



J Adv Ceram 2026, **15**: 9221361

<https://doi.org/10.26599/JAC.2026.9221361>

Research Article

Oxidation of multi-principal component diborides at 2300 °C under ultra-fast heating

Yizhou Cao, Ji-Xuan Liu*, Weiqiang Cheng, Jingyuan Wang, Wenbo Xie, Pai Peng,

Guo-Jun Zhang*

State Key Laboratory of Advanced Fiber Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

*Corresponding author.

E-mail: J.-X. Liu, jxliu@dhu.edu.cn,

G.-J. Zhang gjzhang@dhu.edu.cn

Received: July 18, 2026; Revised: August 23, 2026; Accepted: August 23, 2026

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Abstract: Multi-principal component diboride (MEB) ceramics are promising candidates for ultra-high-temperature thermal protection systems. However, their intrinsic oxidation behavior above

2000 °C remains poorly understood because conventional testing methods have limitations. Here, an ultra-fast heating method with a heating rate of 100 °C/s was applied to investigate the oxidation behavior of $(\text{Zr}_{1/4}\text{Hf}_{1/4}\text{Ta}_{1/4}\text{Ti}_{1/4})\text{B}_2$, $(\text{Zr}_{1/4}\text{Hf}_{1/4}\text{Ta}_{1/4}\text{Nb}_{1/4})\text{B}_2$, $(\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ta}_{1/3})\text{B}_2$, and monolithic ZrB_2 ceramics at 2300 °C under cyclic oxidation conditions. After five 1-min cyclic exposures at this temperature, totaling 5 min, MEB ceramics form multi-layered oxide scales, while ZrB_2 ceramic develops only a porous and cracked single-layer scale. Among them, the Ti-containing composition exhibits the thinnest scale, the densest outer layer, the least mass loss, and intact scale integrity. Beyond the thermodynamic contribution of configurational entropy, this superior performance mainly arises from the dual role of the functional element Ti. First, it forms a liquid Ti-containing oxide phase that densifies the outer $(\text{Zr}, \text{Hf})\text{O}_2$ -based layer derived from the structural elements Zr and Hf, enabling the outer layer to act as an effective oxygen diffusion barrier. Second, it promotes the formation of a porous needle-like Ta_2O_5 network in the inner layer during cooling, which can relieve thermal stress and prevent interfacial separation during cyclic heating and cooling. This work establishes a rapid-heating evaluation protocol and shows that oxidation resistance in these materials is governed by elemental functionality rather than entropy alone, offering a design principle for both equimolar and non-equimolar multi-principal component non-oxide ceramics for reusable thermal protection applications.

Keywords: Oxidation resistance; Ultra-fast heating; Ultra-high temperature; Multi-principal component ceramics; Boride

1 Introduction

ZrB_2 and HfB_2 -based ultra-high temperature ceramics (UHTCs) are recognized as critical thermal protection materials for extreme hypersonic applications, owing to their ultra-high melting points and excellent high-temperature performance [1-3]. The relentless advancement of hypersonic

vehicles imposes increasingly stringent demands on oxidation resistance, necessitating performance breakthroughs beyond conventional diborides.

Recently, the multi-principal component design, including medium- and high-entropy ceramics, has emerged as a highly effective strategy for tailoring the high-temperature performance of UHTCs, particularly their oxidation resistance [4-18]. Gild et al. [5] synthesized $(\text{Ti}_{1/5}\text{Zr}_{1/5}\text{Hf}_{1/5}\text{Nb}_{1/5}\text{Ta}_{1/5})\text{B}_2$ and found that its oxidation resistance at 1000-1500 °C surpassed the average of its five constituent diborides, demonstrating the effectiveness of entropy engineering in improving the oxidation resistance of diboride ceramics. Subsequent studies have confirmed that the high-entropy effect and the sluggish diffusion effect can significantly enhance the oxidation resistance of diboride ceramics [6, 15-18]. Beyond these effects, the specific identities of constituent elements also play a crucial role. Group IV elements Zr and Hf are considered ideal matrix components for designing oxidation-resistant high-entropy diborides, as their oxides possess high thermodynamic stability and melting points, forming a solid oxide skeleton that provides structural support and maintains scale integrity at ultra-high temperatures [9]. Additionally, isothermal oxidation tests at 1400 °C show that $(\text{Ti}, \text{Zr}, \text{Hf})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta})\text{B}_2$ ceramics develop thinner oxide scales than monolithic ZrB_2 ceramic, owing to densification promoted by Ti-rich and (Ti, Ta) -rich melts [11]. Moreover, laser ablation tests at ~2200 °C on $(\text{Ti}_{1/5}\text{Zr}_{1/5}\text{Hf}_{1/5}\text{Nb}_{1/5}\text{Ta}_{1/5})\text{B}_2$ ceramic revealed a dense multilayer oxide scale, with Nb-rich oxide in the outermost region and a Ti-rich oxide sublayer that physically blocks oxygen diffusion [12]. These findings collectively confirm that MEB ceramics containing transition metal elements such as Zr, Hf, Ta, Ti, and Nb exhibit excellent oxidation resistance via diverse and synergistic mechanisms.

Despite these promising advances, a critical knowledge gap persists regarding the intrinsic anti-oxidation mechanisms of MEB ceramics at ultra-high temperatures (>2000 °C), which are directly relevant to real service environments. This gap is not merely a matter of raising the test temperature, but is fundamentally constrained by the limitations of conventional oxidation evaluation

methodologies. An ideal method for assessing intrinsic oxidation resistance should reach ultra-high temperatures while minimizing pre-oxidation and avoiding mechanical disturbance of the oxide scale. However, existing techniques fall short in at least one of these aspects. Conventional furnace tests, while accurate for isothermal kinetics, are typically restricted to temperatures below 1800 °C [5, 6, 8, 10, 11, 13, 14], falling short of the ultra-high temperature region (>2000 °C). Moreover, its slow heating rate inevitably subjects the material to prolonged exposure at intermediate temperatures before the target high temperature is even reached, far from the rapid thermal transients of actual service conditions. Conversely, oxyacetylene flame, plasma, and wind tunnel ablation techniques can achieve ultra-high temperatures [15-20]. However, they introduce complex aerodynamic erosion and non-uniform flow fields that physically remove surface oxide scales, complicating the decoupling of intrinsic oxidation kinetics from thermomechanical erosion effects. Laser heating, while capable of ultra-fast heating to extreme temperatures, suffers from large temperature gradients from the irradiation center to the sample edge [12, 21]. Consequently, each of these techniques has its own merits but falls short of providing a faithful assessment of intrinsic oxidation resistance under well-defined ultra-high-temperature conditions. Moreover, the practical application of thermal protection materials in next-generation hypersonic vehicles increasingly demands reusable thermal protection systems capable of multiple mission cycles, which require both the material and its surface oxide scales to maintain integrity through repeated rapid heating/cooling cycles. However, the cyclic oxidation behavior of MEB ceramics above 2000 °C remains largely unexplored.

