Presented at the NATO ARW- Boron Rich Solids
14-18 December 2009, Orlando, Florida

PROCESSING AND PROPERTIES OF ULTRA-REFRACTORY COMPOSITES BASED ON Zr- AND Hf-BORIDES: STATE OF THE ART AND PERSPECTIVES

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Abstract: High performance Ultra-High-Temperature Composites, based on zirconium and hafnium borides, are characterized by relevant and unique thermo-physical and thermo-mechanical properties, suitable for applications in aerospace hot structures and in many industrial sectors where extreme conditions are present.
In spite of the difficult sinterability of Zr- and Hf- diborides, recent results highlight that these ceramics can be produced with full density, fine microstructure and controlled mechanical and thermal properties, through different procedures: pressureless sintering and hot pressing with proper sintering aids, reactive synthesis/sintering procedures starting from precursors, field assisted technologies like spark plasma sintering (SPS).
A proper selection of reinforcing phase (SiC, B_4C, $TaSi_2$, $MoSi_2$, etc) leads to improvements in mechanical properties and oxidation resistance of ZrB_2 and HfB_2 ceramic composites.
Strength as high as ~ 800MPa at room temperature and at 1500 °C in air can be obtained for HfB_2-based composites, after an accurate tailoring of compositions and processing parameters. SPS proved to be a very rapid fabrication process leading to refined microstructure and improved properties of ultra-refractory diborides -based composites.

Keywords: zirconium diboride, hafnium diboride, composites, sintering, mechanical properties, microstructure

1. Introduction

ZrB_2 and HfB_2-based ceramics belong to the class of ceramics defined as Ultra-High Temperature Ceramics (UHTCs). Besides the top refractoriness, these compounds present a unique combination of properties such as high electrical and thermal conductivity, chemical inertness against molten metals or non basic slags [1, 2]. The principal fields of applications are those associated with atmospheric re-entry, hypersonic flights, propulsion

[1-7], that need materials and structural components capable of operating at temperatures in excess of 1600°C.
The open literature in the field of processing and materials science of UHTCs is nearly scarce up to the eighties of the past century [8-13]. In recent years different routes were attempted to improve fabrication procedures and performances of the Zr- and Hf-based borides and carbides:
i) the incorporation of sintering aids [14-28] associated to a conventional densification technique like hot pressing (HP) or gas-pressure sintering;
ii) reactive processing that relies on chemical conversion of most or all of the precursors to new phases through displacement reactions [28-34], solution-based methods [35-37] or other solid-state reactions [38-41];
iii) innovative densification methods like spark plasma sintering (SPS), successfully used to densify several non oxide ceramics [42-49], and UHTC compounds [50-58];
iv) a careful ñmaterials designò to increase strength, toughness, oxidation resistance, thermal shock resistance through the addition of reinforcing phases [2-4, 17, 19, 59-62], including short fibers or whiskers [63-70].
The durability in oxidizing environment and the thermal and mechanical properties under severe conditions have been widely studied [71-94]. Moreover, the behaviour in a simulated re-entry environment is a key issue for all the space applications [1-3, 95-97].
In this work, recent results achieved in the development of monolithic and composites based on HfB_2 and ZrB_2 are presented and discussed, with reference to the effects of sintering technologies, of the type of sintering aids, of the role of secondary phases on the main materials properties.
Table I lists the starting compositions, processing procedures microstructural and mechanical features of the monolithic and composite ceramics object of this paper.

2. Role of the sintering aids on microstructure

Due to the high melting point and high vapour pressure of the constituents, undoped Zr- and Hf- borides and carbides can be densified to final relative densities in the range 70-90%, at temperatures above 2000°C. The very high sintering temperatures lead to excessive grain growth [10, 11]. The addition of metal sintering aids (Ni, Fe) results in grain boundary phases that deteriorate the high temperature mechanical and physical properties [14, 15]. Ceramic additives like Si_3N_4 [16], AlN [18], HfN [19], disilicides of Mo and Ta [22, 43, 57, 60] improve densification, microstructures and properties of ZrB_2 and HfB_2.

