



Role of mixed oxides in designing the composition of multicomponent transition metal diborides with improved oxidation resistance

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ABSTRACT

Ultra-High Temperature Ceramics involving the co-presence of multiple transition metals have recently attracted significant attention owing to the potential for generating solid solutions with improved oxidation resistance compared to their individual constituents. Along this line, the compositions of binary and ternary Zr–Hf–Ta diborides are engineered *a priori* in this work to enhance their oxidation performance. This is achieved by promoting the formation of thermally stable $A_6Ta_2O_{17}$ ($A = \text{Zr, Hf}$) within the oxide scale upon exposure to oxidizing environments. Systems crafted with a (Zr,Hf):Ta ratio equal to 3:1 are observed to display better oxidation resistance compared to the equiatomic counterparts. Correspondingly, while $A_6Ta_2O_{17}$ is the exclusive or dominant oxidation product generated in the former case, detrimental individual oxides (Ta_2O_5 , and ZrO_2) are also formed in the latter. Thus, compositional tailoring is key to enhancing the oxidation resistance of multicomponent diborides, shifting away from the standard equimolar paradigm.

Given their remarkable high-temperature properties, transition metal diborides (TMBs) involving Zr, Hf, and/or Ta elements are among the most widely investigated Ultra High Temperature Ceramics (UHTCs) for applications under extreme conditions, such as in the aerospace field [1,2]. Recently, the combination of unary TMBs to form high entropy multicomponent solid solutions often resulted in enhanced oxidation resistance with respect to their boride constituents [3,4]. To justify such finding, several investigations, either focused on the preferential oxidation of different metallic elements [5–7], or on boride formation and its stabilization by certain substances, have been addressed [8–10].

Individual TMBs present certain drawbacks that restrict their widespread applicability in harsh environments, for instance in the aerospace sector. Specifically, TaB_2 and HfB_2 have high densities (~ 12.6 and 11.2 g/cm^3) and critical raw constituent metals [11]. Furthermore, TaB_2 and ZrB_2 exhibit poor high-temperature oxidation resistance [12–16]. The latter drawback can be linked to the occurrence of phase transitions/transformations in the generated oxide scale, which are accompanied by steep volume changes that compromise the thermomechanical stability and protective nature of the oxidation products [12–14].

In this regard, based on ZrO_2 – Ta_2O_5 , HfO_2 – Ta_2O_5 or ZrO_2 – HfO_2 – Ta_2O_5 phase diagrams [17–19], it appears that the complex $A_6Ta_2O_{17}$ ($A = \text{Zr, Hf}$) type oxides are not affected by phase transition/transformations, so

that volume changes and defect generation typical of ZrO_2 and Ta_2O_5 can be, in principle, avoided [13]. Accordingly, recent studies focused on these oxides showed that they exhibit remarkable thermochemical stability and generally form dense, adherent layers that act as highly effective oxygen barriers [16,20–27]. For this reason, $A_6Ta_2O_{17}$ oxides have drawn attention in the framework of thermal barrier coatings [21,25–28] and bulk metal carbides [22,23,29–31].

Along this line, the combination of Ta-, Zr-, and/or Hf-diborides can then be considered as a powerful strategy to possibly improve the oxidation resistance of these ceramics, aiming at stabilizing the oxide scale by favouring the formation of $A_6Ta_2O_{17}$ rather than other oxides more prone to phase transitions. Despite the different investigations conducted so far on the fabrication of $(Zr_{1-x}Ta_x)_2B_2$ [13,32–39], $(Hf_{1-x}Ta_x)_2B_2$ [13,40,41], and $(Zr_xHf_yTa_{1-x-y})_2B_2$ [13,42–44] solid solutions in bulk form, only two of them focused the attention on their oxidation resistance [13,43]. Specifically, in our recent study [13], the single-phase $(Zr_{1/3}Hf_{1/3}Ta_{1/3})_2B_2$ solid solution produced with the combined Self-propagating High-temperature Synthesis (SHS) - Spark Plasma Sintering (SPS) approach, exhibited higher oxidation resistance with respect to its individual and equimolar binary constituents. Excluding preferential boride stabilization, the key stabilizing factor was postulated to be the abundant stable $(Zr,Hf)_6Ta_2O_{17}$ phase in the oxide

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Table 1

Characteristics of SHS powders and SPS samples produced in this work. The relative amounts of each phase present in the SHS powders and SPS products were determined by Rietveld refinement. T_D: dwell temperature (°C); t_D: dwell time (min); P: applied pressure (MPa).