In this work, we introduce a rapid-heating furnace equipped with a graphite heating element, capable of elevating specimens to 2300 °C in 30 seconds under flowing air for oxidation testing. This ultra-fast heating profile effectively minimizes pre-oxidation during the transient stage, enabling more accurate evaluation of the intrinsic oxidation resistance of the MEB ceramics under ultra-high-temperature conditions. We systematically investigated the oxidation behavior of three representative compositions: $(\text{Zr}_{1/4}\text{Hf}_{1/4}\text{Ta}_{1/4}\text{Ti}_{1/4})\text{B}_2$, $(\text{Zr}_{1/4}\text{Hf}_{1/4}\text{Ta}_{1/4}\text{Nb}_{1/4})\text{B}_2$, and $(\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ta}_{1/3})\text{B}_2$, denoted as

(ZHT, Ti)B₂, (ZHT, Nb)B₂, and (ZHT)B₂, respectively, with monolithic ZrB₂ as a reference. This study aims to assess the oxidation behavior of MEB ceramics at 2300 °C and provide foundational insights into their oxidation mechanisms by elucidating the roles of constituent elements, while also establishing a rapid-heating evaluation approach for ultra-high-temperature oxidation of thermal protection materials.

2 Experimental procedures

2.1 Sample preparation

(ZHT, Ti)B₂, (ZHT, Nb)B₂, (ZHT)B₂, and ZrB₂ powders were synthesized by boro/carbothermal reduction of corresponding metal oxides (ZrO₂, HfO₂, Ta₂O₅, TiO₂/Nb₂O₅) with B₄C at 1600 °C for 1 h under vacuum. Detailed powder synthesis procedures are described in our previous work [22, 23]. The as-synthesized powders were then consolidated by spark plasma sintering (SPS) at 2000 °C for 10 min under 30 MPa. The relative densities of the obtained bulk ceramics are >98% (except ZrB₂, ~95%). The specimens were cut into disks of 10 mm in diameter and 2 mm in height, and their surfaces were mechanically ground and polished for subsequent characterization and oxidation tests.

2.2 Ultra-high temperature oxidation test

The samples were placed on a graphite heating sheet in a rapid-heating furnace (UHS-3000, Tianjin Zhonghuan Electric Furnace Co., Ltd., China). Before testing, the samples were aligned within the infrared temperature measurement zone. High-temperature oxidation experiments were carried out under a flowing air atmosphere. The gas pressure was maintained at 1.01×10^5 Pa, with the air flow set to 1.5 L/min. As illustrated in Fig. 1, an electric current was applied to the heating sheet, Joule-heating the sample placed on it. The samples were repeatedly subjected to the following cycle: heating to 2300 °C at 100 °C/s, holding at 2300 °C for 1 min, and then naturally cooling to room temperature. Because the graphite heating sheet has limited heating stability, each oxidation cycle time was fixed at 1 min. This cycle was repeated five times, resulting in a total holding time of

5 min at 2300 °C. After the final cycle, the samples were removed from the heating sheet for subsequent characterization.

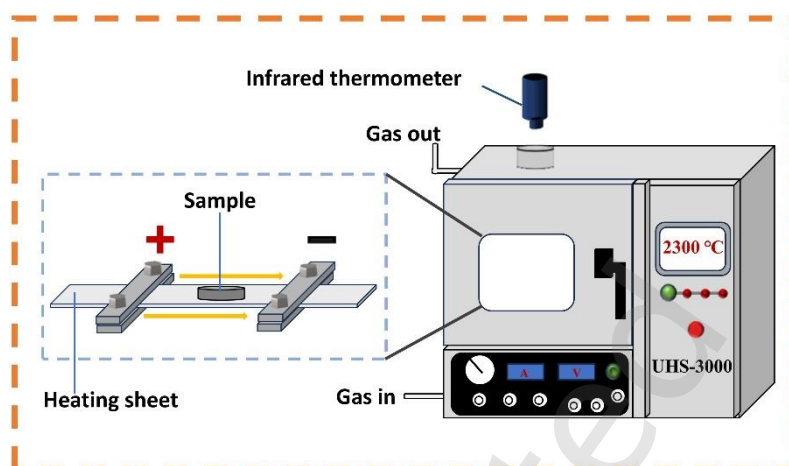


Fig. 1 Schematic diagram of the oxidation process in the rapid-heating furnace.

2.3 Sample characterization

The phase compositions of the samples before and after oxidation were analyzed by X-ray diffraction (XRD, MiniFlex 600, Rigaku, Japan). The microstructures of the samples were characterized using field-emission scanning electron microscopy (FE-SEM, MAIA 3, TESCAN, Czech Republic) coupled with energy-dispersive X-ray spectroscopy (EDS, SU8220, Hitachi, Japan). For cross-sectional microstructural observation by SEM, the oxidized samples were cut in half along the diameter and embedded in phenolic resin. The cross-sections were then ground and polished for SEM observation. The specific mass change ($\Delta m/S$) of the samples after oxidation tests was calculated as $(m_t - m_0)/S$, where S is the initial total geometric surface area of the sample, and m_0 and m_t are the mass of the sample before and after the oxidation test, respectively.

3 Results and discussion

3.1 Phase composition and microstructure of the samples before oxidation

Fig. 2 shows the XRD patterns of the sintered ceramics. All samples exhibit a hexagonal single-phase structure, with no detectable impurity phase, confirming the formation of homogeneous single-phase solid solutions in the MEB ceramics and a single-phase composition in ZrB₂ ceramic. Fig. 3

displays the SEM morphologies and corresponding EDS elemental maps of the sintered ceramics.

