Technical Article

Investigating the Research Conducted on Improving the Properties of Oxidation Resistance and Erosion of ZrB2/SiC Composites

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Abstract

One of the main challenges in advanced industries in the field of future technologies is the existence of materials that can maintain their integrity at temperatures above 2000 degrees Celsius. Ultra-high temperature ceramics (UHTCs) are among the attractive options for meeting this industrial need. Resistance to oxidation and linear and mass erosion is one of the most important and influential properties of these high-temperature ceramics. Hf and Zr diborides are the most important materials among high-temperature ceramics for these components, showing the best resistance to oxidation up to a temperature of 1500 degrees Celsius. Especially ZrB_2 has received more attention due to its low density and low cost. However, two important factors hinder its application: firstly, it contains a high amount of boron. Boron oxides quickly vaporize at temperatures above 1200 degrees Celsius, resulting in severe material loss due to hot gases. Secondly, due to its brittleness and low thermal shock resistance, it is prone to sudden fracture. In order to reduce the evaporation of boron oxides and improve the erosion resistance of ZrB_2, significant attention has been given to adding silicides (such as SiC, $MoSi_2$, etc.) and carbides (such as ZrC) to ZrB_2 to form multiphase ceramics. On the other hand, relatively little attention has been paid to the development of single-phase ceramics with multiple elements. Although ZrC is less prone to evaporation at high temperatures due to the absence of boron, it has lower oxidation resistance compared to diborides (such as ZrB_2) and is weaker. This makes it less suitable for anti-erosion applications. The mentioned factors indicate that high-temperature ceramics are limited in their application in environments with very high temperatures, and new single-phase ceramic materials with lower evaporation rates and better oxidation resistance need to be developed. This research focuses on recent studies on increasing the oxidation resistance of ZrB_2 composites in detail.

Keywords: Oxidation, Ceramic, Composite, Erosion, Zr/B_2.

1. Introduction

Ultra high temperature ceramics (UHTCs) are designed for use in critical environments such as leading edges of hypersonic vehicles or in propulsion components [1]. In recent years, there has been renewed interest in UHTCs, especially in methods to improve their high-temperature capabilities [2-11]. To maintain structural integrity of UHTCs under operating conditions, resistance to oxidation is of particular importance for these ceramics. Transition metal diborides such as hafnium and zirconium have proven to be among the best choices in UHTC materials [12-15]. For the purpose of this investigation, only zirconium diboride-based ceramics will be considered unless research on hafnium diboride provides valuable insights. Several historical research studies on UHTCs have summarized material properties and testing methods [16, 17], and this review considers candidate materials and necessary selection methods for UHTC production that meet stringent environmental requirements [11, 18].

The aim of this study is to summarize recent research advancements that identify possible methods for improving the oxidation resistance of UHTC materials.
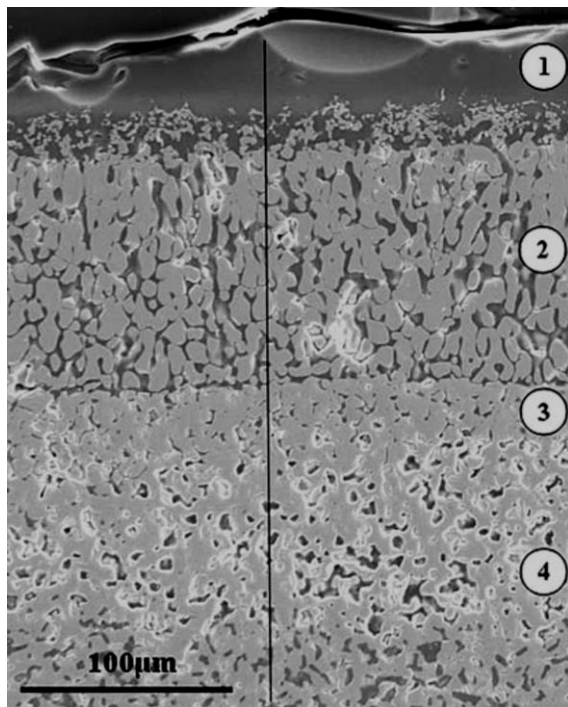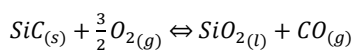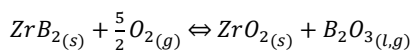
2. Oxidation

Oxidation resistance and methods for improving the oxidation performance of zirconium diboride (ZrB_2) have been studied since 1960 [1, 3, 8-10, 19-43], and the temperature range in which the ceramic has been tested has expanded with improved testing capabilities. For consolidated ZrB_2, the formed oxide is B_2O_3, which remains liquid above 450°C and wets the oxide grains until it evaporates at temperatures above 1000°C [22]. Below 1100°C, the kinetics of oxidation is controlled by oxygen diffusion through the liquid boron surrounding the ZrB_2 grains. Between 1100 and 1400°C, the oxidation kinetics exhibit a linear behavior due to an increase in mass from ZrO_2 and B2O3 formation and a decrease in mass from B_2O_3 evaporation. The significant improvement in properties of high-temperature ceramics based on ZrB_2 by adding SiC has been observed for some time, and it has generally been found that the optimal amount of SiC is between 15 and 20% by volume.

