted that EDS tests are associated with inherent errors. Therefore, five random points were selected in the A1-A4 areas for EDS elemental analysis. The average atomic ratios of each element were calculated to reduce the influence of errors, and the results are shown in Table S7. Fig. 5(g) shows a statistical analysis of Ti content in the oxide scales. The Ti content increases from the A1 to the A4 area. The Ti content in the oxide scales is lower than that in the high-entropy carbide coatings before ablation, which can be attributed to the volatilization of TiO_2 during ablation [51]. According to previous researches [57, 58], a denser oxide scale can form on the surface of Ti-containing high-entropy carbide coatings, indicating the positive role of TiO_2 in promoting oxide scale sintering. In the A1 and A4 areas, the Ti content in the oxide scales of the HEC-Lu coatings is 0.40 ± 0.09 at. % and 2.35 ± 0.34 at. %, respectively, which is higher than that of the HEC-Sm (0.26 ± 0.02 at. % and 1.94± 0.11 at. %) and HEC-Er (0.30 ± 0.06 at. % and 2.02 ± 0.20 at. %) coatings. In the A1 area, the average Ti content in the oxide scale of the HEC-Lu coatings after ablation is increased by 53.85 % and 33.33 % compared with that of the HEC-Sm and HEC-Er coatings, respectively. These results further demonstrate that TiO_2 content may a

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major factor influencing ablation behavior. Ablation tests were performed on the HEC-Sm coatings for different durations (60 s, 120 s, and 300 s) (Fig. S18). It was observed that the Ti-rich oxide phase segregated and accumulated at grain boundaries at the initial ablation stage. As the ablation time prolonged, TiO_2 dissolved into refractory oxide grains to form Ti-containing HEOs. It is worth noting that, as shown in Figs. S18(a-c), TiO_2 cannot be fully dissolved into the solid solution, and a small amount of Ti-rich amorphous phase remains in the oxide scale after ablation for 300 s. Combined with the XRD (Fig. S15) and TEM (Fig. 4) results, the *in-situ* oxide scale of the ablated high-entropy carbide coating consists of crystalline high-entropy oxides and amorphous Ti-rich phase. For *in-situ* oxide scale generated on three high-entropy carbide coatings, the difference in Ti content may be due to the incorporation of different rare-earth elements. However, the specific mechanism by which rare-earth elements affect TiO_2 content remains unclear and requires further investigation.

The above compositional analysis confirms the inhomogeneous distribution of Ti in areas A1-A4 of the *in-situ* formed oxide scale. However, Fig. S15 only shows a single XRD pattern, which is insufficient to verify whether the entire oxide scale is composed of the high-entropy oxide phase. To address this, $(Hf\text{-}Zr\text{-}Ti\text{-}Sc\text{-}Y\text{-}Lu)O_{2-\delta}$ high-entropy oxide powders with varying Ti contents were synthesized via solid-state reaction, with their detailed compositions summarized in Table S8. Fig. S19(a) displays the corresponding XRD patterns. High-entropy oxides with different Ti contents exhibit highly similar diffraction profiles, all corresponding to a single-phase fluorite structure. From the locally magnified (111) diffraction peak (Figs. S19(b-e)), slight shifts in peak position are observed among the five oxide powders, with their lattice constants ranging from 5.079 Å to 5.094 Å. These results confirm that variations in Ti content do not significantly alter the crystal structure or lattice parameters of $(Hf\text{-}Zr\text{-}Ti\text{-}Sc\text{-}Y\text{-}Lu)O_{2-\delta}$. Thus, despite compositional inhomogeneities across different regions of the *in-situ* oxide scale formed on the ablated high-entropy carbide coatings, the crystalline phase can still be regarded as a high-entropy oxide.