System ID	Nominal composition	SHS powders composition (wt%)	SPS conditions (T _D /t _D /P)	SPS samples composition (wt %)	ρ [%]	Reference
ZTB_E	(Zr _{1/2} Ta _{1/2})B ₂	(Zr _{0.26} Ta _{0.74})B ₂ (20.6); (Zr _{0.35} Ta _{0.65})B ₂ (10.4); (Zr _{0.08} Ta _{0.92})B ₂ (32.6); ZrB ₂ (16.7); TaB ₂ (19.4)	1950/20/20	(Zr _{1/2} Ta _{1/2})B ₂ (>99.9)	97.0 ±0.5	[13]
ZTB_NE	(Zr _{3/4} Ta _{1/4})B ₂	(Zr _{0.85} Ta _{0.15})B ₂ (23.1); (Zr _{0.5} Ta _{0.5})B ₂ (10.5); (Zr _{0.1} Ta _{0.9})B ₂ (6.0); ZrB ₂ (55.6); TaB ₂ (4.8)		(Zr _{3/4} Ta _{1/4})B ₂ (>99.9)	>99.9	This Work
HTB_E	(Hf _{1/2} Ta _{1/2})B ₂	(Hf _{0.76} Ta _{0.24})B ₂ (32.4); (Hf _{0.42} Ta _{0.58})B ₂ (20.2); HfB ₂ (26.3); TaB ₂ (20.4); m-HfO ₂ (0.7)	2050/20/20	(Hf _{0.59} Ta _{0.41})B ₂ (93.7) (Hf _{0.25-0.32} Ta _{0.68-0.75})B ₂ (6.3)	95.4 ±1.4	[13]
HTB_NE	(Hf _{3/4} Ta _{1/4})B ₂	(Hf _{3/4} Ta _{1/4})B ₂ (44.3); HfB ₂ (35.1); TaB ₂ (6.8); HfO ₂ (2.4); Ta (11.4)		(Hf _{3/4} Ta _{1/4})B ₂ (>99.9)	98.9 ±3.8	This Work
ZHTB_E	(Zr _{1/3} Hf _{1/3} Ta _{1/3})B ₂	Ta-rich (Zr,Hf,Ta)B ₂ (16.4); Ta-poor (Zr,Hf,Ta)B ₂ (32.6); ZrB ₂ (13.9); HfB ₂ (22.2); TaB ₂ (12.4); t-ZrO ₂ (2.1); m-HfO ₂ (0.4)	2000/20/20	(Zr _{1/3} Hf _{1/3} Ta _{1/3})B ₂ (>99.9)	97.1 ±0.7	[13]
ZHTB_NE	(Zr _{3/8} Hf _{3/8} Ta _{1/4})B ₂	(Zr _{1/3} Hf _{1/3} Ta _{1/3})B ₂ (4.4); (Zr _{0.25} Hf _{0.25} Ta _{0.5})B ₂ (10.3); ZrB ₂ (24.5); HfB ₂ (46.8); TaB ₂ (11.0); HfO ₂ (2.0); Ta (1.0)		(Zr _{3/8} Hf _{3/8} Ta _{1/4})B ₂ (>99.9)	97.3 ±0.8	This Work

scale, alongside a reduced presence of phase-transition-susceptible TaO₂, Ta₂O₅, and ZrO₂ [13].

Based on the equilibrium phase relations reported for the AO₂–Ta₂O₅ systems, the A₆Ta₂O₁₇ mixed oxide is thermodynamically stable around the 3:1 A:Ta atomic ratio. Accordingly, to maximize the fraction of this stable phase generated during oxidation, the NE binary and ternary borides investigated in this study are tailored to provide the exact same 3:1 proportion.

Thus far, a similar approach has only been considered in the context of Hf-Ta metallic alloys [16] and carbides [30]. In both cases, Hf₆Ta₂O₁₇ was the only oxidation product formed [16,30]. To date, no similar studies are available in the literature involving transition metal borides.

The present work investigates tailored Zr-Hf-Ta-B formulations designed to form exclusively A₆Ta₂O₁₇ oxidation products (A = Zr, Hf). Accordingly, the oxidation resistance of (Zr_{3/4}Ta_{1/4})B₂, (Hf_{3/4}Ta_{1/4})B₂ and (Zr_{3/8}Hf_{3/8}Ta_{1/4})B₂ ceramics produced by SHS-SPS is evaluated and compared to their equimolar counterparts. It is also explored how Zr and Hf (co-)presence affects oxidation to determine if behaviour depends on the specific metals or just the (Zr,Hf):Ta ratio. This will assess if using hafnium can be partially or entirely avoided to mitigate its drawbacks.

The synthesis of (Zr_{3/4}Ta_{1/4})B₂, (Hf_{3/4}Ta_{1/4})B₂, and (Zr_{3/8}Hf_{3/8}Ta_{1/4})B₂ by SHS was performed using zirconium (Alfa Aesar, cod 00847, APS 2-3 μm), hafnium (Alfa Aesar, cod. 10201, < 44 μm), tantalum (Alfa Aesar, cod 00337, < 44 μm), and amorphous boron (Sigma-Aldrich, cod 15580) powders as reactants. The SHS-SPS protocol previously developed for producing bulk equimolar (“E”) samples [13] was extended in this work to process the non-equimolar (“NE”) counterparts, alongside new E samples to be tested under identical conditions. It is specified that, in this work, the term non-equimolar and its acronym NE refer exclusively to systems with an A:Ta atomic ratio of 3:1, where A=Hf and/or Zr. As summarized in Table 1, the NE formulations were sintered under the same SPS conditions previously optimized for the E systems [13]. The particle size distribution of the SHS powder batches was determined by laser light scattering analysis (CILAS 1180, France).