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Addition of SiC through liquid phase sintering via borosilicate liquid formation enhances the sinterability of initial powders [4, 6-9, 21, 22, 24, 44]. The addition of SiC itself further controls the growth of diboride grains leading to improved mechanical properties [4, 45]. Other reported benefits include improved thermal shock resistance and oxidation resistance [8]. The likely influence of low thermal conductivity and brittle glass phases on thermal shock resistance is limited to temperatures below the softening point of around 1000°C [22]. During high-temperature oxidation, silicon from SiC and boron from ZrB_2 oxidize to form a protective borosilicate glass layer according to the following equation:

$$ZrB_{2(s)} + \frac{5}{2}O_{2(g)} \Leftrightarrow ZrO_{2(s)} + B_2O_{3(l,g)}$$

$$SiC_{(s)} + \frac{3}{2}O_{2(g)} \Leftrightarrow SiO_{2(l)} + CO_{(g)}$$

Fig. 1. Scanning Electron Microscope (SEM) image of ZrB_2+ 20 vol% after oxidation in air at a temperature of 1627°C 10-minute cycles: (1) Outer glass layer, (2) ZrO base intermediate layer, (3) Void region, and (4) Unreacted high-ceramic [25].

Generally, several researchers [22, 25, 38, 46] have found that the oxide has a layered structure (Fig. 1. and Fig. 2.). A borosilicate glass layer is present on top of the micrograph. Below this layer, there is an embedded oxide layer with voids filled with a glass phase. The high wetting angle between the oxide grains and the borosilicate glass coating ensures complete surface coverage at temperatures below the evaporation temperature of the glass. In some samples, there are regions beneath this oxide layer that have been depleted in SiC.

Finally, at the bottom of the micrograph, there is unreacted high-density ceramic. Borosilicate glass has higher viscosity, higher boiling point, and lower vapor pressure than boride, which provides more effective oxidation protection. The protective layer's effectiveness increases up to about 20% by volume of SiC. When ZrB_2-SiC materials are exposed to furnace oxidation at 1500°C, the thickness of the borosilicate layer decreases with increasing SiC content. When there is enough SiC present, as the amount of SiC increases, the borosilicate liquid flows from oxidized regions towards the material surface and can effectively fill voids between oxide grains to protect against further oxidation [22].
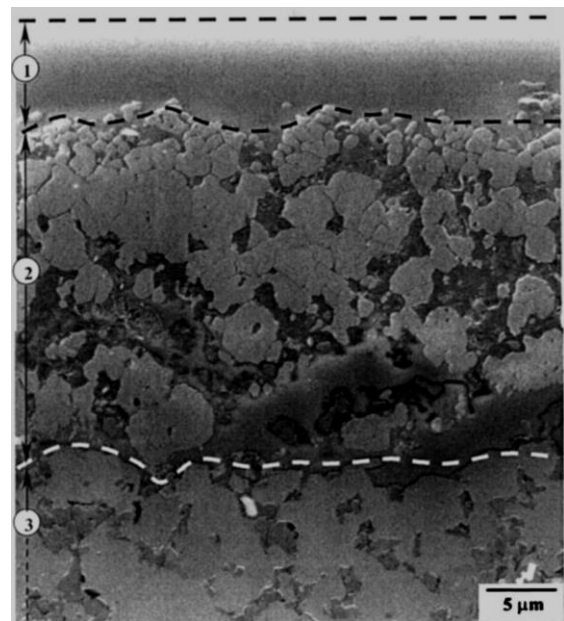

Fig. 2. SEM image of an oxidized sheet in ZrB_2+ 20 vol% SiC+ 5 vol% Si3N4, after non-isothermal oxidation testing up to 1350°C. The numbers in the micrograph indicate: (1) Outer glass layer, (2) ZrO base intermediate layer, and (3) Unreacted high-ceramic [38].

Li [8] precisely explained mechanism of improving the oxidation performance of high-temperature ceramics based on ZrB_2-SiC for both ZrB_2 and SiC. They suggested that better oxidation performance is achieved by developing a "solid column with a liquid roof" structure, where borosilicate glass acts as a diffusion barrier and the ZrO_2 grains remain in a liquid form, providing mechanical stability to the oxide layer. The growth of oriented ZrO_2 grains in the oxidation of ZrB_2-SiC ceramics is induced by gas product generation and liquid transport [24]. The dissolution of ZrO_2 grains occurs through the discharge of SiC gas products with high vapor pressure: carbon monoxide gas is inactive during oxidation, while carbon monoxide and silicon monoxide gases are active during oxidation. ZrO_2 particles can be transferred to the surface of glass layers through convection or reactions between

zirconia, boron, or silica [47]. Optimizing the composition of the glass to prevent oxygen transfer can reduce the rate of progression of the oxide layer into the bulk matrix.

It is believed that the borosilicate liquid moves from the oxidation network to the surface. The formation of silica liquid for zirconia is non-wetting and near the surface, it becomes more viscous due to the evaporation of B_2O_3 by the liquid phase [3, 22, 48]. Karlsdottir and Halloran [22] suggested that sustained sub-scale oxidation recession occurs with a flow of boron-rich liquid in thermal cells between oxide grains, providing pathways for oxygen transport into unoxidized bulk materials.
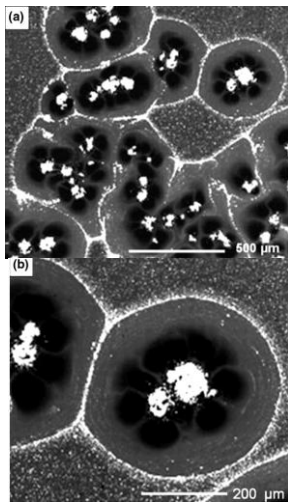
Fig. 3. SEM image of (a) 500 μm backscattered electrons of thermal cells on the surface of (b) 200μm ZrB_2+15 vol% SiC after 30 minutes of oxidation at 1600°C [49].
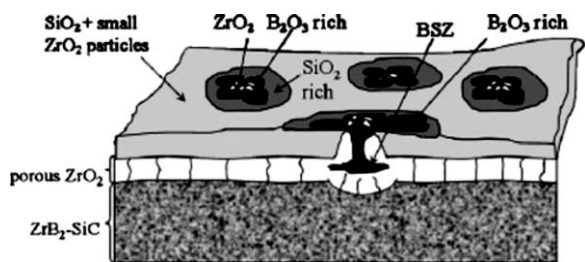
Fig. 4. Schematic representation of heat transfer cell features on the surface of highly temperature-resistant oxidized ZrB_2-SiC ceramics. BSZ is a liquid oxide solution containing boron, silicon, and zirconium [49].
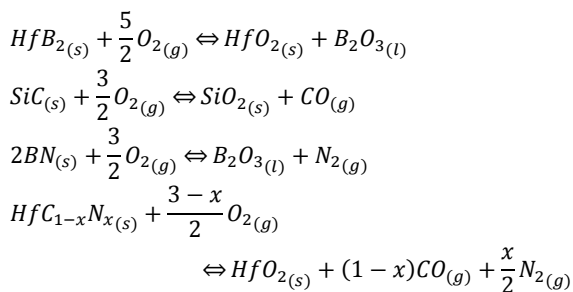
As shown in Fig. 3. and Fig. 4., thermal cells are formed in the borosilicate liquid from the zirconia deposition on the oxidized surface. The amount of SiC should be controlled so that the protective glass formed during oxidation is present in sufficient quantity. However, if the amount of SiC exceeds the infiltration threshold [6, 14, 31, 32, 37] - for example, if it forms a continuous three-dimensional network - then open porosity channels between oxide grains will remain until further oxidation.