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3.5 Stability mechanism of TiO_2

To elucidate the effects of rare-earth introduction on the high-temperature stability of TiO_2 and the ablation resistance of carbide coatings, ZrC (ZC), $(Hf_{0.54}Zr_{0.36}Ti_{0.1})C$ (HZTC) and $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.15}Y_{0.15})C$ (HZTSYC) coatings were fabricated via SAPS with identical parameters. Plasma ablation tests were conducted on all three carbide coatings, with the corresponding results displayed in Fig. S20. The ZC coating exhibits the poorest ablation resistance and completely fails after ablation for 100 s. Benefiting from the formation of dense, intact oxide scales, both HZTC and HZTSYC coatings provide effective protection for C/C substrates within a short ablation duration (100 s). Nevertheless, upon extending the ablation time to 300 s, the oxide scales covering HZTC and HZTSYC suffer severe damage, leading to coating failure and severe ablation of the underlying C/C substrates. Microstructural observations of the *in-situ* oxide scales (Fig. S21) combined with EDS analysis (Fig. S22) reveal the underlying degradation mechanism of ZC coatings. Owing to the absence of Ti, the *in-situ* generated ZrO_2 grains cannot be sintered into a continuous dense oxide scale under ablation environments. The loose and porous ZrO_2 scale is gradually stripped off until coating failure. In contrast, both HZTC and HZTSYC deliver outstanding short-term ablation resistance due to the rapid formation of dense oxide scales. However, EDS quantification of A1 area within the *in-situ* oxide scales of HZTC and HZTSYC demonstrates drastically reduced Ti concentrations of 0 at.% and 0.46 ± 0.02 at. %, respectively, confirming the evaporation of TiO_2 at high temperatures. Prolonged thermal exposure eventually triggers the breakdown of protective oxide scales. Collectively, these experimental results verify that the incorporation of Sm, Er and Lu rare earth elements substantially enhances coating ablation resistance and suppresses high-temperature volatilization of TiO_2 within oxide scales.

By comparing the ablation resistance of carbide coatings with different numbers of constituent elements and different rare earth (RE) dopants, a compositional design framework for improving the ablation resistance of carbide coatings is proposed, as illustrated in Fig. S23. With the gradual increase

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in the number of components in the carbide solid solution, the sintering behavior of the *in-situ* formed oxide scale during ablation is promoted via the multi-component synergistic effect, thereby achieving enhanced ablation resistance. Additionally, with the substitution of rare-earth elements in the carbide solid solution from Sm to Er and Lu, the volatilization of TiO_2 within the densely structured *in-situ* oxide scale is effectively suppressed, which further improves the ablation resistance of the coating.

Because of the lack of in situ characterization methods to directly determine the stabilizing effect of rare-earth dopants on TiO_2, DFT calculations, AIMD simulations, and Joule heating experiments were applied to indirectly evaluate the ability of lanthanide dopants to suppress TiO_2 volatilization based on the change in Ti content.

DFT calculations were performed to unravel the intrinsic mechanism by which Sm, Er and Lu stabilize TiO_2 in the *in-situ* oxide scales. Supercell models of three rare-earth-containing high-entropy oxides (HEOs), i.e., $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Sm_{0.1})O_{2-\delta}$ (HEO-Sm), $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Er_{0.1})O_{2-\delta}$ (HEO-Er) and $(Hf_{0.36}Zr_{0.24}Ti_{0.1}Sc_{0.1}Y_{0.1}Lu_{0.1})O_{2-\delta}$ (HEO-Lu), were constructed. Fig. 6(a) presents the electron localization function (ELF) of HEO-Sm, HEO-Er and HEO-Lu structures. Electrons are highly localized around individual atoms, with negligible electron density observed along interatomic bonding paths, demonstrating that Ti-O and RE-O (RE = Sm, Er, Lu) bonds in these HEOs feature predominant ionic bonding character. Fig. 6(b) summarizes the averaged Mulliken populations of Ti-O and RE-O bonds within the three HEO lattices. A higher Mulliken population corresponds to stronger chemical bonding [59]. The average Mulliken populations of Ti-O bonds in HEO-Sm, HEO-Er and HEO-Lu are 0.268 ± 0.134, 0.274 ± 0.139 and 0.279 ± 0.140, respectively, establishing a bond strength sequence of HEO-Lu > HEO-Er > HEO-Sm. This indicates that Lu doping yields the most pronounced strengthening effect on Ti-O bonds. Formation energy (E_f) calculations of supercell models were further adopted to quantitatively compare the stabilizing effects of different rare earth dopants on HEO lattices, as defined by Equation (6):