The oxidation resistance of sintered samples was evaluated based on thermogravimetric analysis (TGA) using a synthetic air atmosphere and furnace experiments conducted in ambient air conditions. Dynamic TGA tests from room temperature (RT) to 1450°C (2°C/min, 0.1 L/min air flow) were performed with a STA 409PC Luxx machine (NETZSCH, Germany). In addition, a tube furnace (volume: 1.24 L, NRTH50/150/1700/3Z, Nabertherm, Germany) was used to conduct oxidation experiments in stagnant air: cuboid samples (about 3 × 3 × 13 mm) were

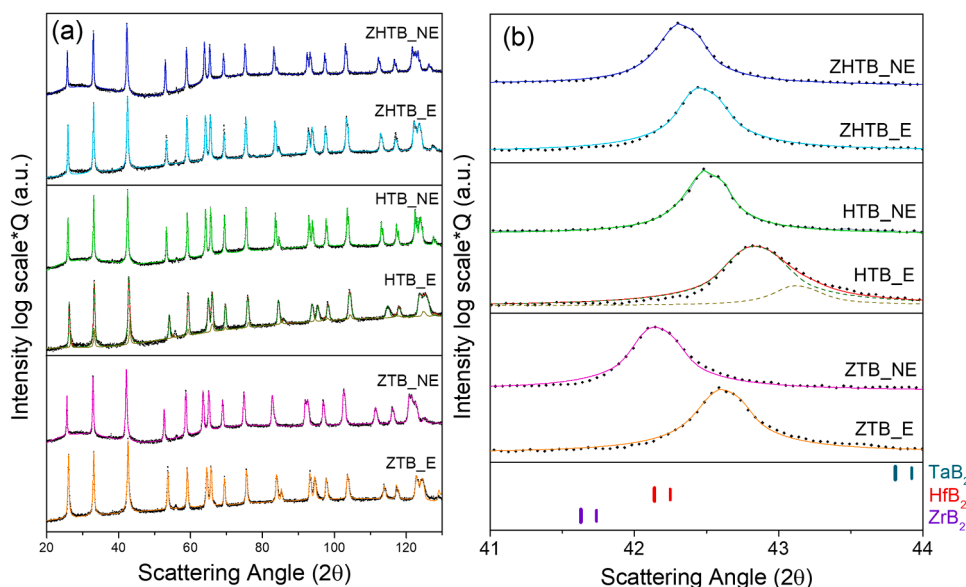


Fig. 1. General (a) and detailed (b) views of XRD patterns (black dots) and related Rietveld profiles relative to bulk samples produced in this work by SPS. ZTB_E (orange line), ZTB_NE (purple line), HTB_E ((Hf_{0.59}Ta_{0.41})B₂ phase: dark green dashed line; (Hf_{0.25-0.32}Ta_{0.68-0.75})B₂ phase: dashed olive line; calculated pattern: red solid line), HTB_NE (light green line), ZHTB_E (light blue line), ZHTB_NE (dark blue line). The related structural parameters are reported in Table S3. ZrB₂, HfB₂ and TaB₂ stick patterns have been reported in (b) to evidence the peak shift towards the Zr- and Hf-boride reflections in the non equimolar compositions. The small, unassigned peaks at approximately 55° (2θ) stem from the sample holder used for the XRD analysis.

