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Synthesis, densification and characterization of TaB_2–SiC composites

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Abstract

The TaB_2–27.9 vol% SiC composite was synthesized by self-propagating high-temperature synthesis starting from mechanically activated Ta, B_4C and Si reactants. The obtained powders were spark plasma sintered at 1800 °C and 20 MPa for 30 min total time, thus obtaining a 96% dense product. The latter one was characterized in terms of microstructure, hardness, fracture toughness, and oxidation resistance. The obtained results, particularly the fracture toughness, are promising when compared to those related to analogous materials reported in the literature and fabricated with similar and different processing routes.

Keywords: Tantalum diboride; Ball milling; Self-propagating high-temperature synthesis; Spark plasma sintering

1. Introduction

It is well known that the combination of their high melting temperature, hardness, electrical and thermal conductivities, and good chemical resistance makes transition metal diborides such as ZrB_2, HfB_2, TiB_2, TaB_2, etc., potential candidates for high temperature structural applications [1–3]. Among them, all belonging to the general class of Ultra-High Temperature Ceramics (UHTCs), only few investigations have been dedicated so far to tantalum diboride based materials, as compared to the other UHTC systems. The effect of TaB_2 addition on the characteristics, mainly the oxidation resistance, of some refractory composites was studied by different authors [4–7]. Talmy et al. [4] found that oxidation resistance of ZrB_2–SiC materials was significantly improved when partially replacing ZrB_2 with TaB_2. More specifically, when comparing the effect of the addition of 10 mol. % of various metal diborides, i.e. TiB_2, NbB_2, VB_2, CrB_2, and TaB_2, the latter one was found to guarantee the higher protection to the modified ZrB_2–SiC when exposed to air at 1300 °C for 5 h. More recently, the study of the influence of the TaB_2 content on the oxidation resistance of ZrB_2-based ceramics received renewed attention [5,7]. The improvement in the oxidation resistance of the ceramic composite as a consequence of the addition of TaB_2 beyond 3.32 mol.% was confirmed at 1200 and 1400 °C, while this property became worsen at 1500 °C. Moreover, the beneficial influence of tantalum diboride on the oxidation resistance, densification behaviour and mechanical properties of TaC–10 wt.% TaB_2, as compared to monolithic TaC, was also demonstrated [6]. In this study, tantalum diboride was synthesized by reducing Ta_2O_5 with B_4C and graphite in a tube furnace under Ar atmosphere, as described in a previous investigation [8], where the resulting powders were subsequently consolidated by HP at 2100 °C to obtain a 98% dense product.

The preparation of TaB_2–TaC composites by combustion synthesis starting from Ta, B_4C and graphite was recently studied [9]. Due to the non-sufficiently high enthalpy of the synthesis reaction, the reactants were firstly preheated at 200 °C to make the process self-sustaining after ignition.

In the present work, the fabrication of dense TaB_2–27.9 vol% SiC composite is attempted for the first time following a processing route successfully used for the obtainment of bulk ZrB_2–25 vol% SiC [10], ZrB_2–40 vol%

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ZrC–12 vol% SiC [11], HfB_2–26.5 vol% SiC, and HfB_2–40.6 vol% HfC–11.2 vol% SiC [12]. This method basically consists of firstly obtaining *in situ* the UHTC composite by self-propagating high-temperature synthesis (SHS) and, subsequently, consolidating it by spark plasma sintering (SPS), where the powders and the die containing them are directly crossed by a pulsed current [13]. It is well established that heating processes are strongly accelerated during SPS in contrast with the relatively long processing times (typically on the order of hours) encountered in conventional HP.

To promote the SHS character in the synthesis process, the mechanical activation by ball milling of the starting reactants is also considered in this investigation.

2. Experimental materials and methods

The raw materials utilized in the present study were Ta (Alfa-Aesar, −325 mesh, 99.9% purity), B_4C (Alfa-Aesar, 1–7 μm particle size, >99.4% purity) and Si (Aldrich Chemical, −325 mesh, >99% purity) powders. The starting mixture to be reacted by SHS was prepared by mixing reactants according to the following stoichiometry:

$$2Ta + B_4C + Si \rightarrow 2TaB_2 + SiC \qquad (1)$$

where the TaB_2–27.9 vol% SiC composite, which will be indicated as TS in what follows, is expected to be formed.

