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Qualitative Analysis of Hafnium Diboride Based Ultra High Temperature Ceramics Under Oxyacetylene Torch Testing at Temperatures above 2100°C.

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Abstract

Oxidation tests were carried out on HfB_2-SiC, HfB_2-HfC, HfB_2-WC-SiC, and HfB_2-WSi_2 ceramics using an oxyacetylene torch. The samples were oxidized between 2100 and 2300°C. From cross-sectional images, scale non-adherence was noted as a limiting factor in oxidation resistance. The sample with the best scale adherence was HfB_2-WSi_2. Factors involving scale non-adherence such as vapour pressure, coefficient of thermal expansion mismatch and phase transformations were considered. In comparing the scale adherence of the samples it was hypothesized that vapour pressure build-up is the principal contributing factor in the scale adherence differences observed among the tested samples. However, the coefficient of thermal expansion mismatch and HfO_2 phase transformation cannot be neglected as contributing factors to scale non-adherence in all samples.

Key Words

Hafnium diboride, Silicon Carbide, Tungsten Silicide, Oxidation, Ultra High Temperature Ceramics

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1. Introduction

Transition metal borides and carbides with melting temperatures exceeding 2700°C are commonly referred to as ultra-high temperature ceramics (UHTCs) and have been studied as primary candidates for extreme environment thermal protection systems such as those found at the sharp leading edges of hypersonic vehicles. [1,2] Most commonly explored are the ZrB_2-SiC and HfB_2-SiC (MeB_2-SiC) systems with and without various additives. Most oxidation resistance testing of UHTCs has involved either resistive-element furnace heating or arc jet heating. Over the past decade the cost and limited availability of arc jet testing and the temperature and heating rate limitations of furnace heating have led many laboratories to develop new testing methods in order to probe higher temperatures. The first widely reported test, direct electrical resistance, developed primarily under J. Halloran, [3,4] provided insight into the volatile nature of the oxidation products of ZrB_2-SiC at temperatures up to 2100°C. Observations of mixing between the ZrO_2 and SiO_2 led to a better understanding of the dynamic characteristics occurring at testing temperature. Using this technique, oxidation resistance and mechanical strength retention comparisons between samples with different chemistries can easily and rapidly be examined. [5,6] The main drawback of this method, the internal heating, has limited its widespread use. Laser testing of UHTC materials has been utilized by researchers to reach temperatures from benign to beyond the melting points of the UHTC materials. [7,8] Laser heating technology is versatile and more economical than arc jet testing, yet is also not widely available. As such, several laboratories have developed oxyacetylene torch testing as a rapid screening tool for UHTC materials at temperatures up to 3400°C. [9-14] The oxyacetylene torch test is naturally ablative owing to the high velocity gas flow associated with the flame. The oxidation characteristics of the oxyacetylene torch can be controlled by the acetylene to oxygen ratio, while at a given ratio temperature is controlled by the distance to the flame. The torch has

been used as a standard test method for oxyacetylene ablation testing of thermal insulation materials (ASTM E285-08).

As UHTCs have been tested using these various techniques with parameters that include higher temperatures (> 1800°C) and high velocity flow, [14-20] it has become apparent that there is a point at which the protective SiO_2-MeO_2 scale that is formed on MeB_2-SiC begins to fail. Above a critical temperature, the viscosity of glassy SiO_2 will be too low to remain integral to the scale. Under these conditions the SiO_2 will flow out of the pores of the MeO_2 and from the sample surface resulting in a less protective porous outer scale. [20] Oxide scale non-adherence at temperatures in excess of 2000°C has also been observed during oxidation testing of MeB_2-SiC materials. [9,21,22] The loss of scale adherence could be a result of many factors including stress induced by the difference in thermal expansion coefficient (CTE) of the MeB_2 and MeO_2-based layers upon heating/cooling, phase transformation of the MeO_2 and its associated volume increase upon cooling or fracture caused by the escape of gaseous by-products of oxidation such as CO, SiO and B_2O_3.