These residual SiC channels will undergo further oxidation and lead to areas devoid of SiC. Peng et al. [46] concluded that the SiC-depleted region is a result of a wicking process. The internally formed borosilicate liquid is transferred to the existing borosilicate liquid on the surface through wicking. Increasing the amount of SiC beyond the infiltration threshold increases the thickness of the SiC-depleted region [47]. It has also been observed that the SiC depletion zone acts as an initiation site for material cracking and spalling during oxidation at temperatures around 1900°C. ZrB_2 grains adjacent to the SiC-depleted regions remain exposed to residual oxygen [47]. The particle size of SiC powder also affects the properties of high-temperature ceramics. Compared to materials produced with standard-sized powders with much larger particle sizes, the use of fine SiC with sub-micron particle sizes can produce ZrB_2-SiC composites with improved mechanical and thermomechanical properties [21]. This is due to the more uniform dispersion of particles, which inhibits the growth of diboride grains and results in a finer microstructure that is more effective in deflecting cracks and bridging gaps. Additionally, fine SiC enables the production of materials through hot pressing at 1900°C without the need for sintering aids [50] and improves resistance to oxidation [2, 50-52]. The flexural strength of ZrB_2-SiC composites with fine SiC particles increases after oxidation, while the flexural strength of composites with larger SiC powder (with an average particle size of approximately 6 μm) decreases after oxidation [2]. As the temperature increases, a transition from inactive to active oxidation occurs between 1600°C and 1700°C during SiC oxidation in air under atmospheric pressure [2, 19, 51, 52], such that above this temperature range, any protection provided by a layer of glassy oxide is largely lost.
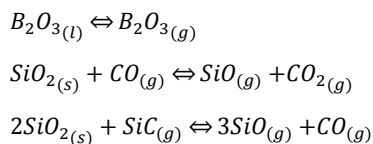
2.1. Oxidation Kinetics

Extensive oxidation studies have been conducted to determine the oxidation kinetics of ZrB_2 and ZrB_2-SiC composites [18]. For the oxidation of ZrB_2 without SiC, oxygen diffusion through the borosilicate glass layer at 1200°C was identified as the rate-limiting step. The protective liquid phase above this temperature evaporates, so the oxidation rate is dependent on oxygen diffusion through the zirconium oxide layer. High-temperature ceramics containing SiC maintain the protective glass layer at higher temperatures compared to samples without SiC. However, SiC only improves resistance to oxidation at temperatures above 1350°C - the temperature at which silicon oxide forms. Below this temperature, SiC components remain in the oxide layer.

Hinze et al. [2] found that the rate-limiting step for the overall kinetics of these materials, as calculated by their fractional contribution, is oxygen diffusion through the borosilicate glass; This idea has also been observed in recent research. Monteverde and Bellosi studied the oxidation resistance of HfB$_2$-SiC composites through isothermal and non-isothermal treatments in air at temperatures below 1600°C. They found that the oxidation kinetics of the composite follows a pseudo-linear rule until the rupture of a portion of the oxide scale, after which the weight gain is proportional to time. The fractional contribution of the results is attributed to the growth of an external oxide scale, which gradually provides another diffusion path for oxygen upon the formation of a diboride-oxide interfacial region. A negative linear contribution is calculated for volatile products (likely B$_2$O$_3$ or SiO$_2$) released from the outer borosilicate layer. The HfB$_2$-SiC composite also contains HfO$_2$ and cubic solid solution HF(C, N) as secondary phases formed during hot pressing, which have a negligible effect on oxidation resistance at temperatures below 1350°C. As expected, SiC improves resistance to oxidation at temperatures above 1350°C. In their study of HfB$_2$-SiC materials, MonteverdeandBellosi [53] proposed the main reactions involved in the oxidation process. Depending on the selected temperature range, these reactions include mass gain as follows:

$$HfB_{2(s)} + \frac{5}{2}O_{2(g)} \Leftrightarrow HfO_{2(s)} + B_2O_{3(l)}$$

$$SiC_{(s)} + \frac{3}{2}O_{2(g)} \Leftrightarrow SiO_{2(s)} + CO_{(g)}$$

$$2BN_{(s)} + \frac{3}{2}O_{2(g)} \Leftrightarrow B_2O_{3(l)} + N_{2(g)}$$

$$HfC_{1-x}N_{x(s)} + \frac{3-x}{2}O_{2(g)}$$
$$\Leftrightarrow HfO_{2(s)} + (1-x)CO_{(g)} + \frac{x}{2}N_{2(g)}$$

