Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 1985–1989

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Pressureless sintering of $Ta_{0.8}Hf_{0.2}C$ UHTC in the presence of $MoSi_2$

S.A. Ghaffari[a,*], M.A. Faghihi-Sani[a], F. Golestani-Fard[b,c], S. Ebrahimi[b]

[a]*Department of Materials Science and Engineering, Sharif University of Technology, Tehran 11365-9466, Iran*
[b]*School of Metallurgy and Materials Engineering, Iran University of Science and Technology, P.O. Box 16845-161, Tehran, Iran*
[c]*Center of Excellence for Advanced Materials, Iran University of Science and Technology, P.O. Box 16845-195, Tehran, Iran*

Received 1 August 2012; received in revised form 15 August 2012; accepted 16 August 2012
Available online 24 August 2012

Abstract

$Ta_{0.8}Hf_{0.2}C$ ceramic has the highest melting point among the known materials (4000 °C). However, this high melting point makes the ceramic difficult to be sintered at temperatures lower than 2300 °C, pressurelessly.

The purpose of this study is to consolidate $Ta_{0.8}Hf_{0.2}C$ UHTC by pressureless sintering at 2000 °C using $MoSi_2$ as sintering aid. In this regard, effect of different amounts of $MoSi_2$ on sintering behavior of $Ta_{0.8}Hf_{0.2}$ UHTC was investigated.

It was observed that condensation of the UHTC after sintering at 2000 °C was enhanced by increasing $MoSi_2$ content and the highest relative density of 95% was obtained in the presence of 24 vol.% $MoSi_2$. XRD pattern of the sintered UHTC confirmed the formation of single phase TaC–HfC solid solution. SEM micrographs revealed the presence of $MoSi_2$ as a residual phase. Oxidation test of $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ sample by oxidized flame at 3000 °C showed the formation of double protective oxide layers on the surface of UHTC.

Keywords: Carbides; Sintering; Thermal application

1. Introduction

Tantalum and hafnium carbides are refractory transition metal carbides from the fifth and fourth groups of the periodic table [1]. They possess interesting engineering properties, such as high melting point (TaC: 3983 °C; HfC: 3693 °C), high hardness (TaC: ~19 GPa; HfC: ~20.0 GPa), high elastic modulus (TaC: 537 GPa; HfC: 425 GPa) and high electrical conductivity. So they're capable to withstand temperatures above 1600 °C in an aggressive environment [1–3]. Within this solid solution region, $Ta_{0.8}Hf_{0.2}C$ has been reported to have the highest melting point among the ever known refractory substances ($T_m = 3940$ °C) [4–6]. However, monolithic TaC or HfC are difficult to be traditionally sintered due to their high covalent bonds and low self-diffusion coefficients. Therefore, hot pressing has been typically used to enhance the densification of TaC or HfC [1,7,8]. Sciti et al. [1] hot pressed TaC bodies containing 15 vol% $MoSi_2$ or $TaSi_2$ at temperatures in the range of 1750–1850 °C and achieved a high relative density of about 97%. Hackett et al. [9] prepared TaC ceramic with a relative density of 97.1% by hot pressing at 1800 °C. Also, Zhang et al. [3] fabricated a near theoretical density TaC ceramic by hot pressing.

Due to unavailability of hot press, pressureless sintering of ceramic bodies is more favorable. Kislyi et al. [10] pressurelessly sintered TaC powders containing 2.4 wt.% Fe at 2400–2700 °C, but still 11% porosity was left in the best condition. Moreover, Liu et al. [11] prepared TaC ceramics with a relative density of 97.5% by pressureless sintering at 2300 °C without sintering aids. Silvestroni et al. [12] also pressurelessly consolidated TaC and HfC ceramics up to 98.4 and 99.1% (respectively) at 2000 °C using $MoSi_2$ additive.

It was also observed that 10 vol.% $MoSi_2$ was enough to reach high density for single phase carbides at 2000 °C [13]. In this research, fabrication of $Ta_{0.8}Hf_{0.2}C$ UHTC has been studied by pressureless sintering in the presence of different amounts of $MoSi_2$ as sintering aid.