The present paper focuses on evaluating the relative performance of four different compositions among the HfB_2 containing UHTCs, at temperatures above 2100°C for long duration, using an oxyacetylene torch. A baseline sample of HfB_2-SiC was tested and compared to W-containing samples. W has been found to be a beneficial additive for both ZrB_2 and HfB_2-based UHTCs when samples are tested under furnace heating up to 2000°C, [21,23,24] and as such two chemistries including W, HfB_2-WC-SiC and HfB_2-WSi_2, were tested. A qualitative analysis of the differences in behaviour is presented.

2. Materials and Methods

Commercially available HfB_2 (Materion ,99.9%, -325 mesh), WC (Materion ,99.5%, -325 mesh), WSi_2 (Materion ,99.5%, -325 mesh), Hf (Materion ,99.8%, -325 mesh), C (Materion ,99.5%, -325

mesh), and β-SiC (Materion, 99.9%, 1μm) were used to prepare four different sample compositions: HfB_2-20vol.%SiC (HS), HfB_2-20vol.%SiC-4vol.%WC (HSW), HfB_2-4vol.%WSi_2 (HW), and HfB_2-4vol.%HfC (HH). For the HH sample, Hf and C were added in a 1:1 molar ratio to produce HfC during reactive sintering. The powder mixtures were ball milled in isopropanol for 24 h with SiC grinding media, dried at room temperature, and subsequently dry milled for 12 h. Typical weight loss of the SiC grinding media after milling was 0.2 mg (0.2 wt.% of the total batch). The powders were sieved through an 80-mesh (177 μm) screen.

Sample composition and sintering conditions are summarized in Table 1. Milled powders were loaded into a 20 mm diameter graphite die to produce a 13 mm thick cylinder. A layer of BN and graphite foil separated the powder from the die with the powder in contact with the graphite foil. The powder-filled dies were cold pressed at approximately 50 MPa. The powders were sintered using field assisted sintering (FAS: FCT Systeme GmbH, Model HPD 25-1, Rauenstein Germany) at 2100°C (HSW, HH, HW) or 1940°C (HW) for 25 min (HS), 15 min (HSW and HW), or 50 min (HH) under a 32 MPa load. The controlled heating and cooling rates were 50°C/min. The load was applied during heating to 1600°C and released on cooling to 1000°C. The graphite foil was removed from the sample by manual grinding, and the faces of the disks were polished to 45 μm for exposure to the torch.

Samples were oxidized using the oxyacetylene torch apparatus developed at Loughborough University. [13,14] Samples were held in place using a carbon-carbon foam insert in a water-cooled graphite holder. The surface of the sample was 25 mm from the exit point of the torch. During the test, the temperature of the exposed face was recorded using a 2 colour pyrometer (Marathon MR1SCSF, Raytek GmbH, Berlin, Germany) while the back face temperature was measured by a J-type thermocouple. An oxygen rich flame was chosen for testing the UHTC samples. The acetylene to oxygen ratio was 1:1.35 with flow rates of 0.8 $m^3 \cdot h^{-1}$ and 1.1 $m^3 \cdot h^{-1}$

respectively. The heat flux was measured at 25 mm using the same acetylene to oxygen flow rates and ratio with a water-cooled gardon gauge (TG1000-54, Vattel Corp., Christiansburg, VA). Oxidized samples were analysed by X-ray diffraction (XRD: D8 Bruker AXS limited, Coventry, UK), and then mounted in epoxy and cut in half. The cross section of the oxidized face was then polished to 1 μm. The microstructures were characterized using scanning electron microscopy (SEM: Quanta, FEI, Hillsborough, OR) along with energy dispersive spectroscopy (EDS: Pegasus 4000, EDAX, Mahwah, NJ) for elemental analysis. Wavelength dispersive spectroscopy (WDS: SX100, Cameca, France) was used for the chemical analysis of W and Si. Transmission electron microscopy (TEM:Phillips CM200 FEI, Hillsborough, OR) samples were prepared by focused ion beam milling (FIB: DB235, FEI, Hillsborough, OR).