or mass loss as follows:

$$B_2O_{3(l)} \Leftrightarrow B_2O_{3(g)}$$

$$SiO_{2(s)} + CO_{(g)} \Leftrightarrow SiO_{(g)} + CO_{2(g)}$$

$$2SiO_{2(s)} + SiC_{(g)} \Leftrightarrow 3SiO_{(g)} + CO_{(g)}$$

To maintain the oxidation resistance of a high-temperature material, the protective oxide layer must be preserved. MonteverdeandBellosi observed the rupture of the oxide scale in $_{ZrB2}$-SiC ceramics after furnace oxidation testing in several thermal cycles from room temperature to 1700°C. The cracking and spalling of the oxide scale are attributed to the phase transition in ZrO$_2$ particles occurring during thermal cycles. At high temperatures, this oxide exists in a tetragonal form, while at lower temperatures, it is monoclinic.

In pure ZrO$_2$, the martensitic monoclinic-to-tetragonal transformation occurs at temperatures of 1170°C during heating and 950°C during cooling [49]. It is evident that undergoing thermal cycles with rapid and unstable thermal conditions is undesirable for a material. Additionally, oxides have higher coefficients of thermal expansion (CTEs) and lower thermal conductivity compared to diboride matrix materials. This, along with phase transformation, leads to the cracking of the oxide scale, which promotes bulk oxidation.

3. Additives

Oxidation products form when the materials are exposed to an oxidizing environment, and they largely contribute to the high-temperature performance of these materials. The extent of protection against subsequent oxidation is determined by the thickness of the oxide layer that can shield the underlying material. The physical and chemical processes occurring at the surface depend on the microstructure and composition of the oxidized material. It can be concluded that modifying the microstructure and composition can have beneficial (or detrimental) effects on oxidation resistance. Additives can be used in various ways to improve the oxidation resistance of high-temperature ceramics. The main areas of interest include: Increasing the viscosity of borosilicate liquid phase,Preventing polymorphic transformations of particles, Using alternative options for introducing silicon, Formation of long-lasting protective phases at high temperatures,Modifying the microstructure of the sheet. Additives can be used in various ways to improve the oxidation resistance of high-temperature ceramics. The main areas of interest include: Increasing the viscosity of borosilicate liquid, Preventing polymorphic transformations of particles, Using alternative options for introducing silicon, Formation of protective long-lasting phases at high temperatures, Modifying the microstructure of the sheet ZrO$_2$

3.1. Viscosity of Borosilicate Liquid

Increasing the viscosity of the borosilicate liquid phase prevents oxygen penetration into the non-reactive bulk, preserves the protective liquid phase at higher temperatures, and prevents boron evaporation from the glass phase. The diffusion in a viscous liquid has an inverse relationship, as demonstrated by the Stokes-Einstein equation: $D = kT/6\,\eta\,\pi\,r$, where D is the diffusion constant, k is the Boltzmann constant, T is in Kelvin, η is the viscosity, and r is the radius of spherical particles. The viscosity of borosilicate glass can be significantly increased by adding specific elements to the bulk materials. Adding tungsten in 10% and

20% volume to ZrB_2-SiC ceramics significantly increases the viscosity of borosilicate glass phases but reduces thermal shock resistance and structural stability at high temperatures, which is undesirable for sharp and precise materials [18]. The oxidation resistance of ZrB_2+25 vol% SiC composites improves with the addition of diborides of Cr, Ti, Ta, Nb, and V [48]. These additives lead to the formation of corresponding oxides in the glass. The improvement in oxidation resistance is due to the fact that borate and silicate glasses containing oxides of these elements (Group IV-VI transition metals) are immiscible and undergo phase separation. Such systems contain compounds with high viscosity and liquid temperature. The improvement in oxidation resistance is well correlated with the strength of the cationic field in the related modifying additive. Opila et al. [12] investigated the effect of adding tantalum on the oxidation performance of zirconium diboride. They found that adding $TaSi_2$ enhances the oxidation resistance of the ZrB_2+20 vol% SiC composite. The oxidation rate decreased with the addition of reducing agents at a temperature of 1627°C. They concluded that further research is needed to confirm whether the improvement in oxidation is due to the addition of tantalum rather than silicon. It has been suggested that Ta leads to the formation of an immiscible liquid phase, which increases the viscosity of the liquid phase and forms a protective layer that is more resistant to evaporation. The immiscibility on the surface of ZrB_2-20vol% SiC-ZrB_2-20vol% $TaSi_2$ after oxidation in air at 1627°C for 100 minutes is shown in Fig. 5.
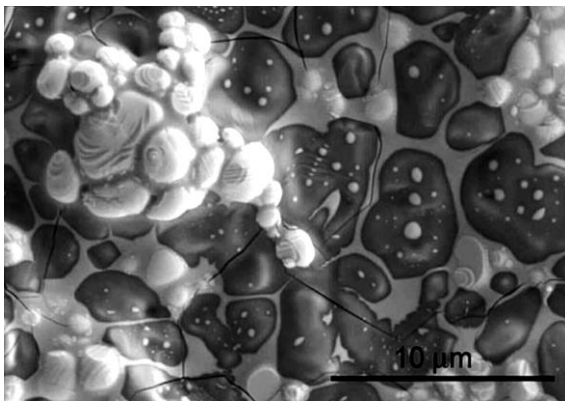
Fig. 5. SEM image with backscattered electrons showing immiscibility on the surface of 20 vol % $TaSi_2$-ZrB_2-20 vol% SiC after oxidation in air at 1627°C for 100 minutes. The bright contrast phase is ZrO_2, the medium contrast is silicate glass with impurities, and the dark phase is SiO_2 [12].