The MEB ceramics are essentially pore-free, and the monolithic ZrB_2 ceramic is also relatively dense despite containing only minor closed pores. EDS elemental maps confirm uniform elemental distribution of MEB ceramics without elemental segregation or local agglomeration, in excellent agreement with the single-phase solid solution nature revealed by XRD. Overall, all samples achieved single-phase composition, high relative density, and homogeneous elemental distribution. This effectively removes interferences from microstructural artifacts, including residual porosity and elemental segregation, for the subsequent oxidation test, so the intrinsic effects of chemical composition on oxidation resistance can be isolated and evaluated.

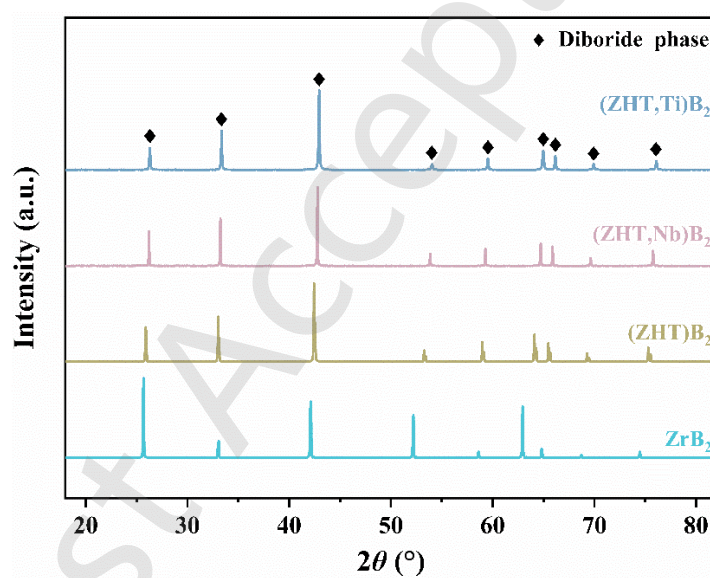


Fig. 2 XRD patterns of the sintered MEB and ZrB_2 ceramics.

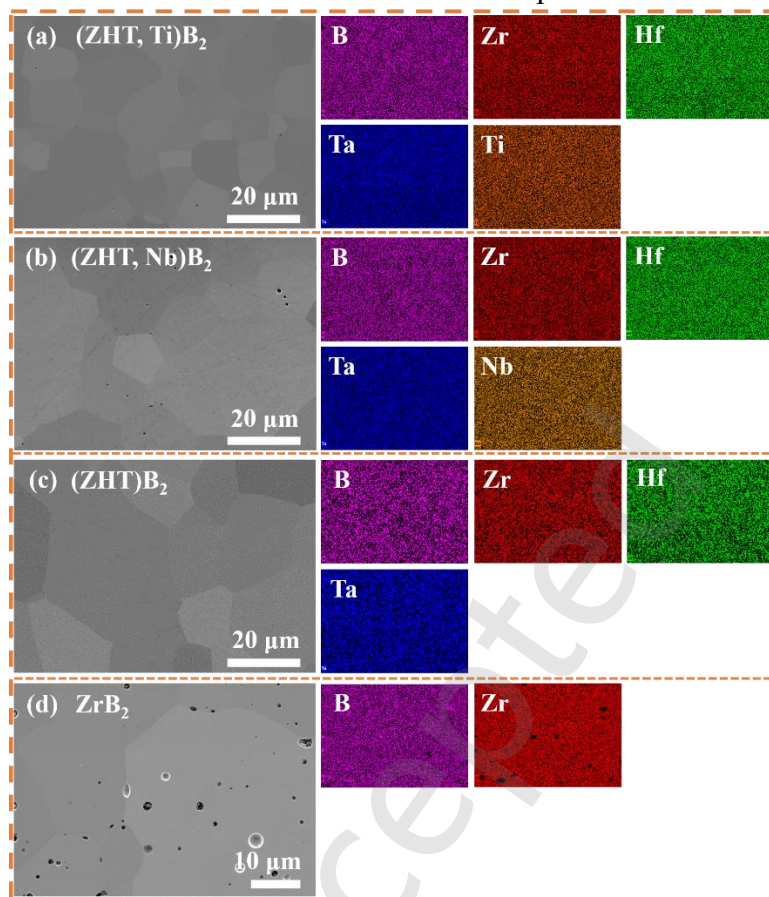


Fig. 3 SEM morphologies and corresponding EDS elemental maps of the sintered MEB and ZrB_2 ceramics. (a) $(\text{ZHT, Ti})\text{B}_2$, (b) $(\text{ZHT, Nb})\text{B}_2$, (c) $(\text{ZHT})\text{B}_2$, (d) ZrB_2 .

3.2 Macroscopic characteristics of the samples after oxidation at 2300 °C

3.2.1 Macroscopic morphology evolution of the samples during oxidation

Fig. 4 shows the macroscopic morphology of MEB and ZrB_2 ceramics after oxidation at 2300 °C for various exposure times. The morphological evolution of the oxidized MEB ceramics shows a clear time dependence. As oxidation time increases, the surfaces of all the MEB ceramics become rougher, and solidified droplets begin to appear. After oxidation at 2300 °C for 5 min, the MEB ceramics are covered with abundant solidified droplets on both the surface and edges, with some located beyond the sample edges, indicating the fluidity of their molten oxidation products at the oxidation test temperature. In addition, compared with these MEB ceramics, the surface of the monolithic ZrB_2 ceramic remains relatively flat and smooth, with no droplets during oxidation at all tested times.