Starting composition (wt%)	Sint. tech.	rd %	E GPa	HV1.0 GPa	σ RT (MPa)	σ HT (MPa)
ZrB_2 [17]	HP	~85	346	8.7	351±31	312±14 (1200°C) 220±7 (1400°C)
ZrB_2+2$MoSi_2$ [14]	HP	100	500	18.1	750±160	240± 25 (1500°C)
ZrB_2+4Ni [15]	HP	~98	496	14.4	371±24	15±1 (1200°C)
ZrB_2+2.5AlN [18]	HP	~92	407	9.5	600±35	300±25 (1400°C) 200±20 (1500°C)
ZrB_2+2.5Si_3N_4 [17]	HP	~99	419	13.4	595±90	240±20 (1200°C)
HfB_2+2.5Si_3N_4	HP	~99			478±45	227±11 (1400°C)
ZrB_2+12SiC+2Si_3N_4 [17]	HP	~98	421	14.2	725±98	280±20 (1200°C)
ZrB_2+ 5$MoSi_2$	PLS	~96	516	15.2	569±54	533±87 (1200°C) 487±46 (1500°C)
ZrB_2+ 20$MoSi_2$ [22]	PLS	100	489	13.9	530±70	655± 45 (1200°C) 500 ±49 (1500°C)
ZrB_2-15$MoSi_2$ [57]	SPS	100	479	16.2	643±97	357±48 (1500°C)
ZrB_2-15$MoSi_2$	HP	~99	452	14.9	704±98	333±31 (1500°C)
ZrB_2-15$TaSi_2$	HP	~99	444	17.8	840±33	598±25 (1200°C) 374±5 (1500°C)
ZrB_2+33ZrC+6SiC[51]	SPS	~99	474	19.8	780±80	594±33 (1200°C) 418±57 (1500°C)
HfB_2+6.5SiC+2Si_3N_4 [85]	HP	~99	421	20.4	560±98	150±25 (1500°C)
HfB_2+6.5SiC+4HfN 19]	HP	~98	506	22.3	650±50	465±45 (1500°C)
HfB_2+32ZrB_2+8SiC+ 5.5HfN [19]	HP	~99	497	22,0	765±20	250±45 (1500°C)
HfB_2+11SiC [53]	SPS	~99	512	26.0	590±50	600±15 (1500°C)
HfB_2+1$MoSi_2$ [55]	SPS	~94	562	21.1	663±65	570 (1500°C)
HfB_2+3$MoSi_2$ [55]	SPS	~96	584	22.0	750±34	650 (1500°C)
HfB_2+9$MoSi_2$ [55]	SPS	~99	583	21.9	652±40	820 (1500°C)
HfB_2+7.5SiC+8HfC[21]	RHP	~99	520	24.0	770±35	315±15 (1500°C)
HfB_2+12.2$MoSi_2$ [43]	PLS	~98	482	18.0	388±65	548±30 (1200°C) 577±50 (1500°C)
HfB_2+15$MoSi_2$ [60]	HP	~99	530	20.6	742±151	664±28 (1200°C) 548±20(1500°C)
HfB_2+15$TaSi_2$[60]	HP	~99	528	21.9	698±58	704±24 (1200°C) 597±46 (1500°C)

Table I. Comparison of relative densities (rd) and mechanical properties of some UHTCs. HP: hot pressing; PLS: pressureless sintering; SPS: spark plasma sintering; RHP: reactive hot pressing; HV1.0: Vickers microhardness, 9.81 N; E: Youngôs modulus (resonance frequency method); σ: 4-pt flexural strength (specimens 25 x 2.5 x 2 mm^3) at room temperature (RT) and high temperature (HT).

As examples of these statements, the microstructures of two materials produced by SPS are compared in Fig. 1. Monolithic HfB_2 sintered at 2200° C shows an extensive porosity (Fig. 1a). Instead, HfB_2 with 1 vol% $MoSi_2$ as sintering aid and sintered at 1750°C highlights high final density and grain size refinement (Fig. 1b). In the composite, the majority of the HfB_2/HfB_2 boundaries appears flat and depleted of secondary phases that are mainly concentrated at the triple points. The darker areas on the polished surfaces in Fig. 1b correspond to SiC. In addition to HfB_2 and SiC, Hf-O secondary phases were detected.