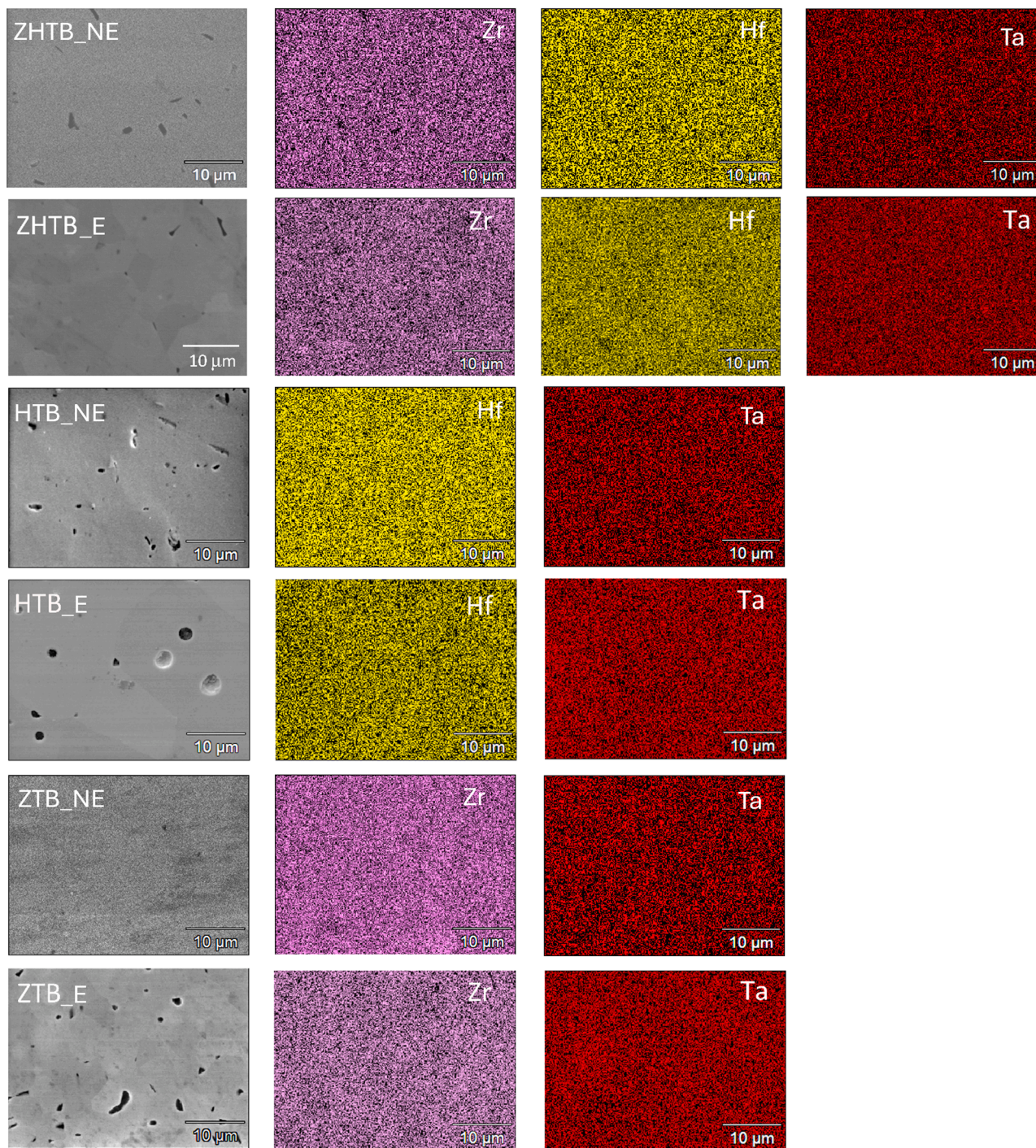


Fig. 2. SEM micrographs and associated EDS metal maps of ZTB_E, ZTB_NE, HTB_E, HTB_NE, ZHTB_E and ZHTB_NE products obtained by SPS from SHS powders.

heated at 4°C/min from RT to 1200°C, then maintained for 1 h at the target temperature, and finally cooled at 5°C/min.

The densities of SPS products were determined by the Archimedes' method, using distilled water as immersion medium. The theoretical reference values of 7.55, 11.47, 9.49 g/cm³ for ZTB_NE, HTB_NE and ZHTB_NE, respectively, were estimated using the phase lattice parameters of the different solid solutions [13].

SHS powders, SPS products, and oxidized samples were analyzed by X-Ray Diffraction (XRD), using a Bruker D8 Advance diffractometer (Bruker, Germany) (2 θ =20°-130°, steps of 0.05°, 0.5s per step). Phases content and microstructural parameters were estimated via the Rietveld method using the MAUD program [45]. The microstructure and

elemental distribution across the bulk products were examined by a HRSEM (mod. S4000, Hitachi, Tokyo, Japan) equipped with an UltraDry EDS Detector (Thermo Fisher Scientific, Waltham, USA). Cross sections of the oxidised samples were analysed with an EM40 SEM (Coxem, ROK) and a Quantax ED-XS probe (Bruker, Germany).

As observed for the E systems [13,38], the synthesis of the NE formulations investigated in this work also exhibited a self-sustaining behavior. The complete transformation of initial precursors to the expected diborides was not achieved by SHS while various secondary phases were also formed (Table 1 and Supplementary Table S1). This agrees with previous findings on other multicomponent systems [13, 46–48] and it is ascribable to the extremely short timescales of SHS