Peng and Speyer [31] investigated the effect of $TaSi_2$ and TaB_2 on the oxidation resistance of ZrB_2-B_4C-SiC composites in the temperature range of 1150 to 1550°C. Adding compounds containing Ta improves the oxidation resistance of the materials in the entire temperature range studied, but $TaSi_2$ performs better due to its ability to form a higher amount of protective silica-rich glass phase compared to TaB_2. Peng et al. [31] also studied the effect of SiC, TaB_2, and $TaSi_2$ on the oxidation resistance of ZrB_2 at elevated temperatures. They found that increasing SiC reduces both the thickness of silica-rich glass layers and the SiC-depleted zone. TaB_2 was more effective than $TaSi_2$ in improving oxidation performance. It is suggested that both compounds contribute to improvement through the formation of a solid solution of zirconium tantalum boride. After solid solution oxidation, finer particles (approximately 1 μm) of ZrO_2 and TaC are formed from the pure ZrB_2 liquid phase. The finer particles are more effective in trapping the liquid phase within the ZrO_2 layer and preventing oxygen transfer through the liquid. Additives are only effective at low concentrations (approximately 3.32 mol%) and at higher concentrations, they disrupt oxidation resistance due to the formation of zirconia dendrites, which act as pathways for oxygen diffusion into the bulk material. Zhang et al. [55] found that adding 3 vol% yttria improves the wettability of the parent phases and prevents grain growth by reacting with surface oxides of the initial powders. Grain size modification enhances the fracture toughness and flexural strength of the materials. Adding LaB_6 to high-temperature ZrB_2 + 20 vol% SiC ceramics significantly increases fracture toughness compared to the same ceramics without LaB6 [40], as it deflects and bridges cracks near SiC particles. $MoSi_2$ has a beneficial effect on the mechanical and oxidation properties of ZrB_2-SiC ceramics and is an effective sintering aid for ZrB_2-SiC composites produced by hot pressing [31, 41] and spark plasma sintering [56]. Zhang et al. [37] found that adding tungsten carbide to ZrB_2, produced by pressureless sintering at 1600°C, increases oxidation resistance by forming a solid solution with ZrB_2, which leads to the formation of a liquid ZrO_2 phase during oxidation. This process results in a significant reduction in the thickness of the oxide layer in WC-containing ceramics [2, 57].

3.2. Polymorphic Transformations in ZrO_2

Prevention of polymorphic transformations in ZrO_2 can improve the integrity of the oxide layer by inhibiting polymorphic transformations in ZrO_2 and their associated volume changes. In low-temperature systems, this integrity has been achieved by adding stabilizing cations such as Mg, Ca, and Y. However, these cations are obtained from the ZrO_2 lattice at relatively low temperatures, and alternative cations are desired for UHTCs. Adding a cation such as Ta to replace the cation on the Zr lattice in ZrO_2 particles leads to a reduction in oxygen vacancy concentration due to the high capacity of the cation (Ta forms Ta_2O_5 upon oxidation).

This reduces oxygen diffusion through the oxide layer and stabilizes the oxide phase, resulting in increased adhesion of the oxide layer to ZrB_2-SiC materials. The cation should have a higher capacity and also form a slow-growing oxide layer. Additionally, candidate additives should act as a slow-growing phase and form a slow-growing oxide. Two of the best candidates based on niobium and tantalum, but tantalum in the form of Ta_2O_5 is preferred because it has a melting temperature of °Cl880 (compared to °Cl880 for Nb_2O_5) [48].

Tantalum can be added in elemental form or in the form of a carbide, boride, or silicide. The formation of intermediate phases should be considered. For example, adding Ta_2O_5 can lead to the formation of Ta_2O_5 or the formation of $6ZrO_2$ by adding ZrO_2. This phase has a lower melting temperature than pure oxides and can have beneficial or detrimental effects on the oxidation behavior of the composite.
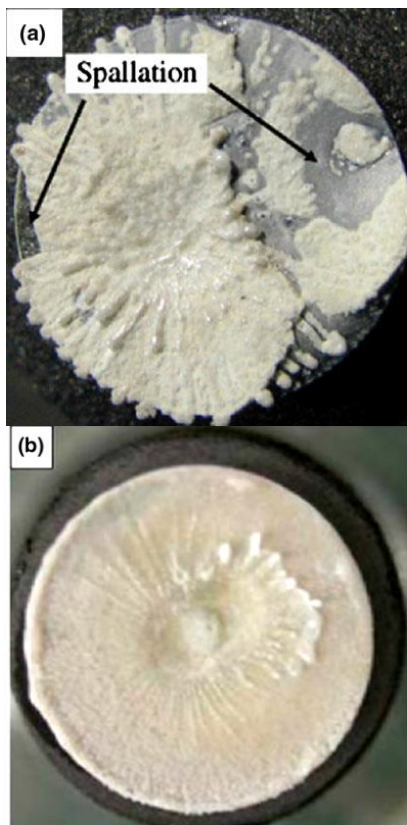
Fig. 6. Image (a) ZrB_2-20 vol% SiC and (b) ZrB_2-20 vol% SiC-10 vol% LaB_2 after oxyacetylene flame test at 2400°C for 600 seconds [13].

3.3. Silicon

The use of SiC substitutes for introducing silicon has been investigated as alternative methods to introduce Si into the system. Ceramics in the ZrB_2-Ta_5Si_3 system have been studied because Ta5Si3 has a higher melting point than SiC (2500°C and 1300°C, respectively). Ta_5Si_3 provides tantalum for glass immiscibility and silicon for the formation of a

borosilicate glass protective layer in the oxidized layer [30]. Composites of ZrB_2 and HfB_2 with $TaSi_2$, produced by hot pressing [58], form a solid solution upon entering the boride phase field. HfB_2-$TaSi_2$ exhibits better mechanical properties compared to the ZrB_2 base materials. Substituting Ti for SiC in UHTC systems has been proposed as it significantly reduces the evaporation rate compared to SiO_2 [40].