Mechanochemical activation (MA) of reactants was carried out by co-milling them in a SPEX 8000 (SPEX CertiPrep, USA) shaker mill apparatus with two steel balls (13 mm diameter, 8 g weight) for 20 min milling time interval and ball to powders or charge ratio (CR) equal to 1.

About 10 g of the MA powders were uniaxially pressed to form cylindrical pellets with a diameter of 10 mm, height of 30 mm and a green density of ~50% of the theoretical value. The synthesis process was conducted inside a reaction chamber under Ar atmosphere. The reaction front was generated at one pellet end by using a tungsten coil maintained electrically heated for few seconds until the synthesis reaction was initiated. The temperature during SHS evolution as well as the average velocity of the combustion wave was determined using thermocouples (W-Re, 127 μm diameter, Omega Engineering Inc.) embedded in the pellet. About 4 g of the obtained SHS product to be densified by SPS was first ground for 20 min by the mill apparatus described above using a stainless steel vial with two steel balls (13 mm diameter, 8 g weight). Particle size distribution of the resulting powders was determined by means of a laser light scattering analyser (CILAS 1180, France).

The densification step of MA-SHS powders was carried out using an SPS 515 equipment (Sumitomo Coal Mining Co., Ltd., Japan). The powders were first cold compacted into a cylindrical graphite die (outside diameter, 35 mm; inside diameter, 15 mm; height, 40 mm) lined with graphite foils (0.13 mm thick, Alfa Aesar, Karlsruhe, Germany) to protect the die and facilitate sample release after synthesis. The die containing the sample was then placed inside the SPS reaction chamber that was evacuated down to 10 Pa.

The effect of the total sintering time, t_T, on sample densification was investigated by performing all SPS experiments at constant values of the dwell temperature, T_D = 1800 °C, the mechanical pressure, P = 20 MPa, and the heating time, t_H = 10 min, i.e. the time required to reach the T_D value when starting from ambient temperature. For the sake of reproducibility, each experiment was repeated at least twice. Further details on the experimental procedure and set-up used in this work for SHS and SPS can be found in previous works [10–11,14].

The relative density of the SPS products was measured using the Archimedes method. The theoretical density of the corresponding composite, i.e. 9.98 g/cm^3, was calculated through rule of mixture [15], by considering the density values of TaB_2 and SiC as 12.6 and 3.2 g/cm^3, respectively. Phase identification was performed by a Philips PW 1830 X-rays diffractometer using a Ni filtered Cu K_α radiation (λ = 1.5405 Å). The microstructure and local phase composition of end products were examined by scanning electron microscopy (SEM) (mod. S4000, Hitachi, Japan) and energy dispersive X-rays spectroscopy (EDS) (Kevex Sigma 32 Probe, Noran Instruments, USA), respectively.

Vickers hardness and fracture toughness (K_{IC}) evaluation of the SPSed products was performed using a Zwick 3212 Hardness tester machine (Zwick & Co. GmbH, Germany) for both 3 and 10 kg applied loads with a dwell time of 18 s.

Oxidation resistance was determined by thermogravimetric analysis (TGA) using a NETZSCH (Germany) STA 409PC Simultaneous DTA-TGA Instrument under 0.1 L/min air flow. Non-isothermal tests, consisting of heating slowly (2 °C/min) the specimen from room temperature to 1450 °C, as well as isothermal runs at 1450 °C for about 4 h, have been performed.