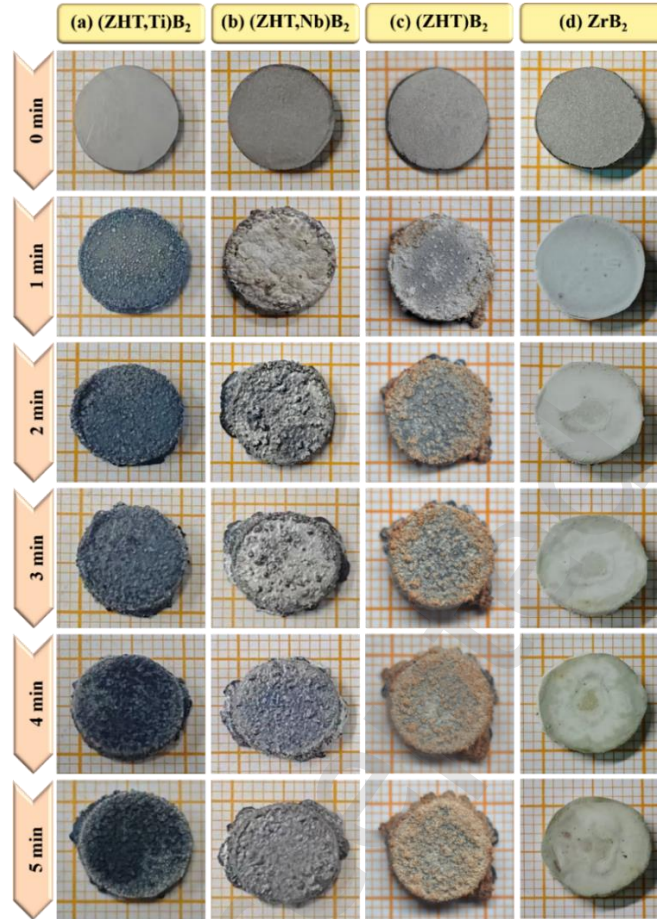


Fig. 4 Macroscopic morphology of MEB and ZrB₂ ceramics after oxidation at 2300 °C for various exposure times.

(a) (ZHT, Ti)B₂, (b) (ZHT, Nb)B₂, (c) (ZHT)B₂, (d) ZrB₂.

3.2.2 Mass change of the samples during oxidation

Fig. 5 presents the mass change per unit area of MEB and ZrB₂ ceramics during oxidation at 2300 °C for various exposure times. Two classical kinetic models are often employed to analyze the rate-controlling factors in the oxidation of boride UHTCs [24, 25]. When a continuous protective oxide scale forms on the surface of UHTCs and oxygen transport becomes the rate-limiting step, the mass change follows parabolic kinetics, as shown in Equation (1). Conversely, when no effective protective oxide layer exists and the chemical reaction at the gas-solid interface controls the oxidation process, the mass change follows linear kinetics, as shown in Equation (2).

$$\left(\frac{\Delta m}{S}\right)^2 = K_p t + C \quad (1)$$

$$\frac{\Delta m}{S} = K_l t + C \quad (2)$$

In these equations, $\Delta m/S$ is the mass change per unit area ($\text{mg}\cdot\text{cm}^{-2}$), t is the oxidation time (min), K_p and K_l are the parabolic and linear oxidation rate constants, respectively, and C is an integration constant.

As shown in Fig. 5, the monolithic ZrB_2 ceramic exhibits nearly linear specific mass change throughout the test, and the measured values at different oxidation times agree well with the dashed line fitted using Equation (2), suggesting a reaction-controlled oxidation process without the formation of an effective protective scale. In contrast, the MEB ceramics show more complex mass change behavior that cannot be directly fitted by Equations (1) or (2), indicating that the oxidation kinetics of these materials are more complex and likely involve other processes that the simple parabolic or linear models do not capture. Theoretically, the oxidation of diboride ceramics involves the replacement of B by O. Since O has a larger atomic mass, this reaction should lead to mass gain. In the present experiments, however, all MEB ceramics exhibit an initial mass gain followed by mass loss as the oxidation time increases from 1 to 5 min. This transition is attributed to the formation of molten oxide droplets on the sample surface during the oxidation test. As oxidation proceeds, these molten droplets become increasingly abundant. The oxide melt can partly volatilize at 2300 °C, contributing to mass loss. In addition, a small fraction of molten droplets may detach completely from the sample edges, further reducing the sample mass.

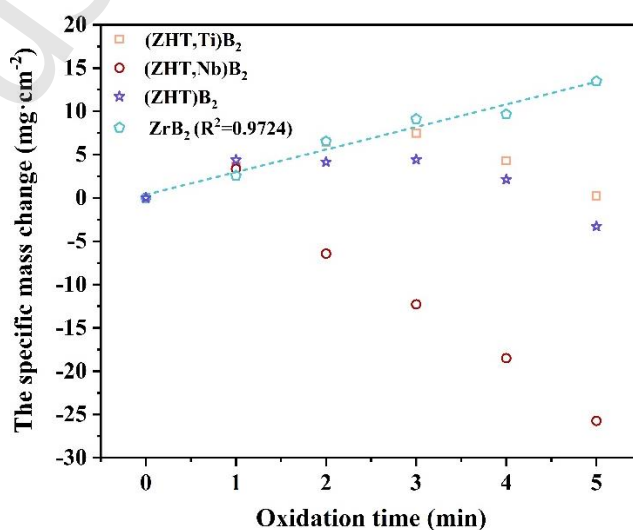


Fig. 5 Mass change per unit area of MEB and ZrB_2 ceramics after oxidation at 2300 °C for various exposure times.