3. Results

3.1 Oxidation Test Parameters

The oxyacetylene torch test is one that is gaining commonality in use, but is not completely characterized. Sample temperature is dictated by sample composition (its heat capacity and thermal conductivity), the sample distance from the flame, and the oxygen to acetylene ratio. In addition, the oxyacetylene flame environment is complicated by the presence of carbon species that depend on the flame chemistry. [25,26] The heat flux can be measured by calorimetry. When the flow rates, gas ratio and distance to the flame are set, the heat flux as measured by the calorimetry is fixed. The heat flux was measured to be 880 $W \cdot cm^{-2}$ at 25 mm from the torch exit using an acetylene to oxygen ratio of 1:1.35 with flow rates of 0.8 $m^3 \cdot h^{-1}$ and 1.1 $m^3 \cdot h^{-1}$ respectively.

The pyrometer data recorded during sample oxidation is plotted in Fig. 1. Tests were targeted for an 8 minute duration and this was achieved for all but the HS sample, which was liberated from a degraded holder after 3.6 minutes. The samples were positioned 25 mm from the torch

nozzle after it had been lit. Transient heat up time was about 90 s. The samples reached peak temperatures between 2100 and 2300°C. The average temperature value noted in Fig. 1 is the average of the last 60 s of exposure. The back face temperature reached approximately 1200°C for the HSW, HW, and HS samples, while the back face temperature of the HH sample was approximately 1100°C.

3.2 Analysis of the Oxide Scales

Optical photographs of the sample surfaces are shown in Fig. 2. The hottest part of the flame was slightly off-centre creating a cooler crescent-shaped region (evidenced by less extensive oxidation) on the sample surface. Evidence of oxide non-adherence was observed in each sample. The oxide scale was white in all samples except the HSW and HW samples, which had areas coloured light green that could be evidence of WO_3. XRD analysis (Fig. 3) of the oxidized sample surfaces showed that in all cases monoclinic HfO_2 was the primary crystalline constituent. In the HS and HSW samples, peaks of HfB_2 were observed; probably as a result of the cracks in the oxide exposing the underlying bulk material. The HSW sample contained a peak near 40°, not seen in any of the other samples. Considering the sample chemistry, the peak could be attributable to various W-containing species such as W or W_xSi_y.

SEM analyses of the sample cross sections across the centre of the hot zones clearly show the non-adherent nature of the oxide scales (Fig. 4). The images in Fig. 4 are from the centre of the sample. Samples HS (Fig. 4a), HSW (Fig. 4b), and HH (Fig. 4d) exhibit multiple oxide layers, with each subsequent oxide scale forming on surfaces below which the scale had previously disadhered. Adherence was limited to the sample perimeter, where the scale was thinner and the sample has been shown in previous experiments to be cooler by a thermal imaging camera. Fig. 4 shows an overview of the oxide scale of each sample. Magnified images of the oxide scales are shown in Fig. 5. The outer oxide layers were HfO_2 in the HS and HH samples, while

HfO_2 and a W-phase were observed in the HSW sample. Oxide scale layers between the outermost oxide layer and the bulk of the HS and HSW samples retained SiO_2 glass while SiO_2 could also be found at the interface between the non-adherent layers and the bulk sample. SiO_2 was likely removed by the flowing gases as velocities up to 70 m/s have been reported at distances 15-30 mm from an oxyacetylene cutting torch. [27] EDS of the W-phase found with HfO_2 in the HSW sample showed primarily W, but because of the small size of the phase, the high absorption coefficient of W and the surrounding oxide, a precise phase identification was not achieved. A W-phase with similar morphology has also been observed in furnace and direct electrical resistance heating of W-containing HfB_2-based samples heated to 2000°C and above. [21,22]