3. Results and discussion

All the attempts carried out to make the synthesis reaction (1) self-sustaining failed when starting from simply blended reactants, in contrast with the classical SHS behaviour displayed by the analogous binary $2ZrB_2$–SiC (ZS) and $2HfB_2$–SiC (HS) systems, recently fabricated following the same approach [10,12]. This outcome is consistent with the corresponding enthalpies of reaction, i.e. $-\Delta H_r^o = 348.364\,\mathrm{kJ(TS)}$, 647.266 (ZS) and 674.042 kJ (HS) [16], significantly lower for the Ta-based composite. Thus, in the latter case, the MA of starting mixture under the ball milling (BM) conditions reported in Section 2 was required to promote the self-propagating behaviour in reaction (1). Correspondingly, the measured combustion temperature and front velocity were equal to 1850 ± 50 °C and 4.5 ± 0.5 mm/s, respectively.

The need of reactants activation manifested in this work is in agreement with the behaviour recently observed during the preparation of TaB_2–TaC by SHS starting from Ta, B_4C and graphite, where the support of the combustion synthesis process was achieved by preheating the reacting pellet at 200 °C [9].

The diffraction pattern of the SHS product obtained in our study is reported in Fig. 1 along with those of the corresponding original reactants before and after the mechanical activation.

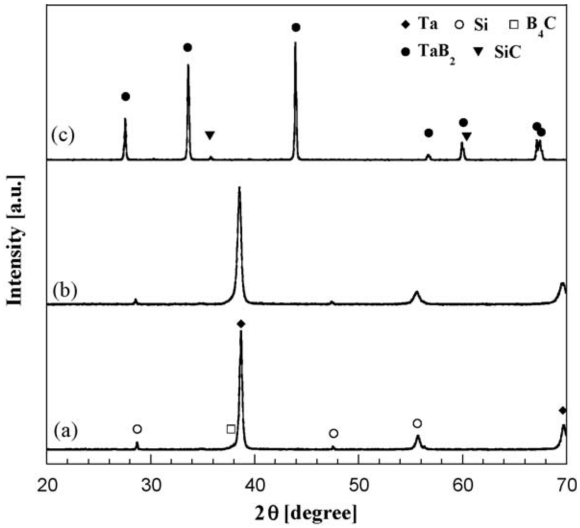

Fig. 1. Comparison of XRD patterns of (a) original reactants, (b) mechanochemically activated reactants and (c) products obtained by MA-SHS according to reaction (1).

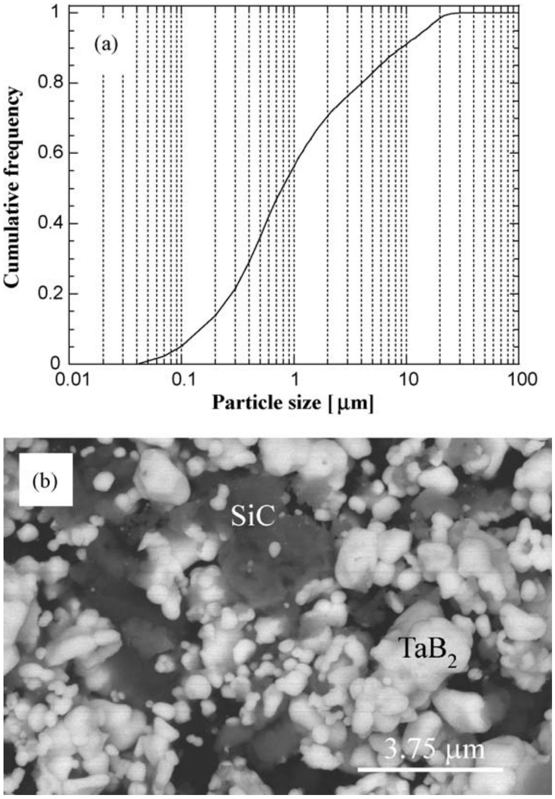

Fig. 2. Size distribution (a) and SEM back-scattered micrograph (b) of TaB_2–SiC SHS powders after 20 min ball milling.

No remarkable effects induced by the BM treatment are evidenced from the XRD results, other than a slight peaks broadening as an indication of crystal size refinement and internal strain increase in the processing powders. The enhancement of chemical reactivity of starting powders as a consequence of their mechanical treatment can be mainly ascribed to the interfaces formation among reactants, which allows to overcome diffusion limitations.