3.3 Phase composition of the samples after oxidation

Fig. 6 shows the XRD patterns of the top surfaces of MEB and ZrB_2 ceramics after oxidation at 2300 °C for 5 min. The oxide scale on the monolithic ZrB_2 ceramic consists predominantly of ZrO_2 , as B_2O_3 , another oxidation product of ZrB_2 ceramic, can rapidly volatilize at 2300 °C [1-3, 26]. This indicates a relatively simple oxidation behavior of ZrB_2 ceramic. In contrast, the phase composition of the oxidation products of MEB ceramics is more complex. All MEB ceramics share $(\text{Zr}, \text{Hf})\text{O}_2$ as a common oxidation product. Beyond this common phase, each sample exhibits unique oxidation products. The oxidation products of $(\text{ZHT}, \text{Ti})\text{B}_2$ and $(\text{ZHT})\text{B}_2$ ceramics both contain Ta_2O_5 , with the former also showing $(\text{Zr}, \text{Hf})\text{TiO}_4$ and the latter $(\text{Zr}, \text{Hf})_6\text{Ta}_2\text{O}_{17}$. Meanwhile, $(\text{ZHT}, \text{Nb})\text{B}_2$ ceramic features $(\text{Nb}, \text{Ta})_2\text{O}_5$ and $(\text{Zr}, \text{Hf})_6(\text{Nb}, \text{Ta})_2\text{O}_{17}$. Among these products, $(\text{Zr}, \text{Hf})\text{O}_2$ and $(\text{Zr}, \text{Hf})_6\text{Ta}_2\text{O}_{17}$ are expected to have high melting points [11, 27, 28], thus remaining as solid skeletons at 2300 °C. In contrast, TiO_2 , Ta_2O_5 , $(\text{Nb}, \text{Ta})_2\text{O}_5$, and $(\text{Zr}, \text{Hf})\text{TiO}_4$ have relatively low melting points below 2000 °C [11, 27-29], and are thus molten to form fluid liquid phases at the test temperature. Some of these liquid phases flowed to the surfaces and edges of the samples and solidified upon cooling, forming the solidified droplets observed in Fig. 4.

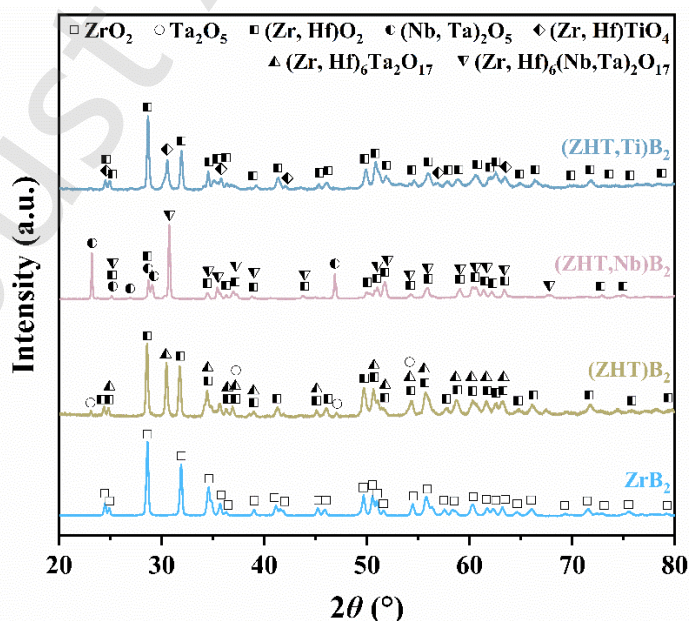


Fig. 6 XRD patterns of the top surfaces of MEB and ZrB_2 ceramics after oxidation at 2300 °C for 5 min.

3.4 Microstructure of the samples after oxidation

3.4.1 Microstructure of the top surfaces of the samples after oxidation

Fig. 7 shows the SEM morphologies of the top surfaces of MEB and ZrB_2 ceramics after oxidation at 2300 °C for 5 min. All MEB ceramics exhibit protrusions on their oxidized surfaces. EDS analysis of the related cross-sections (see Fig. 8 and Table 1) reveals that these protrusions are predominantly composed of $(\text{Zr}, \text{Hf})\text{O}_2$, along with minor amounts of sample-dependent complex oxides. Such protrusions are commonly observed during high-temperature oxidation of boride ceramics. For example, in the oxidation of ZrB_2 -SiC ceramic, similar protrusions have been reported to form as ZrO_2 precipitates from a B_2O_3 - SiO_2 - ZrO_2 liquid when B_2O_3 evaporates at the surface, with the remaining liquid phase solidifying around the ZrO_2 cores and leaving elevated islands [26].

Despite sharing the common features mentioned above, the oxidized surfaces of the three types of MEB ceramics exhibit different pore densities and diameters (see Fig. 7 and the inserted enlarged images). $(\text{ZHT}, \text{Ti})\text{B}_2$ ceramic shows a relatively dense oxidized surface, with only a few pores, approximately 10-20 μm in diameter, located at the protrusion centers (see Fig. 7a). $(\text{ZHT}, \text{Nb})\text{B}_2$ ceramic exhibits an oxidized surface that appears relatively dense, yet actually contains some fine pores ranging from 1 to 9 μm in diameter (see Fig. 7b). In addition, no obvious cracks appear on the surfaces of $(\text{ZHT}, \text{Ti})\text{B}_2$ and $(\text{ZHT}, \text{Nb})\text{B}_2$ ceramics after oxidation at 2300 °C for 5 min, suggesting that liquid phases formed to seal cracks during ultra-high temperature oxidation. In contrast, the $(\text{ZHT})\text{B}_2$ ceramic has microcracks and more pores with diameters of about 30-80 μm on the oxidized surface (see Fig. 7c) than the other MEB ceramics. Compared with the MEB ceramics, the monolithic ZrB_2 ceramic forms a more porous and extensively cracked ZrO_2 scale, indicating poor structural integrity (see Fig. 7d). This is attributed to the rapid volatilization of B_2O_3 at 2300 °C, leaving no residual liquid phase to seal cracks. Such porous, cracked surface morphologies indicate that the oxide scale of ZrB_2 ceramic fails to provide an effective diffusion barrier, leaving open

pathways for inward oxygen transport that can not effectively inhibit oxidation of the underlying substrate [1, 26, 30].

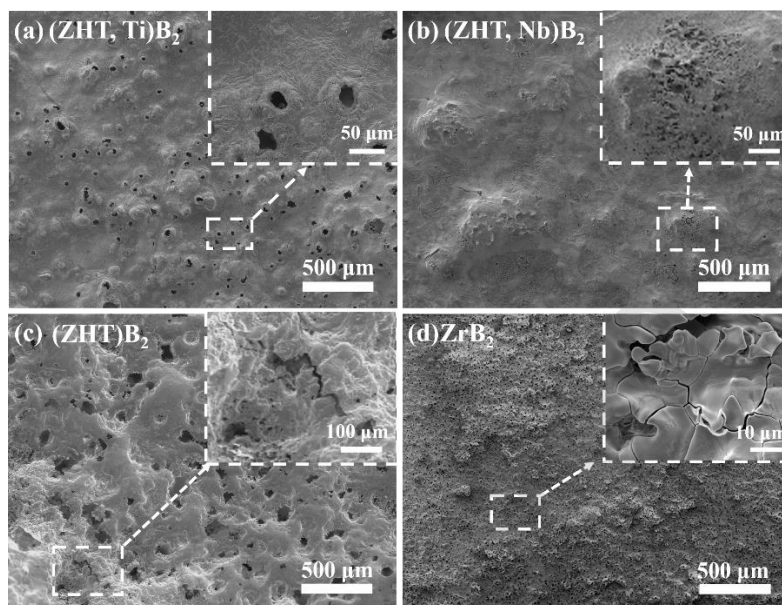


Fig. 7 SEM morphologies of the top surfaces of MEB and ZrB₂ ceramics after oxidation at 2300 °C for 5 min.