The oxide scale in the HW sample (Fig. 4c and Fig. 5c) was distinctly different. Although some separation between the scale and bulk sample was observed, areas of adhered scale were also found near the centre of the sample. Additionally, the regions of non-adherent oxide were a single layer that broke away from the underlying bulk. A comparison of the W-containing phases in HSW and HW are indicated in Fig. 6. In the HW sample, the W-phases were present in the denser outer oxide scale (Fig. 6(b)) and in the more porous inner scale (Fig. 6(c)), while W-phases were only found in the interior porous HfO_2 of the oxidized HSW sample. A Cu impurity in the WSi_2 (0.001 vol.%, as reported) manifests as Cu found with W at the bulk-oxide interface and in some instances with the W-phase in the oxide scale. After annealing at 200°C, thin films of 45 to 72 at% Cu in W can be formed, but at room temperature the systems show negligible mutual solubility. [28] EDS estimates place the Cu content at 7-9 at.% if a Cu-W alloy is assumed. However, the low symmetry electron diffraction patterns cannot be matched to a W-Cu solid solution. As shown by TEM (Fig. 6(d)) a W-containing grain boundary phase exists between the large W-containing phases and HfO_2 in the oxide scale. The volume of this phase precludes its identification.

4. Discussion

The common aspect of the oxidation behaviour among HS, HSW and HH is the formation of multiple layers, presumably from repeated separation of scale from the bulk. There are at least three possible reasons why the oxide scale may separate from the bulk sample during testing: (1) vapour pressure build-up at the scale-bulk interface; (2) CTE mismatch between the oxide scale and the bulk; and (3) the phase transformation between monoclinic and tetragonal HfO_2 and its associated volume change.

When a vapour species or combination of vapour species at the bulk/oxide interface exceeds 1 atm (1×10^5 Pa) pressure the oxide scale may be disrupted. Thermodynamic calculations made by Opeka et al [29] and Fahrenholtz [30,31] on the ZrB_2-SiC system at 2227°C reveal that the vapour pressure of Zr (and Hf) oxides are at least 4 orders of magnitude lower than the 1 atm limit. It has been shown that B_2O_3 does exceed the 1 atm criteria at 1950°C, [29] but its vapour pressure is sufficiently high above 1200°C to cause evaporation from the surface long before the internal pressures exceed 1 atm. The SiO partial pressures can exceed 1 atm at the interface at temperatures above 1865°C, while the vapour pressure of CO is much higher than this. The dissimilarity in the appearance of the HW oxide scale suggests a different set of mechanisms are at work. Unlike in the HS, HSW and HH samples, there are no C-containing phases in the HW sample, suggesting that CO evolution may play a role in the lack of oxide adherence during testing. This mechanism would be active during heating of the sample.

In addition, prior studies of SiC oxidation report bubble formation within the SiO_2 scale at 1700°C, attributed to CO partial pressures up to 7.5 atm. [32] Luthra [33] argues for a SiC oxidation mechanism that involves both diffusion limited and interface limited reactions where CO gas bubbles can form if the permeabilities or diffusion rates of CO are substantially lower than that of oxygen or the SiC or bulk-oxide interface is C-rich. Such C-rich deposits have been

observed at the bulk-oxide interface in oxidized MeB_2-SiC systems. [22,34] Bubbling of the SiO_2 scale has also been reported in MeB_2-SiC systems between 1500-2200°C. [2,6,10,22] But it is possible that for HfB_2-based systems heated to ~2300°C, sintering of the outer HfO_2 could hinder vapour escape and lead to spallation as a result of the build-up of vapour . In fact, sintering of the outer HfO_2 scale is suggested in Fig. 5 and has been reported in ZrB_2-based oxidation studies at temperatures in excess of 1800°C. [10,35]

The CTE difference and phase transformations may also be playing a role, particularly considering that there was non-adherence of the scale in the HW sample suggestive of such mechanisms – a singular layer removed from the un-oxidized bulk. No tetragonal phase stabilization was found in either the HSW or HW sample, as expected. [36] As for CTE modification, hafnium and zirconium tungstates are known to have a negative CTE, but are only stable in a narrow temperature regime, 1276-1105°C for HfW_2O_8. [37,38] The latter can be quenched to room temperature with fast cooling rates, but if decomposition occurs the by-products are HfO_2 and WO_3. [37] It is possible with the rapid cooling experienced by the samples some HfW_2O_8 remains. Although the phase was not observed by XRD, the concentration could be below the detection limit or sufficiently deep within the oxide to avoid detection. EDS scans of the W-containing phases from the dense outer oxide scale in the HW oxide scale show the presence of W and Cu. A grain boundary phase is found between the large W-phase and HfO_2 grains. This phase has not been previously reported or observed in oxidized W-containing HfB_2 samples. Because of the small volume of the phase a precise composition could not be determined. A WO_3-HfO_2 liquid phase can form at temperatures above 1280°C, [39] suggesting that such a phase could form during testing.