All major peaks corresponding to TaB_2, as well as the {1 1 1} and {2 2 0} reflections of SiC were detected by XRD. In addition, no other secondary phases were found in the final product. In conclusion, it is possible to state that the MA treatment allows for SHS to proceed to completion with the formation of the desired composite constituents according to reaction (1).

Once converted in powder form, SHS products have been characterized in terms of particle size distribution and microstructure. The obtained results are shown in Fig. 2(a and b). Rather fine particle powders are obtained, being about 50% less than 1 μm in size. In particular, all powders have particle size less than 30 μm and $d_{50} = 1.19 \pm 0.09$ μm.

The densification of the TS powders was investigated by examining the effect of the total sintering time (t_T) during SPS in the range 0–30 min, when setting $T_D = 1800$ °C, $P = 20$ MPa, and $t_h = 10$ min. The conditions above were chosen on the basis of the results found in previous studies, where the consolidation by SPS of SHSed $2ZrB_2$–SiC [10] and $2HfB_2$–SiC [12] powders was performed.

Typical sample shrinkage and temperature time profiles recorded during the SPS process are reported in Fig. 3(a and b) for the case of $t_T = 30$ min along with the corresponding electrical behaviour showing the current and voltage mean values. The most significant sample displacement change is observed to occur after about 6 min from the beginning of the current application, when the temperature is above 1000 °C. This increase continued until the T_D value was achieved, while no relevant changes were evidenced during the isothermal stage. As far as the electrical behaviour of the system is concerned (cf. Fig. 3b), it may be seen that the current and voltage are augmented during the non-isothermal heating (0–10 min), to satisfy the selected thermal program. It should be noted that the current almost reached the maximum value (1500 A) allowable with the SPS apparatus used in the present work. Afterwards, first rapidly, then smoothly, both parameters decrease down to the corresponding stationary mean values, i.e. about 1300 A and 5.5 V, respectively.

The situation described above also includes the experiments carried out when the SPS process duration was shorter than 30 min, while keeping the same all the other experimental parameters. Thus, the considerations made here hold also true in these cases. Regarding the corresponding SPSed products density, as shown in Fig. 4, it increases from about 91% of the theoretical value at the end of the non-isothermal heating stage up to about 96% when maintaining the sample at 1800 °C for 20 more minutes.

Two back-scattered SEM micrographs at different magnifications of the 96% dense product are reported in Fig. 5(a and b). A rather homogeneous and fine microstructure consisting of TaB_2 (brighter) and SiC (darker) phases well distributed all over the sample is obtained.

The result obtained by TGA in the temperature range 700–1450 °C during the non-isothermal oxidation test is compared in Fig. 6 with that of monolithic TaB_2 reported in literature [6]. While mass gain monotonically increases with temperature in the latter case, a relative maximum is displayed at about

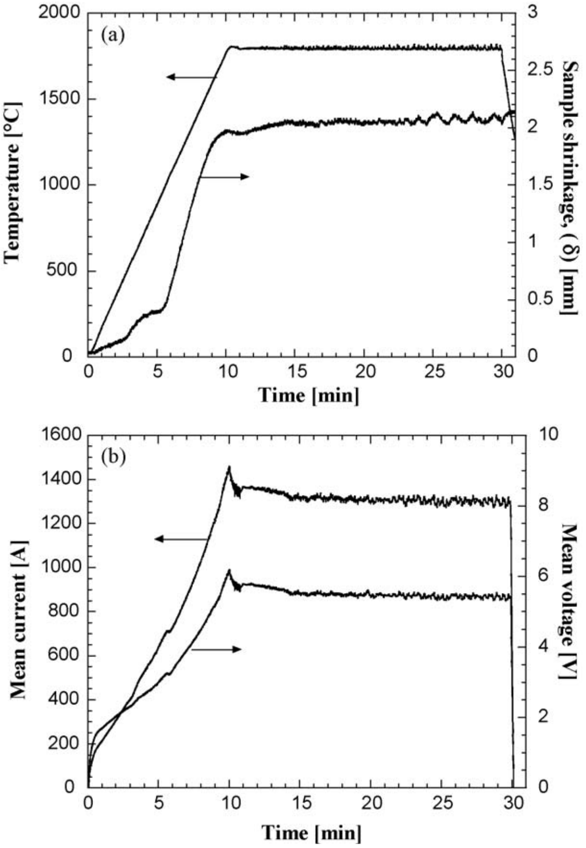

Fig. 3. SPS outputs temporal profiles recorded during the fabrication of dense $2TaB_2$–SiC: (a) temperature and sample shrinkage, (b) mean current intensity and mean voltage ($T_D = 1800$ °C, $t_H = 10$ min, $t_T = 30$ min, $P = 20$ MPa).