3.4. Phases at High Temperatures

The formation of protective slow-growing phases at high temperatures has been extensively studied in terms of introducing additives to ZrB_2-SiC ceramics. An alternative approach is the use of additives in the form of a solid dopant at high temperatures, which can provide resistance against oxidation at temperatures higher than the base materials, thus protecting the underlying matrix and preventing further oxidation. Promising candidate additives for this method include rare earth elements, particularly lanthanum. In fact, zirconium diboride (ZrB_2) has been investigated as an additive to improve oxidation resistance, and it was found to be effective up to a temperature of 1300°C [41].

Zhang et al. [38] fabricated a hot-pressed ZrB_2-20 vol% SiC-10 vol% $LaB6$ ceramic and compared its oxidation performance with that of ZrB_2-20 vol% SiC ceramic using an oxyacetylene flame test. Both samples were subjected to oxidation up to a temperature of 2400°C, and it was observed that the ceramic containing LaB_6 exhibited significantly less spalling and cracking compared to the ZrB_2-SiC sample (Fig. 6). Additionally, weight changes for ZrB2-SiC to LaB6 and ZrB_2-SiC were 0.2% and 0.33%, respectively. Energy-dispersive X-ray diffraction analysis of the oxide surfaces revealed that the sample containing LaB6 formed an oxide layer consisting of m-ZrO_2, t-ZrO_2, La_2O_3, and $La_2Zr_2O_7$. The addition of LaB6 not only inhibits the transformation of ZrO_2 from tetragonal to monoclinic during cooling but also forms an oxidation barrier containing lanthanum zirconate, which is self-generated and has a much higher melting temperature than SiC. Elemental mapping showed that after oxidation at 2400°C, neither silicon nor boron was present in the outer oxide layer, but the effects of lanthanum remained on the surface of the compacted sheet.

Lanthanum was also added in the form of La_2O_3 to ZrB_2-SiC [59], but it resulted in the formation of an amorphous interfacial phase and significant grain growth of ZrB_2 and SiC. Similar studies have shown that other rare earth oxide additives (Y_2O_3 and Yb_2O_3) have positive effects on the densification, hardness, and fracture toughness of ZrB_2-SiC, but their impact on oxidation resistance has not been investigated yet. Jayaseelan [7] examined the effect of adding compounds containing multiple rare earth (RE) elements to ZrB_2 + 20 vol% SiC.

Samples were prepared with 10 vol% LaB_6, La_2O_3, or Gd_2O_3 and subjected to oxidation testing at 1600°C. All samples formed a dense $RE_2Zr_2O_7$ layer during oxidation in a thickness less than 100 μm (Fig. 7). These zirconates have a high melting temperature above 2300°C and provide oxidation protection when the borosilicate phase evaporates from the surface exposed to oxygen.

Additionally, the reaction between RE and ZrO_2 particles is extensive, resulting in the formation of voids in the oxide surface through the volatilization of species such as B_2O_3 .
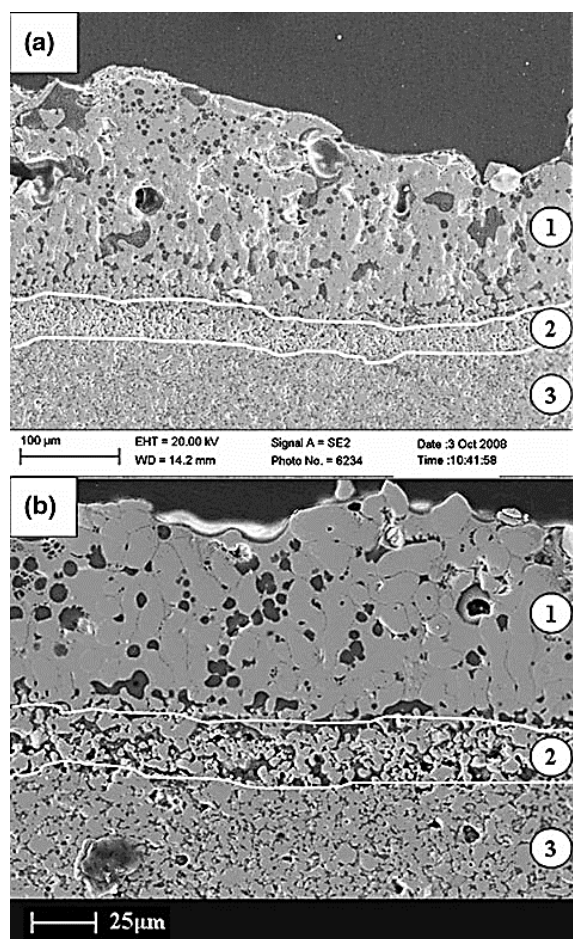
Fig. 7. Secondary electron image of the oxidized sheet in (a) ZrB₂-20 vol% SiC-10 vol% LaO₃ and (b) ZrB₂-20 vol% SiC-10 vol% LaB₆ after 1 hour of oxidation at 1600°C showing (1) dense layer containing La, (2) intermediate layer containing unreacted ZrO₂ and borosilicate [7].

3.5. Microstructure of ZrO_2

Another new technique for modifying the microstructure of ZrO_2 sheets is the use of additives to alter the particle microstructure of ZrO_2. By introducing a liquid-phase sintering route for ZrO_2 particles, the densification of the sheets can be reduced, preventing further oxygen penetration into the bulk material. Since ZrO_2 particles have a melting point of 2715°C, a dense sheet exhibits effective resistance to oxidation at temperatures higher than the evaporation temperature of boron or borosilicate phases (1600°C).