Determination of the mechanisms leading to non-adherence may allow engineering of UHTC compositions that form more resilient oxide scales. Further information regarding chemical

composition of the oxide scale and whether the oxide scale spalls during the hold at testing temperatures (most likely to be as a result of vapour pressure effects) or upon cooling (corresponding to CTE mismatch or phase transformations) could improve this understanding.

5. Conclusion

Oxyacetylene torch testing is an aggressive test for assessing the oxidation and ablative resistance of ultra-high temperature ceramics. All samples formed outer HfO_2-based oxide scales. In the HS, HSW, and HH samples, the oxide scale consisted of multiple layers that were non-adherent to the underlying bulk material. From the multiple layers and the presence of new layers forming on the non-oxidized bulk, it is possible that as each layer broke away from the surface oxygen was able to penetrate and form new oxide layers. The HW sample was distinct in that its oxide scale consisted of a single, partially adherent layer. The differences in the samples suggest that the evolution of CO during oxidation may adversely impact scale adherence. However, the CTE mismatch and HfO_2 phase transformation cannot be ruled out as important factors in establishing adherence of the oxide scales.

6. Acknowledgement

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Table 1. Sample composition and sintering parameters with sample ID

Sample ID	Composition	Sintering temp., hold time, pressure
HS	HfB_2-20vol.%SiC	2100°C, 25 min, 32 MPa
HSW	HfB_2-20vol.%SiC-4vol.%WC	2100°C, 15 min, 32 MPa
HH	HfB_2-4vol.%HfC	2100°C, 50 min, 32 MPa
HW	HfB_2-4vol.%WSi_2	1940°C, 15 min, 32 MPa

Figure 1. Plot of the measured pyrometer temperature readings during oxyacetylene torch testing of the HfB_2-based samples. Temperature was measured at the centre of the front face of the sample and is plotted from the beginning of the test until the torch was extinguished. The average temperature was calculated from the last 60 s of exposure.

Figure 2. Photographs taken after oxyacetylene torch testing of the HfB_2-based UHTCs. The samples were 20 mm diameter and 15 mm thick.

Figure 3. XRD plot of the four HfB_2-based UHTC monoliths after oxyacetylene torch testing. All peaks are HfO_2 except the peaks labelled * (HfB_2) and ~ (possibly a W-phase).

Figure 4. SEM micrographs of an overview of the oxide scale formed on (a) HS, (b) HSW, (c) HW, and (d) HH after oxyacetylene torch testing. Spallation is evident in all samples with multiple layers forming on the HS, HSW, and HH samples. The dark continuous phase is mounting epoxy while the light regions correspond to (O) the oxide scale, (B) the bulk, unoxidized sample, and (D) the SiC-depleted layer.

Figure 5. SEM micrographs of a magnified view of the oxide scale formed on (a) HS, (b) HSW, (c) HW, and (d) HH after oxyacetylene torch testing. Labelled regions are (a) A=primarily HfO_2 and B=HfO_2/SiO_2; (b) C=primarily HfO_2 and D=HfO_2/W-phase; (c) E=dense HfO_2/W-phase, F= porous HfO_2/W-phase and G=HfB_2/W-phase/Si-phase; and (d) H=HfO_2.

Figure 6. SEM micrograph of the W-containing phases (lighter) found with HfO_2 after oxyacetylene torch testing of (a) HSW and (b,c) HW. The phases in (b) are found at the porous inner oxide, while the phases in (c) are found in the dense outer oxide of the HW sample. The W-phase in (a) and (b) are similar in morphology and chemistry (see inset EDS in (b)). The W-phases found in the dense layer of the HW sample are larger and in some cases contain Cu. The C in the EDS is an artefact of the C-coating applied for SEM analysis. WDS (see inset WDS

in (c)) confirms W and Cu without Si. (d) TEM micrograph of a W-containing phase in HW from the dense outer oxide scale. Phase 1 was shown by TEM-EDS to contain W and Cu, while phase 2 is a grain boundary phase potentially composed of Hf, W, and O.