---

*Corresponding author. Tel./fax: +98 21 88220571.
E-mail address: amirghaffari@gmail.com (S.A. Ghaffari).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.08.050

2. Experimental procedures

To fabricate high density $Ta_{0.8}Hf_{0.2}C$ ceramic, commercial powders of TaC (Treibacher, < 5 μm, 99%), HfC (Treibacher, < 5 μm, 99%) and $MoSi_2$ (Treibacher, < 5 μm, 99%) were used as starting materials. To investigate effect of sintering aid content, various amounts of $MoSi_2$ (4, 8, 12, 24 and 30 vol.%, based on $Ta_{0.8}Hf_{0.2}C$) were added. To see effect of HfC content in TaC–HfC system, various volume fraction of HfC (0.05, 0,1, 0.15, 0.2) were added to TaC in the presence of fixed 12 vol.% $MoSi_2$. The powder mixtures were milled for 24 h in absolute ethanol using SiC milling media, dried in a rotary evaporator, pressed in 15 mm-diameter discs and cold isostatically pressed under a 500 MPa pressure. Then, the formed discs were pressurelessly sintered in a resistance-heated graphite furnace under a flowing argon atmosphere (~1 atm) at 2000 °C for 1 h.

Density of sintered samples was measured by Archimedes method. Identification of the crystalline phases was carried out using X-ray diffractometer (Philips, Xpert, TW1800), with CuKa radiation, a step size of 0.04 ° and detecting time of 1 s. Microstructural and elemental analysis of the samples were investigated by an scanning electron microscope (TESCAN-Vega II, equipped with EDAX). Thermal wear at oxidation state was investigated by a domestic apparatus in which oxyacetylene flame attacked $10 \times 10\ mm^2$ surface of the sample with $10{,}000\ W/m^2$ power. Temperature of the attacked surface and the flame was measured by a pyrometer. Pore size distribution of the oxidized sample was determined using Clemex image analysis software.

3. Results and discussion

3.1. Microstructure and phase evolution

As illustrated in Fig. 1, final relative density of the $Ta_{0.8}Hf_{0.2}C$ samples was increased when $MoSi_2$ content was raised. It seems that $MoSi_2$ addition above 24 vol.% does not increase the final density, noticeably. Therefore, it can be concluded that 24 vol.% is an optimum amount for $MoSi_2$ as sintering aid.

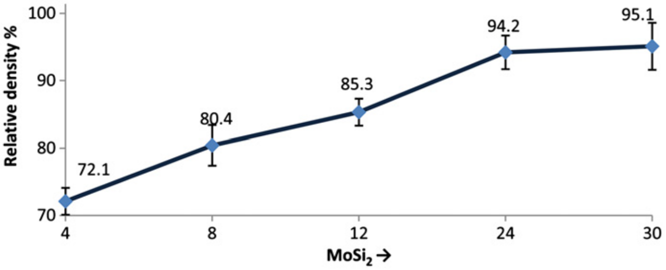

Fig. 1. Relative density of $Ta_{0.8}Hf_{0.2}C$ ceramic after sintering at 2000 °C for 1 h versus $MoSi_2$ content.