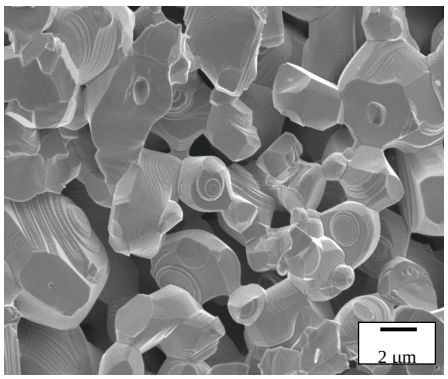

Fig. 1a. Fracture surface of undoped HfB_2 (SPS, 2200°C).

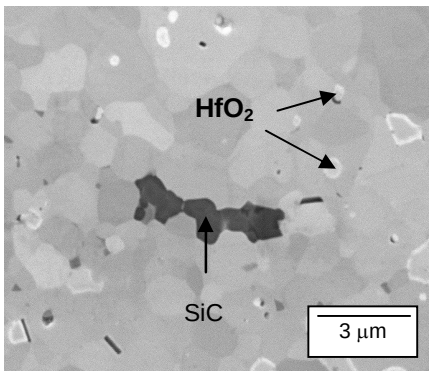

Fig. 1b. Polished surface of HfB_2 with the addition of 1vol% $MoSi_2$ (SPS, 1750°C).

Silicon nitride in an amount of 2.5 wt% allows to achieve full dense ZrB_2 ceramics through hot pressing at 1700°C [17]. The use of AlN as sintering aid greatly limits the formation of secondary grain boundary phases, and good strength values are measured up to 1500°C [18], Table I.
The addition of disilicides ($MoSi_2$, $HfSi_2$, $TaSi_2$) acts either as sintering aid, or as strengthening phases.
The addition of molybdenum disilicide in amounts of 5-10 vol% favors the fabrication of dense materials based on ZrB_2 and HfB_2 even through pressureless sintering [43, 53, 57, 60, 70, 77].

3. Effects of Secondary Phases on Densification, Microstructure, Mechanical Properties and Oxidation Resistance

As the reliability of UHTCs is limited by poor toughness, stress corrosion cracking and high temperature oxidation, many applications of these materials require the addition of second reinforcing phases. Successful efforts

were made to improve mechanical properties and oxidation resistance of Zr- or Hf- diborides based materials, through appropriate additives [1, 2, 4, 17, 41-43, 46-48]. In particular, it was found that Si-supplier compounds, such as SiC and metal silicides, are suitable to increase the oxidation resistance. Among the disilicides, $MoSi_2$ proved to be very effective. SiC is the most diffused additive for the improvement of oxidation resistance and grain refinement. Furthermore, both SiC and $MoSi_2$ offer the advantage to act as sintering aids [3, 4, 17, 39-44, 45, 49, 54-57]. Figs. 2 a,b show the microstructure of ZrB_2-12wt% SiC [17] and HfB_2-6.5wt% SiC [85] produced by hot pressing at 1870 and 1850°C, respectively, with an applied pressure of 30 MPa. The textures of the two SiC-containing composites appear rather similar, with the grain size of the diboride matrix notably refined in comparison to the monolithic ceramics. The SiC particles are mainly distributed in clusters and are often in contact with secondary phases formed during sintering (BN, MeO_2 and B-N-O-Si-Me glassy systems, where Me= Zr, Hf). Data in Table I point out that the proper combination of additives and matrix leads to enhanced high temperature strength.