$$E_f = E_{HEO} - \sum_{i=1}^{n} n_i^M E_i^M - n^O E^O \quad (6)$$

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where the E_{HEO} denotes the total energy of the high-entropy oxide supercell, E_i^M and E^O represent the single-atom energies of metal species and oxygen, while n_i^M and n^O refer to the atomic number of metal cations and oxygen anions in the lattice. Fig. 6(c) compares the calculated E_f of HEO-Sm, HEO-Er and HEO-Lu. HEO-Lu possesses a formation energy of -370.49 eV·atom^{-1}, which is markedly lower than those of HEO-Sm (-336.12 eV·atom^{-1}) and HEO-Er (-362.05 eV·atom^{-1}), evidencing superior thermodynamic stability of the Lu-containing HEO lattice. Combined DFT computational results confirm that the capacity of rare earth dopants to strengthen Ti-O bonds and improve overall lattice stability follows the order Lu > Er > Sm, which is consistent with the EDS results of *in-situ* oxide scales (Fig. 4). The enhanced Ti-O bond strength and the increased lattice stability introduced by Lu are considered to be one of the reasons for inhibiting the high-temperature volatilization of TiO_2 in the *in-situ* oxide scale.

Conventional DFT calculations only characterize bonding and electronic structures under static 0 K conditions and fail to capture high-temperature thermal excitation effects on atomic behavior [60]. AIMD simulations at 2573 K were therefore implemented to clarify the thermal migration behaviors of Ti and O atoms in high-entropy oxide lattices. Fig. 6(d) displays the crystalline structures of HEO-Sm, HEO-Er and HEO-Lu after AIMD simulations at 2573 K for 1000 fs. Pure TiO_2 was simulated under identical computational parameters as a reference system. Atomic trajectories of Ti and O atoms were extracted to calculate the mean squared displacement (MSD), defined by Equation (7):

$$MSD = \frac{1}{N}\sum_{i=1}^{N}[(x_i - x_1)^2 + (y_i - y_1)^2 + (z_i - z_1)^2] \quad (7)$$

where the x_i, y_i and z_i denote the 3D Cartesian coordinates of individual Ti/O atoms at each simulation step, the x_1, y_1 and z_1 stand for the initial coordinates of individual Ti/O atoms. The derived MSD curves for Ti and O atoms in pure TiO_2, HEO-Sm, HEO-Er and HEO-Lu are plotted in Figs 6(e-f). The maximum MSD values of Ti and O atoms in pure TiO_2 are substantially larger than those in all three high-entropy oxides, revealing enhanced atomic mobility and volatilization tendency in monolithic TiO_2. Incorporation of Ti cations into the high-entropy oxide lattice significantly restricts

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atomic migration kinetics. In the regime of classical Brownian motion, MSD exhibits a linear correlation with simulation time, and the slope of the linear curve is proportional to the atomic diffusion coefficient (D), calculated via Equation (8) [61]:

$$D = \frac{1}{2d}\frac{d(MSD)}{dt} \tag{8}$$

where d represents the dimensionality of atomic motion and t is the simulation time. Ti and O atoms undergo unconstrained three-dimensional migration, so d is set to 3. Fig. 6(g) and Fig. S24 presents the derived diffusion coefficients of O (D_O) and Ti (D_{Ti}) atoms in HEO-Sm, HEO-Er and HEO-Lu lattices. The calculated D_O values are $7.083\pm0.050\times10^{-4}$ $Å^2$ fs^{-1}, $6.383\pm0.030\times10^{-4}$ $Å^2$ fs^{-1} and $6.200\pm0.027\times10^{-4}$ $Å^2$ fs^{-1} for HEO-Sm, HEO-Er and HEO-Lu, respectively, following the trend HEO-Sm > HEO-Er > HEO-Lu. This confirms that O atoms exhibit the lowest thermal kinetic stability within the HEO-Lu lattice. Similarly, HEO-Lu also delivers the minimum D_{Ti} among all three high-entropy oxides. Accordingly, we conclude that Lu exerts the most prominent effect on elevating the high-temperature stability of TiO_2.