(a) (ZHT, Ti)B₂, (b) (ZHT, Nb)B₂, (c) (ZHT)B₂, (d) ZrB₂.

3.4.2 Microstructure of the cross-section of the samples after oxidation

Fig. 8 shows the SEM morphologies and elemental maps of the cross-sections of MEB and ZrB₂ ceramics after oxidation at 2300 °C for 5 min. Based on these observations, together with XRD analysis (see Fig. 6) and EDS point analysis (see Table 1), the oxide scales of the MEB ceramics are identified as multi-layered structures, whereas that on monolithic ZrB₂ ceramic consists of only a single layer.

The average thicknesses of the oxide scales on (ZHT, Ti)B₂, (ZHT, Nb)B₂, and (ZHT)B₂ ceramics are 99, 105, and 125 μm, respectively, all substantially thinner than that of ZrB₂ ceramic (230 μm). In terms of layer count, (ZHT, Ti)B₂ ceramic exhibits four layers, while both (ZHT, Nb)B₂ and (ZHT)B₂ ceramics show two layers. Regarding the outermost layer, both (ZHT, Ti)B₂ and (ZHT, Nb)B₂ ceramics develop relatively dense outer (Zr, Hf)O₂-based layers (see Figs. 8a, b), though with different pore characteristics. For (ZHT, Ti)B₂ ceramic, this layer is locally interrupted by only a few pores at the protrusion centers (see Fig. 7a and Fig. 8a). For (ZHT, Nb)B₂ ceramic, by contrast, the

outer scale appears relatively dense but contains some fine pores (see Fig. 7b and Fig. 8b). For (ZHT)B₂ ceramic, the outer (Zr, Hf)O₂-based layer of the oxide scale is porous and cracked (see Fig. 8c). For ZrB₂ ceramic, the oxide scale formed on its surface is completely different from those of the MEB ceramics, which is a more porous and extensively cracked single layer of ZrO₂ (see Fig. 8d). This variation in outer (Zr, Hf)O₂-based layer densification correlates with the wettability of the constituent oxide melts, with the Ti- or Nb-containing melts being the effective in sealing pores and densifying this layer. The relatively dense outer layers on (ZHT, Ti)B₂ and (ZHT, Nb)B₂ ceramics effectively hinder inward oxygen diffusion, limiting continued oxidation of the underlying substrate and resulting in significantly thinner oxide scales than in (ZHT)B₂ and ZrB₂ ceramics.

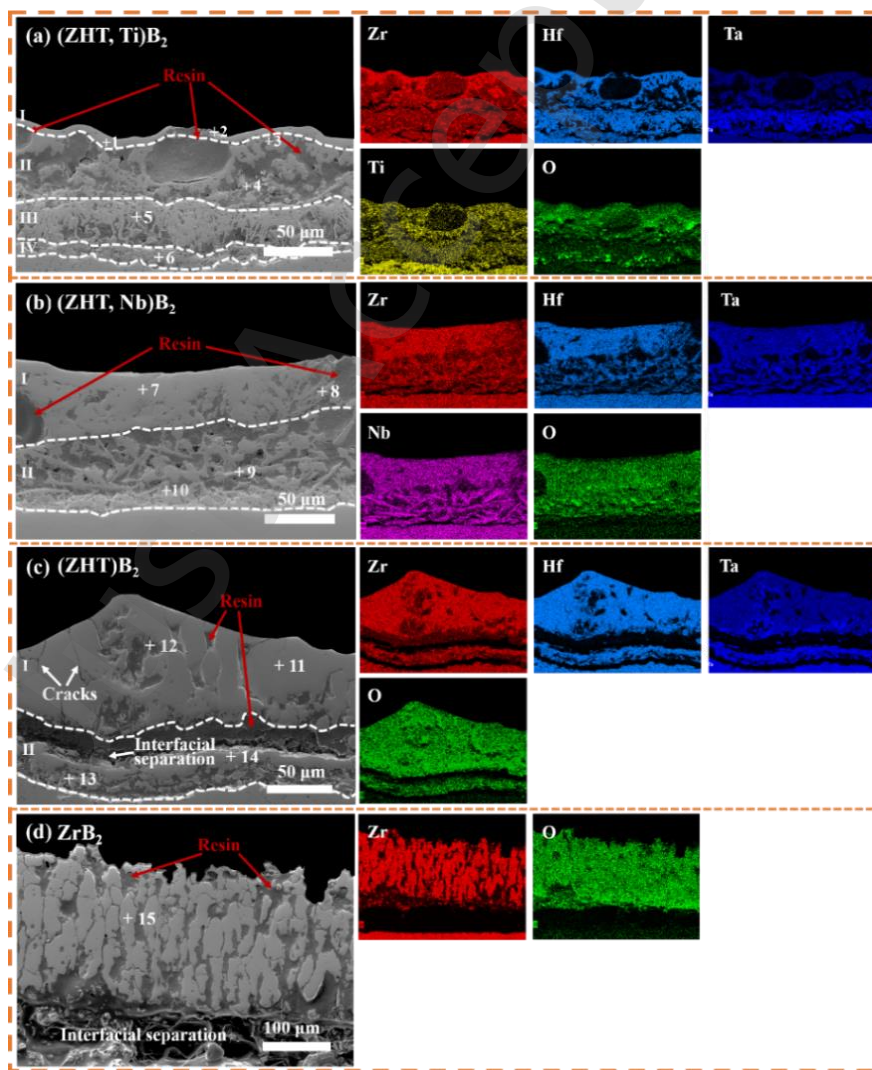


Fig. 8 SEM morphologies and elemental maps of the cross-sections of MEB and ZrB₂ ceramics after oxidation at 2300 °C for 5 minutes. (a) (ZHT, Ti)B₂, (b) (ZHT, Nb)B₂, (c) (ZHT)B₂, (d) ZrB₂.