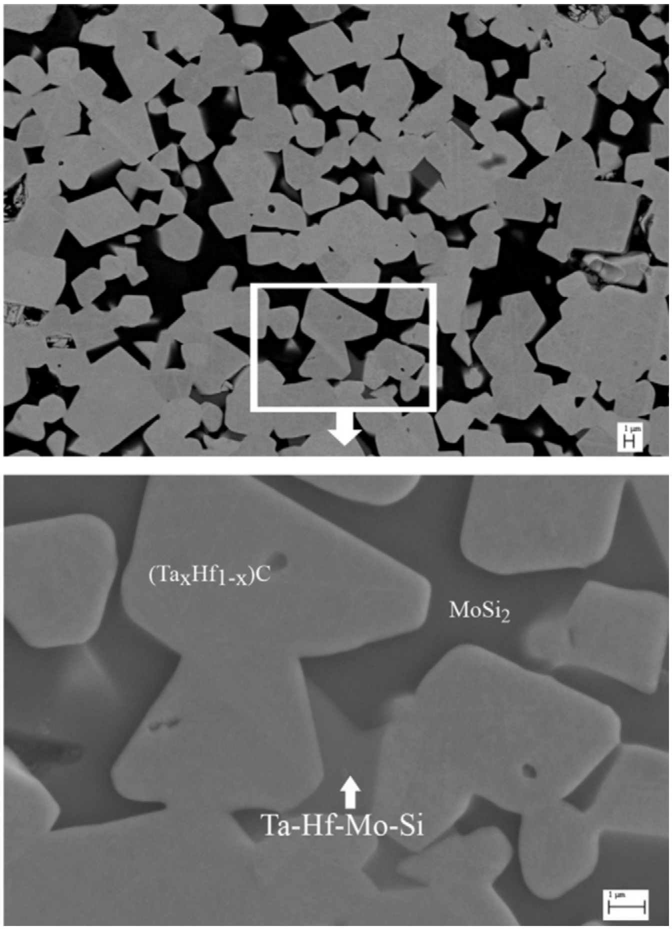

Fig. 2. SEM images of polished section of the $Ta_{0.8}Hf_{0.2}C$/24 vol. % $MoSi_2$ samples after firing at 2000 °C for 1 h in Ar atmosphere.

According to the SEM images shown in Fig. 2, the microstructure of $Ta_{0.8}Hf_{0.2}C$ sample containing 24 vol.% $MoSi_2$ consists of dark pockets ($MoSi_2$ phase) which are distributed within a bright matrix as a single phase. Morphology of the $Ta_{0.8}Hf_{0.2}C$ grains with very low dihedral angles suggests a liquid phase sintering behavior in the presence of $MoSi_2$-based melt. This microstructure reveals that where the amount of $MoSi_2$ is more abundant, the grains retain a round shape with a size of around 1 μm, while where the sintering additive is scarce, the grains grow up to 10 μm. This feature indicates that $MoSi_2$ can act as a grain growth inhibitor for TaC-based composite if its dispersion is improved. SEM image with higher resolution in Fig. 2 showed that Ta–Hf–Mo–Si phase was also formed in the boundary between $Ta_{0.8}Hf_{0.2}C$ and $MoSi_2$ phases, as it was reported before [2]. Formation of these phases suggests a mutual solubility between the two main phases. Moreover, the grains shape, with very low dihedral angles, indicates crystallization of mixed carbide from the liquid phase.

The crystalline phases in $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ sample after sintering were $Ta_xHf_{1-x}C$ and $MoSi_2$, as it revealed in Fig. 3. Position of the carbide phase peaks was between TaC and HfC standard peaks, demonstrating the formation of $Ta_{0.8}Hf_{0.2}C$ solid solution single phase.

Although 10 vol.% $MoSi_2$ is enough for near complete densification of single carbides of TaC or HfC [13], this

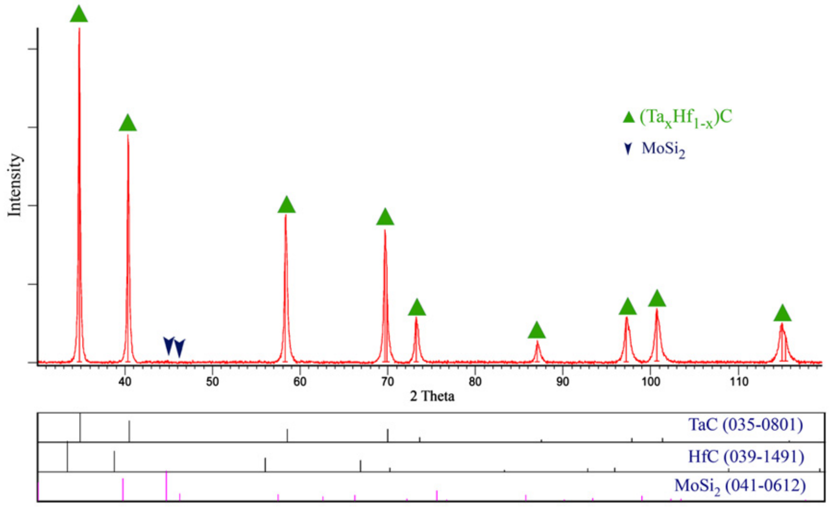

Fig. 3. X-ray diffraction pattern of $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ after sintering at 2000 °C for 1 h in Ar.