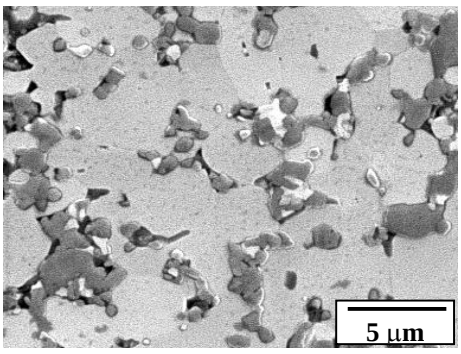

Fig. 2 a. Polished surface of a hot pressed ZrB_2-12wt%SiC composite.

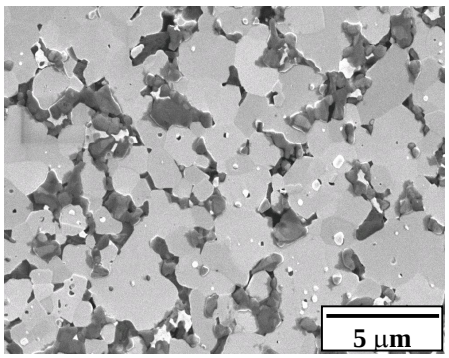

Fig. 2 b. Polished surface of a hot pressed HfB_2+6.5wt%SiC composite.

The use of HfN as sintering aid for HfB_2-SiC composites [19] is suitable to originate highly refractory grain boundary phases, resulting in flexure strength of about 465 MPa at 1500°C. On the contrary the addition of Si_3N_4 as sintering aid leads to strength of about 150 MPa at 1500°C. At the same time, composites based on HfB_2 and HfB_2+ZrB_2, with the same amount of SiC (second phase) and HfN (sintering aid), evidence a great difference in strength measured in air at 1500°C: 465 MPa for the former and 250 MPa for the latter.

UHTCs in the systems ZrB_2- and HfB_2- (5-20 vol%) $MoSi_2$ have been densified to near full density by pressureless sintering and hot pressing [22,

43, 53, 60]. Besides, relevant high temperature mechanical strength was measured on composites based on HfB_2 and densified by spark plasma sintering, in the presence of $MoSi_2$ as secondary phase [55, 57]. The results confirm that $MoSi_2$ acts as second reinforcing phase and as effective sintering aid for the densification of borides. Composites with relative densities higher than 98% can be produced by pressureless sintering at 1850-1950°C, and by hot pressing at 1800-1900°C in the case of ZrB_2- and HfB_2-matrix composites, respectively. The role of $MoSi_2$ can be summarized as follows: it limits the excessive grain growth of borides; it accommodates in the voids left by matrix grains thanks to its plasticity; it promotes oxygen removal from boride particles surface. During sintering, $MoSi_2$ reacts with surface oxides (B_2O_3) of ZrB_2 or HfB_2, forming SiO_2 and Mo-B/Mo-Si-B liquid species that help grain rearrangement and mass transfer. The final microstructure shows the formation of solid solutions around the matrix grains and discrete intergranular pockets [98]. After sintering no residual silica is observed in pressureless sintered composites, due to the reducing sintering atmosphere (Ar flux, graphite crucible and heating elements) and the longer sintering times [22, 43]. Pressure-assisted techniques allow the sintering temperatures to be reduced at 1750-1800°C (Table I), but on the other side, pressureless sintering is also advisable for these materials, since it favors the development of a uniform and fine microstructure without residual glassy phases (Fig. 3) and allows the production of near-net shaped components.

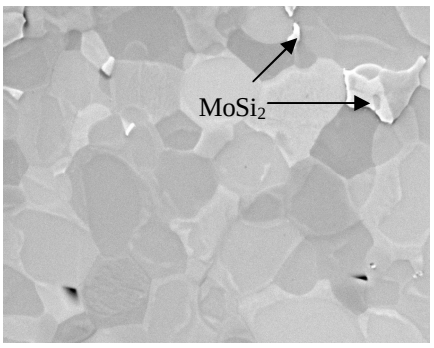

Fig. 3 a. Microstructure of pressureless sintered composites: ZrB_2+5%$MoSi_2$.