In summary, a series of simulation calculations reveal that the effectiveness of rare-earth solution in improving TiO_2 stability follows the order: Lu > Er > Sm. Notably, the HEO-Sm scale with superior radiative cooling capability (Fig. 3(b) and Fig. S12) generated on the HEC-Sm coating. For the HEC-Sm coating, low surface temperatures during ablation reduce the driving force for TiO_2 volatilization. Nevertheless, EDS results acquired on the surface of the ablated HEC-Sm coating exhibit the lowest Ti content, demonstrating that the temperature reduction afforded by radiative cooling cannot compensate for the insufficient lattice stability of HEO-Sm. The TiO_2 stabilization induced by rare-earth elements serves as the dominant factor governing the ablation resistance of the three high-entropy carbide coatings. It should be noted that rare-earth elements also stabilize the crystal structures of HfO_2 and ZrO_2. By suppressing phase transformations during heating and cooling, they preserve the structural integrity of the protective oxide scale, acting synergistically with the suppression of TiO_2 volatilization.

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Fig. 6(h) schematically illustrates the protection mechanism of rare-earth-containing high-entropy carbide coatings during ablation. At the initial ablation stage, the high-entropy carbide coating undergoes oxidation to form an oxide scale consisting of high-melting oxide phases and low-melting Ti-rich phases. Two concurrent processes proceed within the oxide scale during ablation: high-temperature volatilization of TiO_2 and solid-solution formation of Ti into the high-entropy oxide lattice. Once Ti atoms are incorporated into the high-entropy oxide via solid solution, TiO_2 volatilization is drastically suppressed by rare-earth stabilization effect, ultimately generating a gradient Ti content across the coating surface with decreasing Ti concentration from the ablation center to the coating edge. Ti exhibits two competing effects on the *in-situ* oxide scale: Ti-rich phases promote sintering densification, whereas ultra-high-temperature TiO_2 volatilization degrades the protective scale. This competition evolves with ablation time and varies spatially along the A1-A4 temperature gradient. At the initial ablation stage, TiO_2 volatilization dominates with limited sintering. In the intermediate stage, high-entropy solid-solution formation suppresses TiO_2 volatilization, and sintering densification and grain growth prevail. At the late stage, sintering is almost complete and grain size stabilizes. Slow TiO_2 escape from the high-entropy lattice creates a dynamic equilibrium. The temperature decreases gradually from A1 to A4, weakening both sintering and TiO_2 volatilization and mitigating this competitive behavior.

To verify the high-temperature stability behavior of TiO_2 in the oxide scale under rare-earth influence, high-temperature volatilization experiments were conducted using the joule heating method. HEO-Sm, HEO-Er, and HEO-Lu bulk ceramics were fabricated via solid-phase reaction and sintering. Meanwhile, $(Hf_{0.54}Zr_{0.36}Ti_{0.1})O_2$ bulk ceramics (abbreviated as HZTO for simplicity) were also prepared for comparison. Fig. 7 displays the results of the high-temperature volatilization experiments. The four samples were heat-treated under vacuum using rapid Joule heating, with the corresponding schematic illustration shown in Fig. 7(a). The sintered oxide ceramic blocks were placed at the center of the carbon felt. A voltage of 20 V and a current of 60 A were applied to the carbon felt. Due to the

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Joule heating effect, the carbon felt was rapidly heated up to 1700 °C to undergo heat treatment on the ceramic oxide blocks. The carbon felt was held at 1700 °C for 100 s to allow sufficient time for the volatilization of TiO_2 in the oxide blocks. Upon completion of the heating process, the oxide samples were cooled naturally from 1700 °C to room temperature, as presented in Figs. 7(b-c). Fig. 7(d) shows the macroscopic morphology of the oxide blocks before and after Joule heating. All the oxide samples changed from white or light color to black after heating, which can be attributed to the formation of excessive oxygen vacancies in the oxides [62]. Large cracks can also be observed on the oxide surfaces, resulting from thermal stress induced by rapid heating and cooling, which causes brittle cracking of the ceramics [63, 64]. Fig. 7(e) presents the temperature curve of the oxide block during the heating process. The surface temperature remained constant at 1700 °C without obvious fluctuations. The mass of the oxide blocks before and after Joule heating were recorded, and the mass loss (Δm) of the oxide blocks was calculated using the following equation:

$$\Delta m = (m_0 - m_1)/m_0 \tag{9}$$

where m_0 and m_1 stand for the mass of oxide blocks before and after Joule heating. Fig. 7(f) presents the Δm of the ceramic blocks. HZTO exhibited a mass loss of 0.599 %, which is significantly higher than that of the three rare-earth-containing high-entropy oxides, suggesting a positive effect of rare-earth elements on the stabilization of TiO_2. Among the three high-entropy oxides, HEO-Er and HEO-Lu showed similar Δm values, both lower than that of HEO-Sm, indicating a more pronounced stabilizing effect of Er and Lu elements. HEO-Lu possessed the lowest mass loss rate of only 0.237 %, which is consistent with the fact that the HEC-Lu coatings possess the best ablation resistance. During heating, the carbon felt was in direct contact with the oxide blocks, and interfacial carbothermal reduction might also influence the experimental results. To evaluate this effect, XRD characterization was conducted on the contact surfaces between the carbon felt and HEO-Sm, HEO-Er, and HEO-Lu, respectively, as shown in Figs. 7(g-i). No changes in the crystal structure or phase composition were

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observed before and after Joule heating, and all samples maintained a single-phase fluorite structure, verifying that the influence of carbothermal reduction is negligible.

Although the volatilization of TiO_2 under vacuum at 1700 °C has been experimentally verified, there exists a substantial temperature discrepancy between the 1700 °C adopted in the high-temperature volatilization tests and the actual surface temperature (2300-2500 °C) of high-entropy carbide coatings during ablation. Accordingly, we further performed volatilization experiments at elevated temperatures, as illustrated in Fig. 8. It should be noted that the Joule heating equipment only generates a tiny high-temperature zone (< 0.5 mL) at 2300 °C, which fails to achieve uniform heating of sintered ceramic bulks (Fig. 7). Therefore, HEO-Sm, HEO-Er and HEO-Lu powders were selected to conduct the high-temperature volatilization tests. It should be noted that powder samples possess a markedly higher specific surface area and more exposed particle surfaces, which provide abundant gas-solid reaction interfaces [65]. Meanwhile, the irregular particle morphologies and interparticle pores within powder specimens facilitate the outward diffusion of gaseous volatile species [66]. Accordingly, HEO powders undergo more severe TiO_2 volatilization relative to dense HEO bulks, which leads to overestimated mass loss. By comparing the mass loss trends of the three HEO compositions, the relatively high-temperature stability with respect to TiO_2 volatilization can be evaluated. To minimize the measurement uncertainties, all HEO powders were fabricated via an identical preparation route to obtain similar microstructures and sieved using a 300-mesh stainless steel sieve to homogenize the particle size distribution.

About 0.5 g of high-entropy oxide powders were loaded into a sealable graphite tube container to prevent them from spilling out during the heating process, as shown in Fig. 8(a). Prior to Joule heating of the powder samples, the graphite tube were pre-heated repeatedly at 2300 °C for 30 s until their mass remained constant, so as to minimize the mass measurement error. A graphite tube was placed between graphite electrodes and heated to 2300 °C for 30 s via the Joule heating effect (Fig. 8(b)). The mass of the graphite tube loaded with internal powders before and after Joule heating was recorded to

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clarify the high-temperature volatilization behavior of TiO_2 within high-entropy oxides. This testing configuration effectively eliminates measurement errors in powder mass determination. Fig. 8(c) displays the temperature curve of the graphite tube during Joule heating. Under direct current excitation, the graphite tube was rapidly heated up to 2300 °C at a heating rate of 60 °C s^{-1}, followed by a 30 s holding stage to complete heat treatment of the high-entropy oxide powders loaded inside. After Joule-heat treatment, the power was cut off, and the graphite tube was naturally cooled down to room temperature. The Δm values of HEO-Sm, HEO-Er and HEO-Lu are 3.193%, 2.888% and 2.737%, respectively. The HEO-Lu exhibits the lowest Δm value than that of the HEO-Sm and HEO-Er. This trend is consistent with the observations obtained from volatilization tests at 1700 °C (Fig. 7). TiO_2 undergoes much more severe volatilization at 2300 °C. Even with a short heat treatment of only 30 s, its mass loss ratio exceeds that measured after heating at 1700 °C for 100 s. The above results also indicate that Lu possesses the strongest capability to stabilize the TiO_2 in the high-entropy oxide. Fig. 8(e) shows the macroscopic morphologies of HEO-Sm, HEO-Er and HEO-Lu powders before and after Joule heating. Similar to the morphological evolution observed after Joule heat treatment at 1700 °C, all three powders turn dark grey, which originates from oxygen vacancies generated by the volatilization of TiO_2.