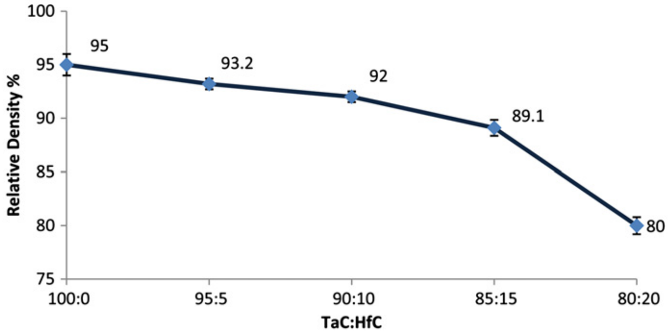

Fig. 4. Variation of final relative density of TaC/HfC composite versus carbides ratio, after sintering at 2000 °C for 1 h in Ar in the presence of 12 vol.% $MoSi_2$.

amount was determined here to be at least 24 vol.% for binary carbide of $Ta_{0.8}Hf_{0.2}C$ (Fig. 1).

Fig. 4 presents effect of HfC addition on densification of TaC in the presence of a fixed $MoSi_2$ content (12 vol.%). As it seems, the final relative density decreases down to 80% when HfC content increases up to 20 vol.%.

Densification of Hf and Ta carbides with $MoSi_2$ occurs via liquid-phase sintering, which is constituted by transition metal silicides. Mo_5Si_3 is likely to be the starting phase for liquid phase sintering. On the other hand, substitution mobility of transition metal carbides decreases from Hf to Ta. Transition metal atoms must substitute Mo in Mo_5Si_3 to form a liquid phase based on Ta–Si or Hf–Si systems [2].

There is a competition between metallic atoms to substitute in TaC–HfC–$MoSi_2$ system. As it was reported before, transition metal carbides, such as TaC and HfC, can be completely dissolved in each other. When HfC dissolves in TaC, lattice parameter increases [14]. Comparing XRD results of $Ta_{0.8}Hf_{0.2}C$ in Fig. 3 with the standard XRD pattern of TaC reveals an increase in the unit cell parameter from 4.459 for TaC to 4.473 nm for $Ta_{0.8}Hf_{0.2}C$.

On the other hand, both Ta and Hf atoms must substitute in Mo_5Si_3 to form enough liquid phases for sintering. Regarding reverse effect of HfC addition on densification of TaC during sintering at constant amount of $MoSi_2$ (Fig. 4), it can be concluded that the formation of TaC–HfC solid solution is more considerable in comparison with $(Ta,Mo)_5Si_3$ or $(Hf,Mo)_5Si_3$ formation. In fact, some parts of $MoSi_2$ can dissolve inside $Ta_xHf_{1-x}C$, with much open structure, in comparison with TaC. So, it is necessary to increase the amount of $MoSi_2$ content to form enough liquid phase for sintering of $Ta_{0.8}Hf_{0.2}C$.

3.2. Thermal behavior

Oxidation rate of the $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ UHTC in direct contact of oxyacetylene flame for 30 s was 0.14 mm/s. Cross section image of the attacked sample in Fig. 5 demonstrates the formation of two different protective layers on the top surface of sample after the flame test, an outer porous layer with 50 μm thickness and an inner layer with 10–30 μm thickness.

The outer layer consists of a mixed oxide of Ta and Hf, while the inner layer is a diffusion barrier based on Ta–Hf–Mo oxycarbide. As reported before, the formed oxycarbide layer is more resistant to oxidation rather than transition metal oxide layer [15–18]. Sciti et al. [1] reported that Mo and Si from the oxycarbide phases escape as a gaseous state during thermal oxidation. The porous morphology of outer layer and high amount of Mo and Si in the inner layer confirm that the origin of porosity in outer layer comes from evaporation of Mo and Si from the inner layer.

The SEM image of outer layer in Fig. 5 also shows a good adherence between outer layer, inner layer and original body. Moreover, this image reveals that the outer layer is smooth, crack free and partially melted during oxidation test. It has also been reported that Ta_2O_5 can be formed on the surface of TaC during the oxidation test [19]. The elemental analysis of the outer layer in this study confirmed that Ta_2O_5 phase, which contains Hf as substitutional atom, is formed on the