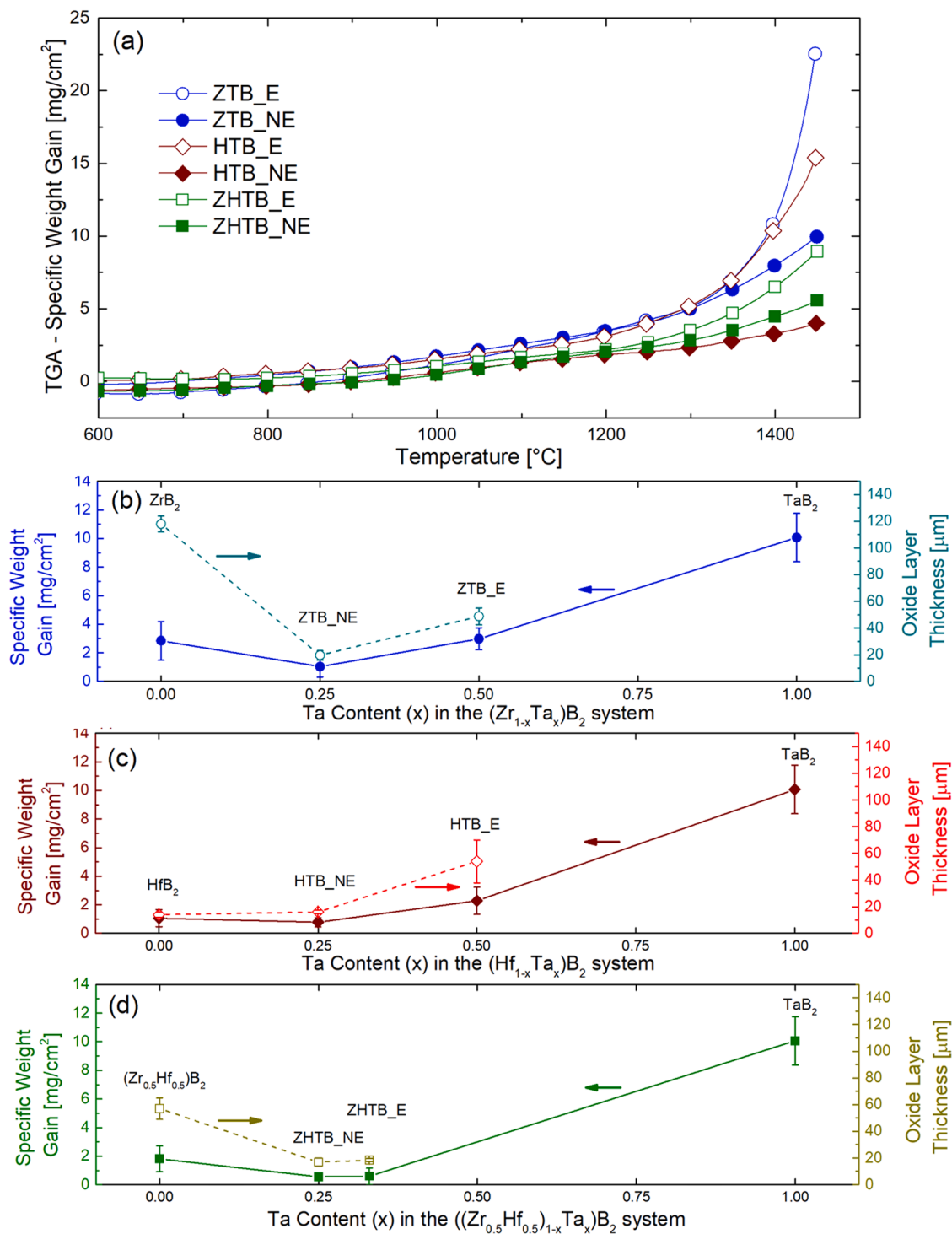


Fig. 3. (a) Specific weight changes of sintered samples during TGA oxidation test in air (ZTB_E: blue empty symbols, ZTB_NE: blue full symbols; HTB_E: wine empty symbols, HTB_NE: wine full symbols; ZHTB_E: green empty symbols, ZHTB_NE: green full symbols). (b)–(d) Specific weight gain (solid lines) and oxide layer thickness (dashed lines) after 1 h in air furnace at 1200°C as a function of Ta atomic content x : (b) $(\text{Zr}_{1-x}\text{Ta}_x)\text{B}_2$; (c) $(\text{Hf}_{1-x}\text{Ta}_x)\text{B}_2$; (d) $((\text{Zr}_{0.5}\text{Hf}_{0.5})_{1-x}\text{Ta}_x)\text{B}_2$. Data for ZrB_2 , HfB_2 , TaB_2 and $(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{B}_2$ systems has been taken from Cappai et al. 2026 [13].

processes (on the order of seconds), which prevent the different metallic species involved from distributing uniformly during this synthesis stage. Particle size analysis, the results of which are reported in **Supplementary Table S2**, indicates that micrometer-sized SHS powders are obtained after the ball milling treatment prior to sintering.

XRD analysis results reported in Fig. 1 and Table 1 prove that the ZTB_NE, HTB_NE, and ZHTB_NE samples obtained by SPS are all single-phase. Further details on the corresponding structural parameters of the

detected phases can be found in **Supplementary Table S3**. SEM/EDX images shown in Fig. 2 confirm the obtainment of highly dense and homogeneous NE solid solutions by SPS. The same outcome was reached when processing the corresponding equimolar diborides, except for HTB_E, where a residual Ta-rich secondary phase persisted after sintering [13]. This discrepancy can be likely attributed to the relatively lower Ta content in HTB_NE, which makes elements homogenization easier compared to the equimolar counterpart. The resulting densification levels are comparable