This approach was investigated by Zhang et al. [39] by adding W to ZrB_2, resulting in the formation of a WO_3-ZrO_2 eutectic at temperatures close to 1275°C. ZrB_2+4 mol% WC ceramics were subjected to TGA under a flow rate of 10 deg/min up to 1500°C and oxidation studies at either 1500 or 1600°C for 1, 2, or 3 hours under an air atmosphere. As normalized mass increased after TGA heating up to 1500°C, it was shown that WC has better oxidation resistance compared to ZrB_2 (5.4 mg/cm2 and 14 mg/cm², respectively). Additionally, ZrB_2+WC exhibited better oxidation resistance in the isothermal oxidation test at 1500 and 1600°C, with a significant decrease in mass gain over time due to the densification of ZrO_2 particles. The addition of WC to ZrB_2-SiC ceramics was also investigated, and the presence of W increased the oxidation resistance of this ceramic.

4. Densification Methods

The common method for densifying UHTCs is hot pressing, which can be done with or without additives. Significant research has explored alternative routes for producing UHTCs to reduce the time and temperature of the process, and therefore, the cost of these techniques. Some of these alternative methods also improve the materials' resistance to oxidation. The presence of secondary phases in the microstructure has a detrimental effect on the high-temperature capability of the materials due to the introduction of grain boundary phases, which may have lower melting temperatures and provide pathways for oxygen diffusion into the materials.

The presence of oxygen impurities can be detrimental to the densification of the initial powders or promote rapid grain growth, as well as contribute to the formation of secondary phases. Nitrides and reducing additives have been added to the powders to enhance their sinterability [13, 21, 60], but these additives create secondary phases in the materials.

The main production techniques employed for forming UHTC materials are as follows:

- Hot pressing [6, 8]
- Pressureless sintering [61, 62]
- Self-propagating high-temperaturesynthesis (SHS)
- Reactive hot pressing [32, 33, 37, 40, 47]
- Spark plasma sintering (SPS) [56]

4.1. Hot Press

Hot pressing is the conventional method for manufacturing UHTCs and has been widely used with typical temperatures ranging from 1900°C and

applied pressures between 30 to 50 megapascals [4, 6, 8, 24, 27, 32, 33, 37, 40, 41, 44, 47, 58, 63]. Hot pressing without the use of sintering aids achieves full densification, although most research utilizes varying amounts of sintering aids such as silicides, borides, metals (such as nickel [5, 15, 64, 65]), or C to reduce the time and temperature of the process and consequently reduce the associated costs of production.

Monteverde et al. [66, 67] conducted extensive studies using hot pressing with different sintering aids. The ceramic ZrB_2 was compared with ZrB_2-TiB_2 and ZrB_2-B_4C composites and it was found that the composite materials have better mechanical properties and perform better in long-term oxidation furnace tests. Full densification of HfB_2+30 vol% SiC ceramics was achieved by hot pressing at 1900°C for 35 minutes using 2 vol% $TaSi_2$ as a sintering aid [66].

4.2. PressurelessSintering

Pressureless sintering of ZrB_2 is challenging due to its high melting point, and in general, pressureless sintering requires a higher amount of sintering aids compared to other sintering techniques.

As a result, materials sintered by pressureless methods often contain amorphous phases, which can be detrimental to the high-temperature capability of the materials. Chamberlin et al. [61] produced ZrB_2 ceramic without sintering aids, achieving 98% of theoretical density but requiring 9 hours of pressureless sintering at 2150°C. Fahrenholtz et al. [18] demonstrated that ZrB_2 cannot be pressurelessly sintered without the presence of sintering aids (in this case, a combination of B_4C and C) that react with oxygen impurities and remove them from the surface of the boride powders. A fully dense material was formed at 1900°C with B_4C and C as sintering aids.

4.3. SHS

Self-propagating high-temperature synthesis (SHS) is not a densification method but utilizes solid-state combustion to produce materials by utilizing internally generated chemical energy from an exothermic reaction. The characteristics of this method include rapid reaction time, low energy requirements, simple experimental setup, and high purity products. However, difficulty in controlling the reactions is a disadvantage of this method. SHS can also be used to prepare ZrB_2 powder using inexpensive raw materials [38].

When used for powder production, high heating and cooling rates are employed to induce defects in the particles, such as stacking faults and linear defects like dislocations, to increase the deformability of the powder by providing a driving force for atomic rearrangement. ZrB_2 powder can be formed by SHS using zirconium and boron [40]. The powders are dry mixed and compacted into cold-pressed discs.

The discs are ignited, and the process results in an explosive-like reaction accompanied by the release of a significant amount of gas. The resulting material is highly brittle and can be used as a precursor material, although X-ray diffraction shows that this material is ZrB_2. SHS has several advantages such as control over excessive grain growth and lower process temperature compared to conventional hot pressing of UHTCs. However, the various issues with the resulting materials have been addressed by hot pressing with the addition of reinforcing phases and modifying the size of the initial powder.

4.4. RHP

Reaction hot pressing (RHP) can be used as an alternative production method to prevent the expensive conditions of hot pressing. RHP involves high-temperature reactions and in-situ solid-state chemical displacement. This benefits the control of fine structure and the equally distributed production of compatible chemistry and phases. The main advantage of RHP compared to SHS, from a process perspective, is the displacement reactions that can occur at much lower temperatures than SHS reactions. The heating rate during the reaction hot pressing should be slow enough (approximately 10°C/min) to prevent self-ignition. Monteverde [53] produced HfB_2-SiC composite by reaction hot pressing. The solid precursor (HF/Si/B_4C) was mechanically mixed, transformed into primary constituents (HfB_2 and SiC), and directly hot pressed at 1900°C to achieve full density.