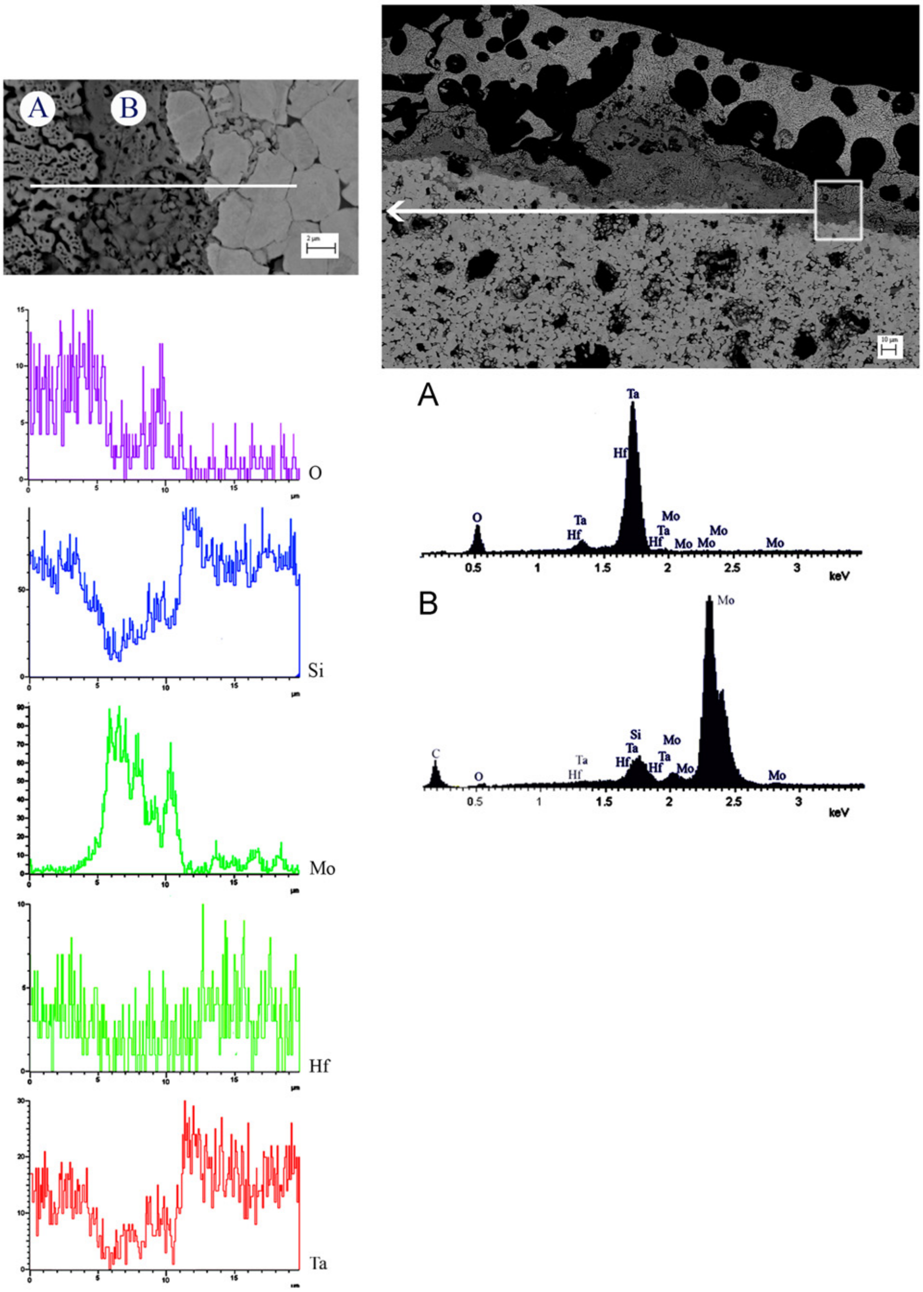

Fig. 5. Point and line scan elemental analyze of the $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ sample after attacking by oxidized flame for 30 s.

surface. Formation of $Ta_2Hf_6O_{19}$ was also confirmed by Courtright et al. [15,20].

Although oxygen was absorbed during flame test, density of samples did not change sensibly after oxidation. In addition, as Fig. 6 shows, the pore size distribution of $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ sample broadened after oxidized flame test, due to the volatilization of carbides.

Formation mechanism of the double layer can be explained as follows:

- At the beginning of flame attack, $Ta_{0.8}Hf_{0.2}C$ begins to catch oxygen from the atmosphere. Carbon, by escaping from the carbide structure in the form of CO gas, expands the carbide structure and enhances diffusion of Mo and Si atoms from the matrix to the oxycarbide layer.
- Mixed oxide of Ta and Hf forms on the surface of oxycarbide inner layer by escaping Ta, Hf, Mo and Si atoms from the origin $Ta_{0.8}Hf_{0.2}C$ body to the outer layer [20].