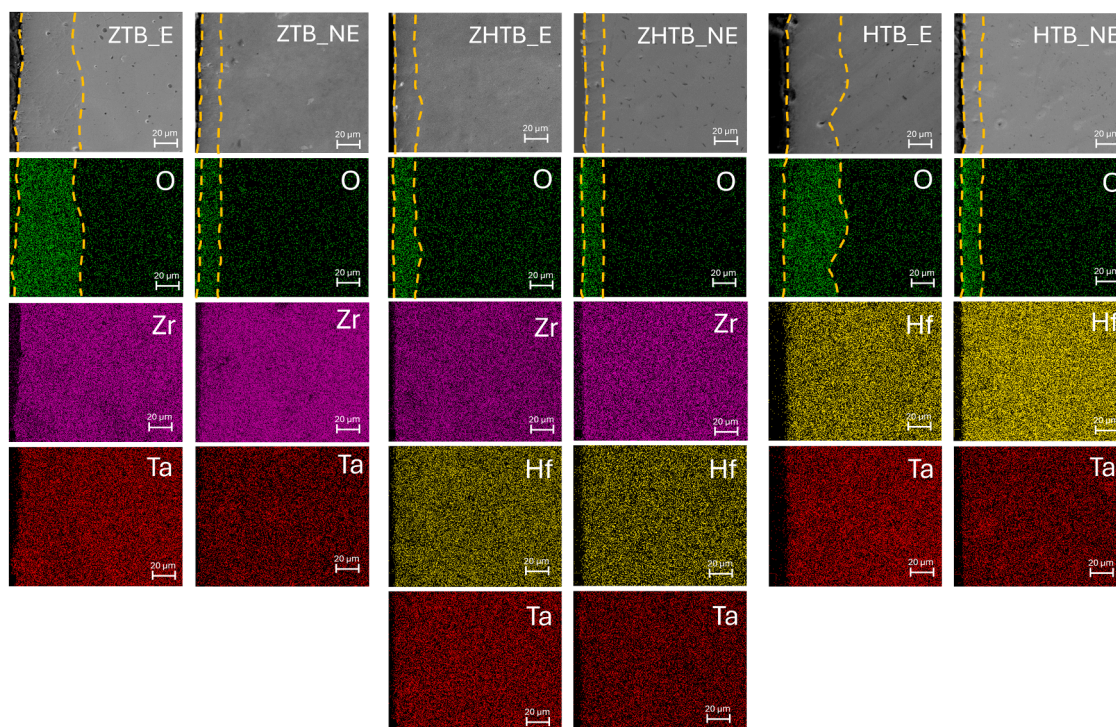


Fig. 4. Cross sectional SEM micrographs and corresponding EDX elemental maps of equimolar and non-equimolar diboride samples after being heat treated for 1h in an air furnace at 1200°C. The oxide layer boundaries have been highlighted with yellow dashed lines.

to (ZHTB), or even slightly higher than (ZTB and HTB), those of the equimolar systems (Table 1).

TGA experiments carried out on the sintered samples clearly reveal that the NE systems (full symbols in Fig. 3a) exhibit lower mass gain during the test with respect to their E counterparts (empty symbols). In the case of the binary borides, more pronounced differences between non-equimolar and equimolar systems were observed, as the latter are characterized by an A/Ta ratio (1:1) that deviates the most from that (3:1) corresponding to $\text{Zr}_6\text{Ta}_2\text{O}_{17}$ and $\text{Hf}_6\text{Ta}_2\text{O}_{17}$. Moreover, all NE diborides behave closely to, or even better than, ZHTB_E, which was identified as the most oxidation resistant among the equimolar systems [13]. TGA outcomes are consistent with specific mass gains measured during air furnace experiments, whose results are shown in Fig. 3b-d. A clear trend emerges, evidencing that the lowest weight gains are always achieved when the relative atomic fraction (x) of Ta in the three diboride systems is 0.25. This condition corresponds to the generation of well adherent and compact oxide scales, as clearly observed in the SEM micrographs shown in Fig. 4 along with the related EDX maps. From these images, it is also apparent that the thickness of oxide layers formed on NE samples is lower than that of their E counterparts, particularly when considering the two binary diborides. The dashed lines plotted in Fig. 3b-d better evidence such a relevant finding. Similar oxide scales, about 15–20 µm thick, were formed regardless of the system when the Ta content was set at 25 at.%, i.e., in the case of the NE solid solutions (Fig. 4). The correspondingly lower mass gain indicates that the generated compact oxide scale provides superior protection against oxidation for the ceramic bulk. Conversely, Figures 3 and 4 show that the equimolar counterparts, particularly HTB_E and ZTB_E, exhibit significantly thicker oxide layers (53.9 ± 16.1 and 48.7 ± 6.3 µm, respectively), consistent with the recorded weight gain.

All the outcomes described above can be readily linked to the different oxide species formed on the surface of the investigated samples. XRD analysis results reported in Fig. 5 and Table 2 indicate that $\text{A}_6\text{Ta}_2\text{O}_{17}$ type oxides were almost exclusively detected on the NE ceramics upon oxidation. In contrast, significantly higher quantities of other oxide species,

including ZrO_2 , Ta_2O_5 , and TaO_2 , were also generated in the case of the equimolar diborides, especially the ZTB_E and HTB_E systems. Their presence is considered detrimental from the oxidation resistance viewpoint, as discussed extensively in [13]. Briefly, ZrO_2 undergoes a monoclinic (m) to tetragonal (t) phase transition around 1120°C [12] within the investigated temperature range. Additionally, detecting both TaO_2 and Ta_2O_5 supports the hypothesis that the formation of the latter species is preceded by that of the former [15]. This phase transformation induces a molar volume change from 6.82 (TaO_2) to 7.62 cm^3/mol (Ta_2O_5), generating thermomechanical stresses that drive cracking and spalling [13].