1200 °C by the two-phases material. Such oxidative behaviour is also typically exhibited by other MB_2–SiC (M = Zr, Hf) systems reported in the literature, including the ZS and HS products [10,12] obtained using the same processing route utilized in this work, except for the mechanical activation. This feature is consistent with the presence of SiC in the composite, being the latter one responsible for the formation of a borosilicate protective layer, as discussed in details by several studies reported in the literature on this subject [5,17–18]. In particular, it is apparent the role played by SiC in protecting the TS material from oxidation at temperatures in the range 1350–1450 °C, since the weight gain of pure TaB_2 becomes more than twice with respect to the TS system and tends to increase in an exponential manner. The fact that the composite material shows a normal weight gain slightly higher than pure TaB_2 at temperatures lower than 1350 °C may be ascribed to the different relative densities of the two samples, i.e. about 96 and 98% for the binary and single phase systems, respectively.

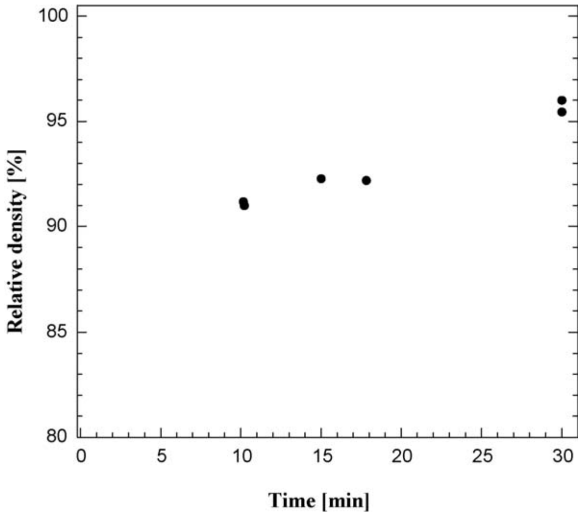

Fig. 4. Effect of SPS time on relative density of sintered $2TaB_2$–SiC powders synthesized by MA-SHS ($T_D = 1800$ °C, $t_H = 10$ min, $P = 20$ MPa).

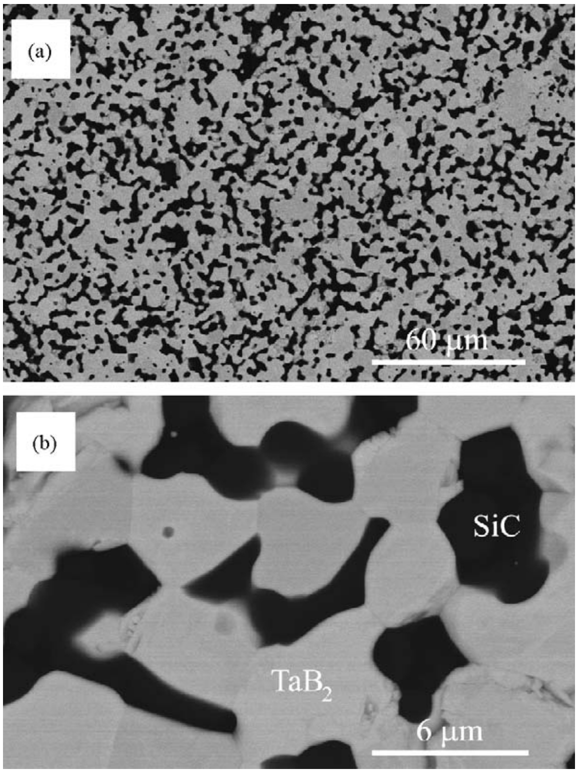

Fig. 5. SEM back-scattered micrographs of dense $2TaB_2$–SiC product: (a) 500× and (b) 5000×.