Table 1 Quantitative EDS analysis results of the cross-section of MEB and ZrB₂ ceramics after oxidation at 2300 °C for 5 minutes.

Sample	Layer	Point	Element contents (at.%)						Possible Phase
			Zr	Hf	Ta	Ti	Nb	O	
(ZHT, Ti)B ₂	I	1	22.80	22.87	5.72	4.74	-	43.88	(Zr, Hf)O ₂
		2	9.51	7.17	5.37	9.97	-	67.99	(Zr, Hf)TiO ₄
	II	3	18.95	18.69	5.33	4.04	-	52.99	(Zr, Hf)O ₂
		4	0.70	4.28	76.98	9.56	-	8.48	Ta ₂ O ₅
	III	5	3.02	5.15	76.75	3.76	-	11.31	Ta ₂ O ₅
	IV	6	23.96	24.58	3.97	5.09	-	42.40	porous (Zr, Hf)O ₂
(ZHT, Nb)B ₂	I	7	21.99	21.08	3.51	-	3.81	49.62	(Zr, Hf)O ₂
		8	14.49	11.35	13.13	-	9.06	51.97	(Zr, Hf) ₆ (Ta, Nb) ₂ O ₁₇
	II	9	8.26	8.00	12.28	-	32.22	39.24	(Nb, Ta) ₂ O ₅
		10	13.90	15.92	11.23	-	30.67	28.28	(Zr, Hf, Ta, Nb)O _x
(ZHT)B ₂	I	11	23.05	18.88	3.07	-	-	55.01	(Zr, Hf)O ₂
		12	17.27	11.19	8.44	-	-	63.11	(Zr, Hf) ₆ Ta ₂ O ₁₇
	II	13	3.37	6.11	81.52	-	-	9.00	Ta ₂ O ₅
		14	23.36	19.05	2.75	-	-	54.84	(Zr, Hf)O ₂
ZrB ₂	I	15	33.73	-	-	-	-	66.27	ZrO ₂

In addition, based on the SEM morphologies (see Fig. 8), quantitative EDS analysis results (see Table 1), and XRD results (see Fig. 6), the inner layers of the oxide scales of the MEB ceramics contain abundant low-melting-point oxides with a distinct needle-like morphology, such as Ta₂O₅ and (Nb, Ta)₂O₅, suggesting that these layers primarily formed by crystallization of the oxide melts during cooling. Notably, such needle-like Ta₂O₅ is barely observed in the inner oxide layer of (ZHT)B₂ ceramic, implying that the presence of Ti or Nb promotes the formation of needle-like Ta₂O₅ during cooling. This porous needle-like Ta₂O₅ skeleton within the inner layer provides local strain-accommodation space, effectively relaxing the accumulation of thermal stresses and preventing crack propagation in subsequent thermal cycles [31]. As a result, (ZHT, Ti)B₂ and (ZHT, Nb)B₂ ceramics retain intact oxide scales with no significant interfacial separation after five cyclic oxidation exposures at 2300 °C. In contrast, (ZHT)B₂ and ZrB₂ ceramics exhibit interfacial separation between the outer and inner oxide layers or at the scale/matrix interface, which compromises the structural integrity of the oxide scale (see Figs. 8c, d), indicating that substantial thermal stresses accumulated during cooling, leading to interlayer cracking and delamination. The

better structural integrity of the oxide scales on (ZHT, Ti)B₂ and (ZHT, Nb)B₂ ceramics compared to those on (ZHT)B₂ and ZrB₂ ceramics suggests that the former two compositions are more promising for reusable thermal protection systems, which require both the ceramic and its oxide scale to maintain integrity through repeated rapid heating/cooling cycles.

3.5 Summary of the superior oxidation resistance of (ZHT, Ti)B₂ and the role of constituent elements

The preceding comparative analysis of post-oxidation appearance, mass change, phase composition, and scale microstructure identifies (ZHT, Ti)B₂ ceramic as the best-performing composition at 2300 °C, with the thinnest surface oxide scale, the densest outer layer, the least mass loss, and intact scale integrity after five thermal cycles. This superiority arises from two synergistic factors. One is the high configurational entropy that thermodynamically increases the phase stability of MEBs under high-temperature oxidizing environments. The other is a rational synergy between the structural elements (Zr, Hf, Ta) and the functional element (Ti) within (ZHT, Ti)B₂, enabled by the multi-component nature of the solid solution itself. Within the oxide scale, Zr and Hf form a stable outer (Zr, Hf)O₂ layer. However, this layer alone is intrinsically porous and prone to cracking. In this context, Ti plays a functional role, as its oxidation product, together with Ta₂O₅, forms a liquid Ti-containing oxide phase (enriched in Ti and Ta) that wets and densifies the outer (Zr, Hf)O₂ layer, creating an effective oxygen diffusion barrier. Simultaneously, Ti in the liquid phase modifies the crystallization environment of Ta₂O₅ during cooling, promoting the precipitation of a needle-like Ta₂O₅ network that constructs a porous skeletal structure within the inner layer, providing local strain-accommodation space and effectively preventing crack propagation in subsequent thermal cycles. While Nb in (ZHT, Nb)B₂ ceramic exhibits similar densification functionality, its lower-melting-point oxides may lead to excessive melt fluidity and pronounced volatilization, resulting in notable mass loss. In contrast, (ZHT)B₂ and monolithic ZrB₂ ceramics lack functional elements altogether, leaving their oxide scales porous and cracked, unable to provide effective oxygen barriers

and prone to severe interfacial delamination after cyclic thermal exposure. Thus, the dual role of the functional element Ti, densifying the outer layer of the oxide scale and constructing a strain-tolerant porous needle-like Ta₂O₅ skeleton in its inner layer, enables the (ZHT, Ti)B₂ ceramic to maintain an intact, adherent oxide scale after cyclic oxidation at 2300 °C, highlighting its potential for reusable hypersonic thermal protection systems.