For the equimolar ternary system (Figures 3 and 4), shifting from E to NE affected oxidation resistance less than in the binaries. This can be explained by the fact that the (Zr,Hf):Ta ratio in ZHTB_E (2:1) is closer to the one needed to form $\text{A}_6\text{Ta}_2\text{O}_{17}$ (3:1), compared to the 1:1 ratio in ZTB_E and HTB_E. Consistently, as reported in Table 2, this complex oxide is found to be predominant in the first system (86 ± 5 wt.%). In contrast, the relative amount of $\text{A}_6\text{Ta}_2\text{O}_{17}$ detected when the two equimolar binary diborides undergo oxidation slightly exceeds 50 wt.% (Table 2), thus making the generated oxide scale less protective.

Supplementary Fig. S2 provides a direct demonstration of the benefits of exclusive $\text{A}_6\text{Ta}_2\text{O}_{17}$ formation during oxidation of NE systems, as ZTB_E and HTB_E exhibit significantly higher degradation and colour change than ZTB_NE and HTB_NE. This effect is less pronounced for ZHTB, agreeing with the minimal differences in weight loss and oxide thickness between the related NE and E samples (Figures 3 and 4). Detailed SEM micrographs of the sample surfaces, shown in **Supplementary Fig. S3** for the system HTB as an example, further highlights these differences: the oxidized surface of HTB_E is highly porous, with an irregular morphology and several cracks (yellow arrows), unlike that of HTB_NE, which appears much more compact. Two types of grains coexist in HTB_E: larger ones, rich in Ta (Hf/Ta at. ratio close to 0.1) and ascribable to Ta-oxides, and smaller mixed oxide grains. Conversely, the grains formed on HTB_NE show similar morphology, size, and EDS spectra, with a Hf/Ta at. ratio very close to 3, which matches the $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ oxide.

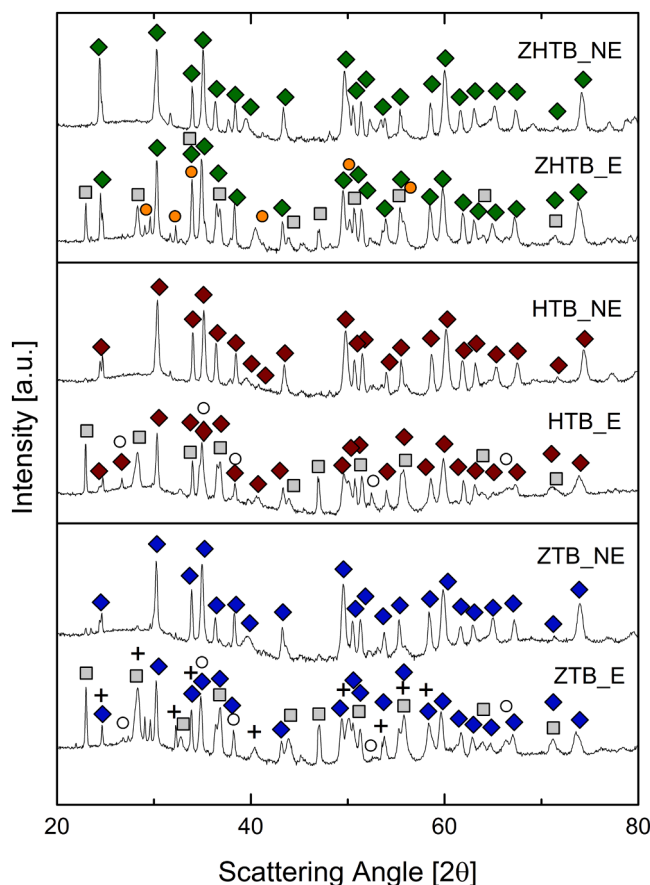


Fig. 5. XRD patterns relative to the surface of equimolar and non-equimolar systems produced in this work after being annealed at 1200°C for 1 h. ◆ $\text{Zr}_6\text{Ta}_2\text{O}_{17}$; ○ ZrO_2 ; □ Ta_2O_5 ; ◆ $\text{Hf}_6\text{Ta}_2\text{O}_{17}$; ◆ $(\text{Zr,Hf})_6\text{Ta}_2\text{O}_{17}$; ○ $(\text{Zr,Hf})\text{O}_2$. XRD patterns in log-scale are reported in **Supplementary Fig. S1** along with the related Rietveld profiles. The relative quantitative outputs are summarized in **Table 2**.

Table 2

Relative content (wt.%) of oxides generated on the surface of equimolar and non-equimolar samples investigated in this work.