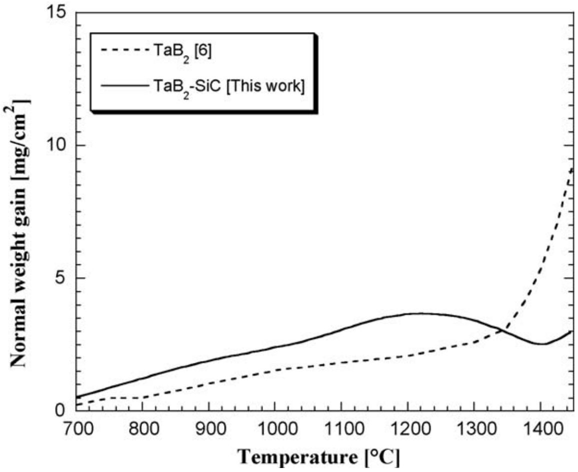

Fig. 6. Comparison among specific weight changes as a function of temperature during non-isothermal TGA oxidation in air of TaB_2 and $2TaB_2$–SiC dense products.

Table 1
Properties of dense ceramic composites.

System	Relative density [%]	Hardness [GPa] (applied load)	K_{IC} [MPa m$^{1/2}$]	Reference
ZS	99.6	16.7 ± 0.4 (1 kg)	5.0 ± 0.3	[10]
HS	>99.9	20.55 ± 0.8 (3 kg)		[12]
		19.2 ± 0.6 (10 kg)	7.0 ± 0.7	
ZZS	98.7	16.9 ± 0.2 (10 kg)	5.9 ± 0.5	[11]
HHS	98.5	17.7 ± 1.5 (3 kg)		[12]
		18.3 ± 1.1 (10 kg)	6.2 ± 0.7	
TaB_2	98	25.6± 0.7(0.5 kg)	4.5 ± 0.3	[8]
$TaC–TaB_2$	98.6	19.4 ± 0.6 (0.5 kg)	3.4 ± 0.1	[6]
TS	96	19.4 ± 0.9 (3 kg)	8.2 ± 0.6	[This work]
		18.9 ± 0.4 (10 kg)	8.4 ± 0.8	

The measured Vickers hardness and fracture toughness properties of the best TS product obtained in this work are reported in Table 1 along with the corresponding values related to the ZS, HS, ZZS and HHS materials fabricated following the same route. For the sake of comparison, the mechanical properties reported in the literature for dense TaB_2 and TaC–10 wt.% TaB_2 are also included in Table 1. As already evidenced in previous papers [10–12], properties of ultra-refractory products obtained by combining SHS and SPS techniques are generally among the best, when compared to those reported in the literature for similar materials produced by other, generally more time and energy-consuming, competitive methods. The combination of the *in situ* synthesis (SHS) of composite powders with a rapid densification technique (SPS) was considered as responsible of the observed advantages. This conclusion is still valid in this study. Furthermore, it is seen from Table 1 that the fracture toughness value (K_{IC}) of the TS ceramic is even higher than ZS and HS.

Such improvement is likely associated to the mechanical treatment provided in this work to the reactants before the SHS process that, other than increasing powder reactivity to guarantee the SHS character of the synthesis reaction, produced powder refinement as well as a better phases distribution in the composite. This aspect leads to a relatively finer and homogeneous microstructure in the final material and, consequently, to an improvement of its mechanical properties.

4. Conclusions

A near fully dense TaB_2–27.9 vol% SiC composite was fabricated by SPS starting from powders synthesized by SHS. The mechanical activation for 20 min (CR = 1) of the Ta, B_4C and Si reactants was required to make the reactive process self-sustained and obtaining *in situ* the desired ceramic constituents. In addition, when the resulting powder products were SPSed for a total processing time of 30 min by setting $T_D = 1800$ °C, $P = 20$ MPa, $t_H = 10$ min, a 96% dense material is obtained.