4 Conclusions

Using an ultra-fast heating technique, this work evaluates the intrinsic oxidation behavior of (Zr_{1/4}Hf_{1/4}Ta_{1/4}Ti_{1/4})B₂, (Zr_{1/4}Hf_{1/4}Ta_{1/4}Nb_{1/4})B₂, (Zr_{1/3}Hf_{1/3}Ta_{1/3})B₂, and monolithic ZrB₂ ceramics at 2300 °C for a cumulative holding time of 5 min achieved through five repeated 1-min cyclic exposures, with a heating rate of 100 °C/s under flowing air. Monolithic ZrB₂ ceramic forms a porous, cracked single-layer ZrO₂ scale with an average thickness of 230 μm that provides negligible protection. In contrast, the MEB ceramics develop multi-layered oxide scales with substantially reduced thicknesses (99-125 μm). Among them, the (Zr_{1/4}Hf_{1/4}Ta_{1/4}Ti_{1/4})B₂ ceramic demonstrates the best overall oxidation resistance, featuring the thinnest surface oxide scale, the densest outer (Zr, Hf)O₂-based layer, the least mass loss, and intact scale integrity without interfacial delamination after five cyclic exposures. By contrast, the (Zr_{1/4}Hf_{1/4}Ta_{1/4}Nb_{1/4})B₂ ceramic, despite forming a relatively dense outer layer, suffers from obvious mass loss. More critically, the (Zr_{1/3}Hf_{1/3}Ta_{1/3})B₂ ceramic lacks a functional element to densify the surface oxide scale, resulting in a porous and cracked structure. Beyond the configurational entropy that thermodynamically stabilizes the MEBs under ultra-high temperature oxidizing environments, the superior performance of (Zr_{1/4}Hf_{1/4}Ta_{1/4}Ti_{1/4})B₂ ceramic arises from the bifunctional role of Ti. It densifies the outer (Zr, Hf)O₂ layer via a Ti-containing liquid phase, forming an effective oxygen barrier, while simultaneously promoting the formation of a porous needle-like Ta₂O₅ network in the inner layer upon cooling that can relieve thermal stress and prevent cracking and delamination during subsequent thermal cycles. These results not only establish a rapid-heating method for conveniently

and efficiently evaluating ultra-high temperature oxidation of materials, but also reveal that the oxidation resistance of multi-principal component non-oxide ceramics is dominated by the synergy between structural and functional constituent elements rather than by configurational entropy alone. This mechanistic insight provides a compositional design principle that can be extended from the present equimolar systems to non-equimolar counterparts for reusable thermal protection applications.

Author contributions

Yizhou Cao: Writing-original draft, Investigation, Data Curation, Formal Analysis. Ji-Xuan Liu: Conceptualization, Methodology, Formal Analysis, Writing-review & editing, Supervision. Weiqiang Cheng: Data Curation. Jingyuan Wang: Formal Analysis. Wenbo Xie: Data Curation. Pai Peng: Formal Analysis. Guo-Jun Zhang: Conceptualization, Writing-review & editing, Supervision.

Acknowledgements

The present work was financially supported by the National Natural Science Foundation of China (No.52332003, 52371023, 52032001).

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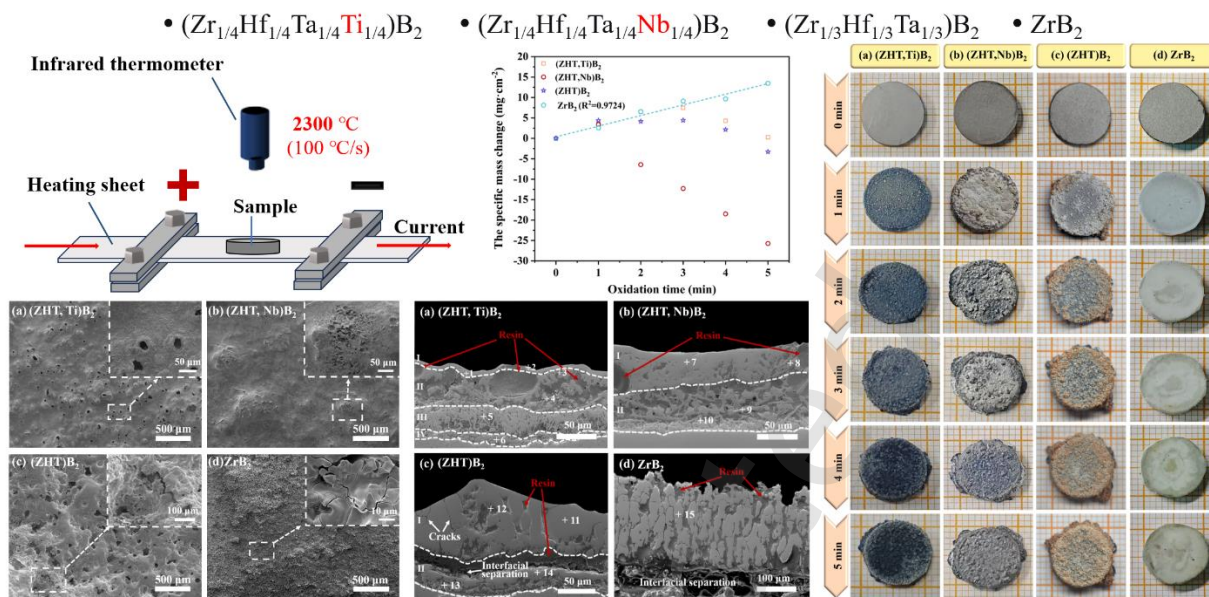
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Oxidation of MEBs at 2300 °C under ultra-fast heating



- Configurational entropy thermodynamically increases the phase stability of MEBs.
- **Structural elements** (Zr, Hf, Ta): protective outer high-melting-point (Zr, Hf)O₂ layer.
- **Functional elements** (Ti, Nb): densify outer (Zr, Hf)O₂ layer to inhibit oxygen diffusion; promote the formation of a porous needle-like Ta₂O₅ skeleton in the inner layer for stress-accumulation avoidance.