Nominal composition	System ID	Oxidised surface composition(wt.%)
$(\text{Zr}_{1/2}\text{Ta}_{1/2})\text{B}_2$	ZTB_E	$\text{Zr}_6\text{Ta}_2\text{O}_{17}$ (53±3); Ta_2O_5 (34±1); ZrO_2 (9±1); TaO_2 (4±3)
$(\text{Zr}_{3/4}\text{Ta}_{1/4})\text{B}_2$	ZTB_NE	$\text{Zr}_6\text{Ta}_2\text{O}_{17}$ (>98%)
$(\text{Hf}_{1/2}\text{Ta}_{1/2})\text{B}_2$	HTB_E	$\text{Hf}_6\text{Ta}_2\text{O}_{17}$ (52±2); Ta_2O_5 (37±1); TaO_2 (11±2)
$(\text{Hf}_{3/4}\text{Ta}_{1/4})\text{B}_2$	HTB_NE	$\text{Hf}_6\text{Ta}_2\text{O}_{17}$ (>98%)
$(\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ta}_{1/3})\text{B}_2$	ZHTB_E	$(\text{Zr,Hf})_6\text{Ta}_2\text{O}_{17}$ (86±5); Ta_2O_5 (11±3); $(\text{Zr,Hf})\text{O}_2$ (3±2)
$(\text{Zr}_{3/8}\text{Hf}_{3/8}\text{Ta}_{1/4})\text{B}_2$	ZHTB_NE	$(\text{Zr,Hf})_6\text{Ta}_2\text{O}_{17}$ (>98%)

The results described above are in line with two literature works on the oxidation of (Hf,Ta) -carbides [30] and alloys [16], respectively. Indeed, 25 at.% was proved to be the optimal content of Ta for enhancing the oxidation resistance of $\text{Hf}_{(1-x)}\text{Ta}_x\text{C}$ ceramics [30]. Similarly, the highest oxidation resistance in $\text{Hf}_{(1-x)}\text{Ta}_x$ alloys was attained with a Ta fraction of 26.7 at.% [16], which is still close to the value identified in the present study for multicomponent diborides (Fig. 3).

As reported in [13], the ZHTB_E system was found to exhibit superior oxidation behaviour compared to its binary equimolar constituents. Rather than a “cocktail effect” resulting from the simultaneous presence of both Zr and Hf metallic elements in the boride, this outcome is mainly attributable to the preferential formation of $\text{A}_6\text{Ta}_2\text{O}_{17}$ (A:Ta=3:1) in the ternary system compared to ZTB_E and HTB_E, due to the corresponding

A:Ta ratios in the original diborides (2:1 and 1:1, respectively). The latter statement is supported by the fact that the ZTB_NE and HTB_NE counterparts, both characterized by an A:Ta ratio of 3:1, display very similar oxidation behaviour, with the former exhibiting only a slightly higher mass gain and oxide layer thickness.

This paves the way for a wider range of non-equimolar materials showing comparable oxidation resistance, whose final selection can be guided by other key factors, such as lightweighting, critical raw materials, cost, etc. Clearly, the expected operating temperature of these materials represents a crucial constraint for their ultimate choice. In this regard, $\text{Zr}_6\text{Ta}_2\text{O}_{17}$ has a melting point of ~1900°C [17] while $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ melts at approximately 2280°C [18]. Therefore, ZTB_NE should be preferred for applications at relatively milder temperatures, given its markedly lower density (approximately -35% with respect to HTB_NE) and the fact that Zr is a less critical element than Hf [11]. Conversely, HTB_NE is better suited for slightly more demanding operating conditions.

In conclusion, this work highlights the key role played by the formation of complex oxides in protecting multicomponent transition metal borides against oxidation. The results obtained call for a shift in perspective from the conventional equimolar solid solution approach toward one focused on Ta-poor compositions, which promote the formation of the more stable $\text{A}_6\text{Ta}_2\text{O}_{17}$ oxide. The proposed approach can also be extended to alternative binary and ternary diborides involving transition metals capable of forming this type of oxide [49].

Moreover, the results obtained in this study can shed light on the oxidation behaviour of more complex high entropy borides, suggesting that mixed oxides generation is one of the phenomena contributing to

their enhanced resistance, as postulated for high entropy alloys [50] and carbides [22,23].

Combining composition-tailoring approach adopted in this work with other literature strategies can further improve TMB oxidation resistance. Complementary methods include boron stabilization [8–10, 51], preferential oxidation of selected metallic elements [5–7], liquid-aided sintering of the oxide scale [12,31], and Si-driven borosilicate glass formation [47,52]. Therefore, all these aspects and strategies must be properly considered to identify the most convenient UHTC system with the highest oxidation resistance.

CRedit authorship contribution statement

Mariano Casu: Writing – original draft, Validation, Methodology, Investigation. **Luca Cappai:** Writing – original draft, Validation, Methodology, Investigation. **Antonio Mario Locci:** Writing – review & editing, Validation, Supervision, Conceptualization. **Giacomo Cao:** Writing – review & editing, Supervision, Funding acquisition. **Roberto Orrù:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Roberto Orrù reports financial support was provided by Sardegna Foundation. Giacomo Cao reports financial support was provided by Ministry for Research and Education, Italy. If there are other authors, they 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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Supplementary materials

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