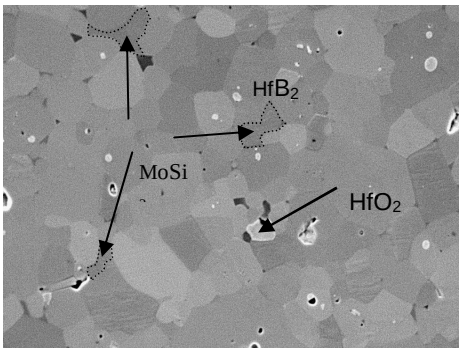

Fig. 3 b. Microstructure of pressureless sintered composites:HfB_2+5%$MoSi_2$.

For the pressureless sintered ZrB_2-20$MoSi_2$ material, the room-temperature flexural strength in air of about 500 MPa was retained up to 1500°C. This property rises to about 600 MPa in the case of HfB_2 matrix.

As this class of advanced ceramics is designed to be exposed frequently to very hot and hostile environments, the high-temperature stability, especially the resistance to oxidation, is a key property. The upper limit of the service temperature is strongly related not only to the characteristics of the matrix, but also to second and/or grain boundary phases, which depend on the sintering aids used. The addition of SiC and/or of $MoSi_2$ to diboride-matrix composites promotes the formation of an external borosilicate glassy layer, which gives much more oxidation protection than B_2O_3. According to Opeka et.al [2], good oxidation performances at hypersonic use temperatures up to 2000°C and above are exhibited by materials that form a multicomponent oxide scale, composed of a refractory oxide skeleton and an amorphous oxide component. This multicomponent oxide can be achieved by compositional modifications with transition metal additives (i.e. Cr- and Ta-compounds) that promote immiscibility in the glassy component of the outermost surface scale.

4. Densification by Spark Plasma Sintering of UHTCôs

In the spark plasma sintering (SPS) process, a pulsed electric direct current is applied in combination with an external mechanical pressure in a graphite die. For electrically conductive materials, heating up is mainly due to the Joule effect. The effectiveness of such a technology in the densification of refractory borides is highlighted by the data on total processing time, which is at least 10 times lower than for conventional hot pressing, and is enough to obtain a final relative density higher than 99%. The micrograph of the composite ZrB_2+9%$MoSi_2$ (Fig. 4 a), treated by SPS at 1700°C, displays fine and uniform grain size (less than 2 µm) and traces of SiC and ZrO_2. The picture in Fig. 4 b shows that the microstructure of a HfB_2-SiC composite heated for 2 min at 2100°C is very uniform, and the mean grain size of HfB_2 grains is about 2 µm. As pointed out from the values shown in Table I, this composite did not undergo strength degradation at 1500°C in air [53]. A plausible explanation is the absence of thermally unstable grain boundary phases that often form from the sintering aids, or from uncontrolled reactions.

A ternary ZrB_2-30ZrC-10SiC composite was fully densified by spark plasma sintering at a temperature of 2100°C and 2 min dwell time [52, 53]. For the densification through hot pressing, the same composition needs the addition of a sintering aid. Introducing 2 wt% Si_3N_4, full density is achieved at T=1870°C. The entire processing time applied to obtain full density through SPS was about 23 min (cooling excluded), significantly shorter than that applied for hot-pressing, i.e. 140 min.

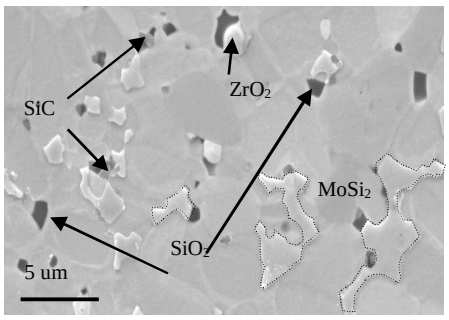

Fig. 4a. Polished surface of the ZrB_2-9 vol% $MoSi_2$ densified by SPS.