The characterization of the composite revealed that it possesses fracture toughness values better than the analogous UHTCs reported in the literature, included the ZrB_2- and HfB_2-products fabricated following the same route, with the exception of the mechanical treatment. Regarding the oxidation behaviour, a significant improvement at temperature higher than 1350 °C is observed as compared to the monolithic TaB_2, as a consequence of the beneficial presence of SiC in the composite material.

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References

[1] K. Upadhya, J.M. Yang, W.P. Hoffmann, Materials for ultrahigh temperature structural applications, American Ceramic Society Bulletin 58 (1997) 51–56.

[2] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium, Journal of American Ceramic Society 90 (2007) 1347–1364.

[3] R. Rapp, Materials for extreme environments, Materials Today 9 (5) (2006) 6.

[4] I.G. Talmy, J.A. Zaykoski, M.M. Opeka, S. Dallek, Oxidation of ZrB_2 ceramics modified with SiC and group IV–VI transition metal diborides, Electrochemical Society Proceedings 12 (2001) 144–158.

[5] F. Peng, R.F. Speyer, Oxidation resistance of fully dense ZrB_2 with SiC, TaB_2, and $TaSi_2$ additives, Journal of American Ceramic Society 91 (5) (2008) 1489–1494.

[6] X. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Densification, mechanical properties, and oxidation resistance of TaC–TaB_2 ceramics, Journal of the American Ceramic Society 91 (12) (2008) 4129–4132.

[7] F. Peng, Y. Berta, R.F. Speyer, Effect of SiC, TaB_2 and $TaSi_2$ additives on the isothermal oxidation resistance of fully dense zirconium diboride, Journal of Materials Research 24 (5) (2009) 1855–1867.

[8] X. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Synthesis, densification, and mechanical properties of TaB_2, Material Letters 62 (2008) 4251–4253.

[9] C.L. Yeh, Y.L. Chen, An experimental study on self-propagating high-temperature synthesis in the Ta–B_4C system, Journal of Alloys and Compounds 478 (1–2) (2009) 163–167.

[10] R. Licheri, R. Orrù, A.M. Locci, G. Cao, Efficient synthesis/sintering routes to obtain fully dense ZrB_2–SiC ultra-high-temperature ceramics (UHTCs), Industrial Engineering Chemistry Research 46 (2007) 9087–9096.

[11] R. Licheri, R. Orrù, C. Musa, G. Cao, Combination of SHS and SPS techniques for fabrication of fully dense ZrB_2–ZrC–SiC composites, Material Letters 62 (2008) 432–435.

[12] R. Licheri, R. Orrù, C. Musa, A.M. Locci, G. Cao, Consolidation via spark plasma sintering of HfB_2/SiC and HfB_2/HfC/SiC composite powders obtained by self-propagating high-temperature synthesis, Journal of Alloys and Compounds 478 (2009) 572–578.

[13] R. Orrù, R. Licheri, A.M. Locci, A. Cincotti, G. Cao, Consolidation/synthesis of materials by electric current activated/assisted sintering, Materials Science and Engineering R Reports 63 (4–6) (2009) 127–287.

[14] A. Cincotti, R. Licheri, A.M. Locci, R. Orrù, G. Cao, A review on combustion synthesis of novel materials: recent experimental and modeling results, Journal of Chemical Technology and Biotechnology 78 (2–3) (2003) 122–127.

[15] F.L. Matthews, R. Rawlings, Composite Materials: Engineering and Science, Chapman and Hall, UK, 1994.

[16] I. Barin, Thermochemical Data of Pure Substances, Wiley-VHC, New York, 1989.

[17] W.C. Tripp, H.H. Davis, H.C. Graham, Effect of a SiC addition on the oxidation of ZrB_2, American Ceramic Society Bulletin 52 (8) (1973) 612–616.

[18] F. Monteverde, A. Bellosi, The resistance to oxidation of an HfB_2–SiC composite, Journal of the European Ceramic Society 25 (7) (2005) 1025–1031.