References

1. Wuchina E, Opeka M, Causey S, Buesking K, Spain J, Cull A, Routbout J, and Guitierrez-Mora F. Designing for ultrahigh-temperature applications:The mechanical and thermal properties of HfB_2,HfC_x, HfN_x and αHf J Mater Sci 2004:39:395939 – 49.

2. Opeka MM, Talmy IG, Zaykoski JA. Oxidation-based materials selection for 2000°C + hypersonic aerosurfaces: theoretical considerations and historical experience J Mater Sci 2004:39:5887 – 904.

3. Karlsdottir SN, Halloran JW. Rapid oxidation characterization of ultra-high temperature ceramics J Am Ceram Soc 2007:90:3233-8.

4. Karlsdottir SN, Halloran JW, Henderson CE. Convection patterns in liquid oxide films on ZrB2–SiC composites oxidized at a high temperature J Am Ceram Soc 2007:90:2863-7.

5. Meng S, Qi F, Chen H, Wang Z, Bai G. The repeated thermal shock behaviors of a ZrB_2-SiC composite heated by electrical resistance method Int J Refract Met Hard Mater 2011:29:44-8.

6. Gangireddy S, Halloran JW, Wing ZN. Non-contact mechanical property measurements at ultrahigh temperatures J Euro Ceram Soc 2010:30 2183-9.

7. Justin JF, Jankowiak A. Ultra high temeprature ceramics: densification, properties and thermal stability The Onera Journal 2011:3:1-11.

8. Jayaseelan DD, Jackson H, Eakins E, Brown P, Lee WE. Laser modified microstructures in ZrB_2, ZrB_2/SiC and ZrC J Euro Ceram Soc 201:30:2279-88.

9. Zhang X, Hu P, Han J, Xu L, Meng S. The addition of lanthanum hexaboride to zirconium diboride for improved oxidation resistance Scripta Mater 2007:57:1036-9.

10. Han J, Hu P, Zhang X, Meng S, Han W. Oxidation-resistant ZrB_2-SiC composites at 2200°C Compos Sci Technol 2008:68:799-806.

11. Zhao D, Zhang C, Hu H, Zhang Y. Ablation behaviour and mechanism of 3D C/ZrC composite in oxyacetylene torch environment Compos Sci Technol 2011:71:1392-6.

12. Wang XG, Liu J, Peng LM. ZrB_2–SiC Composite parts in oxyacetylenic torch tests: experimental and computational assessment of chemical, thermal and mechanical behaviour Mater Sci Eng A 2011:528:6896–906.

13. Paul A., Venugopal S, Binner JGP, Vaidhyanathan B, Heaton ACJ, Brown PM, Lee WE. UHTC–carbon fibre composites: Preparation, oxyacetylene torch testing and characterisation J. Euro Ceram Soc 2013:33:423-32.

14. Paul A., Jayaseelan DD, Venugopal S, Zapata-Solvas E, Binner J, Vaidhyanathan B, Heaton A, Brown P, Lee WE. UHTC composites for hypersonic applications Bull Am Ceram. Soc 2012:91:22-9.

15. Zhang X, Hu P, Ham J, Meng S. Ablation behavior of ZrB_2-SiC ultra high temperature ceramics under simulated atmospheric re-entry condition Comp Sci and Tech 2008:68:1718-26.

16. Scatteia L, Alfano D, Cantoni S, Monteverde F, De Stefano Fumo M, Di Maso A. Plasma torch test of an ultra-high temeprature ceramics nose cone demonstrator J. Spacecraft and Rockets 2010:47:271-9.

17. Parthasarathy TA, Rapp RA, Opeka M, Kerans RJ, A model for the oxidation of ZrB_2, HfB_2, and TiB_2 Acta Mater 2007:55:5999-6010.