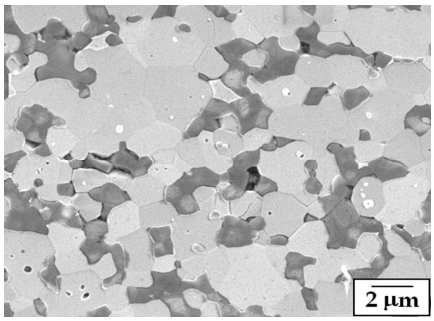

Fig.4b. Polished surface of the HfB_2+12wt% SiC densified by SPS.

5. The Production of UHTCôs through Reactive Processing

The term ñreactive processingò includes a variety of displacement reactions to synthesize materials, as well as several methods such as soft solutions or sol-gel processing [29-40]. Regarding solid-state synthesis, reactive heat treatments like hot pressing, self-propagating high-temperature synthesis, or mechano-chemical synthesis perform well to get rather dense final products, once the starting compositions and processing parameters are optimised. To make clear the potential of these techniques, the current example concerns a reactive hot pressed HfB_2-SiC composite fabricated from a stoichimetric Hf/Si/B_4C powder mixture [21], according to the following reaction:

$$2Hf + Si + B_4C = 2HfB_2 + SiC \qquad (1)$$

The process consists of two stages. The former is a heat treatment up to 1450°C and 60 min holding time under Ar atmosphere, to induce and complete reaction 1 among the solid precursors. The latter implies the hot pressing at 1900°C for 10 min hold time. The final composition of the fully dense composite is HfB_2+22 vol% SiC+ 6 vol%HfC as secondary by-product of the base reaction. The reactive process develops fine microstructures (Fig. 5) with HfB_2 grains in the range 0.5-4 µm and SiC particles (darker particles of about 2 µm in Fig. 5) located at intergranular sites. The mechanical properties are of great interest (Table I), particularly the room temperature flexure strength is higher than the values measured on similar composites produced with other techniques. The strength decrease at 1500°C in air is due to the adverse effect of the oxidation of HfC formed.

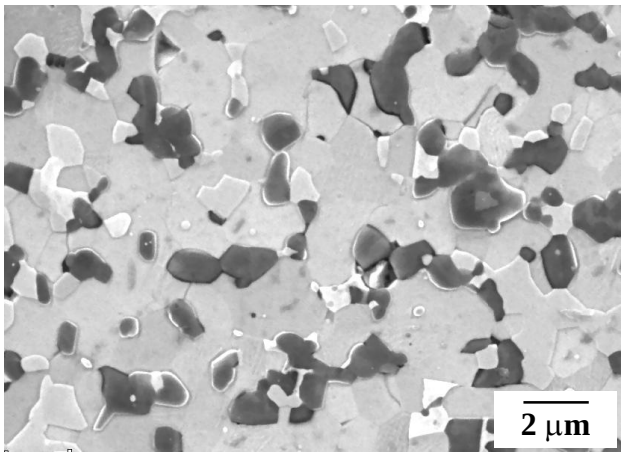

Fig. 5. Microstructure of a HfB_2-SiC-HfC composite sintered by reactive hot-pressing

6. Conclusions

Dense monolithic and composite ceramics based on ultra-refractory compounds like HfB_2 and ZrB_2 can be obtained with addition of SiC, $MoSi_2$, or ZrC as secondary phases and fabricated through different procedures:

- pressureless sintering, provided that $MoSi_2$ is added, at least in amount of 5 vol%;
- hot pressing using sintering aids, specifically Si_3N_4, AlN, HfN, $MoSi_2$, SiC, $TaSi_2$;
- spark plasma sintering, with and without additives;
- reactive hot-pressing from solid precursors.

The composition of the starting powder mixtures and the fabrication route influence microstructure, physical and mechanical properties. A proper selection of sintering aids and the incorporation of second reinforcing phases allow to obtain near fully dense compacts and high strength values. The best values of room temperature strength approach 900 MPa (for hot pressed ZrB_2+$TaSi_2$), the strength at 1500°C in air is about 500 MPa for ZrB_2-$MoSi_2$ composites, while it reaches about 800 MPa for SPS HfB_2-$MoSi_2$-composites.

Improvements in the oxidation resistance can be made with addition of Si-containing species or cations which induce immiscibility in the external glassy layer.

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