4 Conclusion

In this work, three novel rare-earth-doped high-entropy carbide (HEC) coatings, namely (Hf-Zr-Ti-Sc-Y-Sm)C (HEC-Sm), (Hf-Zr-Ti-Sc-Y-Er)C (HEC-Er), and (Hf-Zr-Ti-Sc-Y-Lu)C (HEC-Lu), were successfully fabricated, and their high-temperature ablation resistance was systematically investigated under plasma ablation conditions at 2300-2500 °C for 300 s. The results show that the HEC-Lu coating achieves the optimal anti-ablation performance among the three tailored HEC systems, with a linear ablation rate (R_l) of -0.178 ± 0.012 μm·s^{-1}. This value is 60.36 % lower than that of the HEC-Sm coating (-0.111 ± 0.032 μm·s^{-1}) and 23.61 % lower than that of the HEC-Er coating (-

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0.144 ± 0.022 μm·s^{-1}). Microstructure and compositional characterizations of the in-situ formed oxide scales after ablation confirm the occurrence of gradient dissipation of Ti species, which are driven by the inherent temperature gradient across the coating surface during high-temperature ablation. EDS elemental analysis verifies that the Ti atomic content in all three ablated coatings drops below 10 at. %, evidencing the intense volatilization of TiO_2 at temperatures exceeding 2300 °C. First-principles calculations and ab initio molecular dynamics (AIMD) simulations further uncover a competitive mechanism between the high-temperature volatilization and structural stabilization of TiO_2. At 2573 K, the O and Ti atoms in pure TiO_2 lattice exhibit extremely high diffusion coefficients of 1.798 ± 0.015 × 10^{-3} Å·fs^{-1} and 1.800 ± 0.013 × 10^{-3} Å·fs^{-1}, respectively, demonstrating a strong thermodynamic tendency for TiO_2 volatilization. The introduction of rare earth (RE) elements is verified to effectively promote the in-situ formation of Ti-containing high-entropy oxides (HEOs). RE introducing modulates the electron density distribution around Ti sites and optimizes the Ti-O bonding configuration, thereby strengthening Ti-O bond strength and improving the structural stability of TiO_2 at ultra-high temperatures, which significantly suppresses TiO_2 volatilization. Notably, the three RE elements deliver distinct stabilizing effects, following the order of Lu > Er > Sm, which is highly consistent with the ablation resistance ranking of the HEC coatings. The central region of the ablated HEC-Lu coating exhibits 53.85 % and 33.33 % higher residual Ti content than those of HEC-Sm and HEC-Er coatings, respectively. In line with the experimental results, AIMD simulations reveal that the HEO-Lu system possesses substantially reduced atomic diffusion kinetics, with O and Ti diffusion coefficients of 6.200 ± 0.027 × 10^{-4} Å·fs^{-1} and 5.650 ± 0.055 × 10^{-4} Å·fs^{-1}, respectively, which are markedly lower than those of HEO-Er and HEO-Sm counterparts. This work clarifies the RE element-dependent stabilization mechanism of TiO_2 in high-entropy carbide systems under ultra-high-temperature ablation, and provides a reliable component design framework for the high-performance anti-ablation optimization of rare-earth-containing HEC coatings for extreme environmental applications.

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Lingxiang Guo: Conceptualization, Methodology, Visualization, Writing-Original Draft. **Bing Liu**: Experimental assistance. **Tianyu Liu**: Experimental assistance. **Dou Hu**: Writing-Review & Editing. **Yang Xu**: Writing-Review & Editing. **Laura Feldmann**: Writing-Review & Editing. **Ralf Riedel**: Writing-Review & Editing. **Jia Sun**: Conceptualization, Writing-Review & Editing, Supervision, Funding acquisition.

Availability of data and materials

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

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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