18. Marschall J, Chen Y-K. Modeling surface oxidation intransient aerothermal heating environments AIAA 2004:2004-0485

19. Carney CM. Oxidation resistance of hafnium diboride—silicon carbide from 1400 to 2000 C J Mater Sci 2009:44:5673–81.

20. Hu P, Zhang X-H, Han J-C, Luo X-G, Du S-Y. Effect of various additives on the oxidation behavior of ZrB_2-based ultra-high temperature ceramics J Am Ceram Soc 2010:93:345-49.

21. Carney CM, Parthasarthy TA, Cinibulk MK. Separating test artifacts from material behavior in the oxidation studies of HfB_2–SiC at 2000°C and above Appl Ceram Technol 2013:10: 293-300.

22. Monteverde F, Savino R. ZrB_2–SiC sharp leading edges in high enthalpy supersonic flows J. Am Ceram Soc 2012:95:2282-9.

23. Zhang SC, Hilmas GE, Fahrenholtz WG. Oxidation of zirconium diboride with tungsten carbide additions J Am Ceram Soc 2011:94:1198-1205.

24. Carney CM, Parthasarthy TA, Cinibulk MK. Oxidation resistnace of hafnium diboride ceramic with additions of silicon carbide and tungsten boride or tungsten carbide J Am Ceram Soc 2011:94:2600-7.

25. KleinDouwel RJH, Spaanjaars JJL, ter Meulen JJ. Two dimensional distributions of C_2, CH, and OH in a diamond depositing oxyacetylene flame measured by laser induced fluorescence J Appl Phys 1995:78:2086-97.

26. Kaminski CF, Hughes IG, Ewart P. Degenerate four-wave mixing spectroscopy and spectral simulation of C_2 in an atmospheric pressure oxy-acetylene flame J Chem Phys 1997:106:5324.

27. Ozturk A, Cetegen BM. Experiments on ceramic formation from liquid precursor spray axially injected into an oxy-acetylene flame Acta Materialia 2005:53:5203-11.

28. Subramanian PR, Laughlin DE. Cu-W (Copper-Tungsten) In: Nagender Naidu SV, Rama Rao P, editors. Phase Diagrams of Binary Tungsten Alloys, Calcutta India: Indian Institute of Metals; 1991, p.76-9.

29. Opeka MM, Talmy IG, Zaykoski JA. Oxidation-based materials selection for 2000°C+ hypersonic aerosurfaces: theoretical considerations and historical experience J Mater Sci 2004:39:5887-904.

30. Fahrenholtz WG. Thermodynamic analysis of ZrB_2-SiC oxidation: formation of a SiC-depleted region J Am Ceram Soc 2007:90:142-8.

31. Fahrenholtz WG. The ZrB_2 volatility diagram J Am Ceram Soc 2005:88:3509-12.

32. Mieskowski DM, Mitchell TE, Heuer AH. Bubble formation in oxide scales on SiC J Am Ceram Soc 1984:67:C17-C18.

33. Luthra KL. Some new perspectives on oxidation of silicon carbide and silicon nitride J Am Ceram Soc 1991:74:1095-1103.

34. F. Monteverde, Scatteia L. Resistance to Thermal Shock and to Oxidation of Metal Diborides–SiC Ceramics for Aerospace Application J Am Ceram Soc 2007:90:1130-8.

35. Monteverde F, Savino R, Fumo MD. Dynamic oxidation of ultra-high temperature ZrB_2-SiC under high enthalpy supersonic flows Corr Sci 2011:53:922-9.

36. Chang LY, Scroger MG, Phillips B. Condensed phase relations in the systems ZrO_2-WO_2-WO_3 and HfO_2-WO_2-WO_3 J Am Ceram Soc 1967:50:211-5.

37. Sun L, Sneller A, Kwon P. ZrW_2O_8-contianing composites with near-zero coefficient of thermal expansion fabricated by various methods: comparison and optimization Compos Sci Technol 2008:68:3425-30.

38. Evans JS. Negative thermal expansion materials J Chem Soc Dalton Trans 1999:3317-26.

39. Chang LLY, Scroger MG, Phillips B. Condensed phase relations in the systems ZrO_2-WO_2-WO_3 and HfO_2-WO_2-WO_3 J Am Ceram Soc 1967:50:211-5.