This composite exhibits comparable physical properties to conventional hot-pressed materials. Wu et al. [37] produced ZrB_2-SiC-ZrC composite from a mixture of zirconium, silicon, and B_4C by reaction hot pressing at 1600°C for 60 minutes under a pressure of 20 megapascals in an argon atmosphere. The microstructure was not uniform, containing residual porosity and coarse ZrB_2 grains (up to 10 μm in diameter) due to the relatively large size of the initial powder particles (particle size less than 25 μm). These issues can be mitigated by improving the uniformity of mixing and using smaller particle size initial powders. The size and morphology of the initial powder strongly influence the microstructure in RHP ceramics. Kiang et al. [9] successfully fabricated fully dense ZrB_2-SiC-ZrC composite with a fine microstructure (approximately 1 μm) using RHP at 1900°C. This resulted in increased flexural strength (9 ± 526 megapascals) and fracture toughness

Wu et al. [37] produced ZrB_2-SiC-ZrC composite using RHP at temperatures of 1800°C and1600°C, achieving theoretical densities of 96.8% and 97.3%, respectively.

The materials sintered at 1600°C exhibited comparable mechanical properties to previous reports for materials sintered at higher temperatures. Rangaraj et al. [33] found that non-stoichiometric ZrC_x plays a significant role in the RHP of B_4C-Zr powder mixtures at 1200°C and in the production of ZrB_2-SiC composites at 1600°C. Zhang et al. [37] compared the effect of processing method on microstructure by examining ZrB_2-SiC-ZrC composites fabricated using RHP and hot pressing. The hot-pressed material had a more equiaxed grain structure, while the RHP material exhibited plate-like ZrB_2 grains.This difference in microstructure had an impact on the mechanical properties of the materials: the hot-pressed material had higher flexural strength (681 ± 67 megapascals compared to 654 ± 17 megapascals for the RHP material), while the RHP material showed more effective toughening mechanisms.

4.5. Spark Plasma Sintering

Spark Plasma Sintering (SPS), also known as Field -Assisted Sintering Technique (FAST), is an unconventional method for consolidating powders with relatively weak sinterability in a short period of time. SPS utilizes both conventional heating and pressure, as well as pulsed direct current through a graphite die (and the powder, if it is electrically conductive), as schematically shown in Fig. 8. [56]. The pulsed current enhances grain boundary diffusion and grain rearrangement, leading to increased final density by eliminating closed porosity in the ceramic. SPS offers a processing route for these highly refractory materials that does not require a sintering aid and produces fully dense products at lower temperatures and shorter times than conventional hot pressing [13, 15], which has a beneficial effect on fine-grained microstructure for mechanical properties such as fracture toughness. This technique has been particularly successful when using precursor powders produced by the SHS method [58].
Several researchers have successfully produced dense UHTCs using SPS without the need for sintering aids in the synthesis temperature range of 1900 to 2100°C and custom holding times [56, 68-71]. The materials produced by SPS exhibited comparable or improved mechanical properties and oxidation resistance compared to hot-pressed materials. The improved oxidation resistance may be attributed to the removal of surface oxides during sintering. Holding and processing ZrB_2 (and HfB_2) in air leads to the formation of surface oxides on the powder particles [7]. These surface oxides not only hinder the densification of diboride but also introduce oxides such as B_2O_3 into the bulk material. The presence of these oxides has a detrimental effect on high-temperature mechanical properties and oxidation resistance due to their low

melting temperatures. It is hypothesized that the pulsed electric current used during SPS thermally or electrically decomposes the insulating surface oxides [13, 72], although the complete process by which SPS achieves rapid sintering is not yet fully understood. Figure 8: Schematic of PLC equipment [77]. The parameters of the SPS method can be tailored to produce materials with fine microstructures that tend to have fewer secondary phases compared to materials produced by conventional methods. SPS materials can be produced using sintering aids [34] that still exhibit better oxidation resistance than hot-pressed materials.
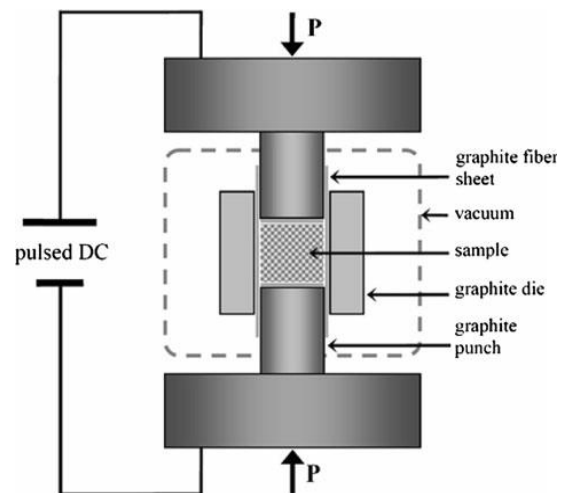

Fig. 8. Schematic of PLC equipment [77].

5.Conclusion

1.Ceramics containing SiC maintain a protective glass layer at higher temperatures compared to samples without SiC. However, SiC only improves oxidation resistance at temperatures above 1350°C, where silicon oxide is present. Below this temperature, SiC components remain in the oxide layer.

2.It can be concluded that microstructure and composition modifications can have beneficial (or detrimental) effects on oxidation resistance .

3.The oxidation resistance of ZrB_2+25 vol% SiC composites improved by adding borides of Cr, Ti, Ta, Nb, and V. These additives lead to the formation of corresponding oxides in the glass.

4.The improvement in oxidation resistance is due to the fact that borate and silicate glasses containing these mentioned oxides (group IV-VI intermediate metals) are immiscible and result in phase separation.

5.Adding $TaSi_2$ enhances the oxidation resistance of ZrB2+20 vol% SiC composite. The oxidation rate decreases at 1627°C.

6.Adding LaB_2 to high-temperature ZrB_2+20 vol% SiC ceramics significantly increases fracture

toughness from 5.7 MPa.m1/2 to 4.8 MPa.m1/2 compared to ceramics without LaB2, as it promotes crack deflection and bridging near SiC particles.

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