4. Conclusion

$Ta_{0.8}Hf_{0.2}C$ UHTC was consolidated up to 94% relative density by using 24 vol.% $MoSi_2$ as sintering aid at 2000 °C. It was declared that HfC addition had a reverse

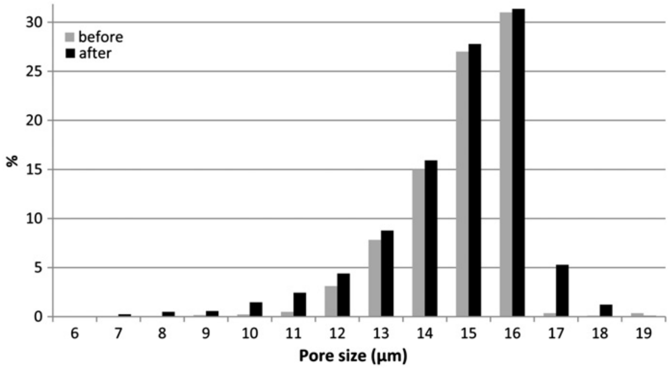

Fig. 6. Pore size distribution of $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ sample before and after attacking by oxidized flame for 30 s.

effect on densification progress of TaC. Thermal oxidation test of $Ta_{0.8}Hf_{0.2}C$/24 vol.% $MoSi_2$ showed the formation of crack free and smooth double protective layer during flame attack.

References

[1] D. Sciti, L. Silvestroni, S. Guicciardi, D.D. Fabbriche, A. Bellosi, Processing, mechanical properties and oxidation behavior of TaC and HfC composites containing 15 vol% $TaSi_2$ or $MoSi_2$, Journal of Materials Research 24 (6) (2009).

[2] L. Silvestroni, D. Sciti, J. Kling, S. Lauterbach, H.J. Kleebe, Sintering mechanisms of zirconium and hafnium carbides doped with Mosi2, Journal of the American Ceramic Society 92 (7) (2009) 1574–1579.

[3] X.H. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Densification and mechanical properties of TaC-based ceramics, Materials Science and Engineering A-Structure 501 (1–2) (2009) 37–43.

[4] D.L. Deadmore, Vaporization of tantalum carbide-hafnium carbide solid solutions, Journal of the American Ceramic Society 48 (7) (1965) 3.

[5] S.Z. Nazarova, E.Z. Kurmaev, N.I. Medvedeva, A. Mowes, Physical properties and electronic structure of TaC–HfC Solid Solutions, Russian Journal of Inorganic Chemistry 52 (2) (2007).

[6] R.A. Andrievskii, N.S. Strel'nikova, N.I. Poltoratskii, E.D. Kharkhardin, V.S. Smirnov, Melting point in systems ZrC-HfC, TaC-ZrC, TaC-HfC, Powder Metallurgy and Metal Ceramics 6 (1) (1967) 3.

[7] X.H. Zhang, G.E. Hilmas, W.G. Fahrenholtz, D.M. Deason, Hot pressing of tantalum carbide with and without sintering additives, Journal of the American Ceramic Society 90 (2) (2007) 393–401.

[8] 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.

[9] K. Hackett, S. Verhoef, R.A. Cutler, D.K. Shetty, Phase constitution and mechanical properties of carbides in the Ta-C System, Journal of the American Ceramic Society 92 (10) (2009) 2404–2407.

[10] P.S. Kislyi, S.A. Shvab, F.F. Egorov, Sintering kinetics of tantalum carbide, Powder Metallurgy and Metal Ceramics 21 (1982).

[11] J.X. Liu, Y.M. Kan, G.J. Zhang, Pressureless sintering of Tantalum carbide ceramics without additives, Journal of the American Ceramic Society 93 (2) 370–373.

[12] D. Sciti, L. Silvestroni, A. Bellosi, High-density pressureless-sintered HfC-based composites, Journal of the American Ceramic Society 89 (8) (2006) 2668–2670.

[13] L. Silvestroni, D. Sciti, Sintering behavior, microstructure, and mechanical properties: a comparison among pressureless sintered ultra-refractory carbides, Advances in Materials Science and Engineering 2010 (2010) 1–11.

[14] H. Pierson, Handbook of refractorycarbides and nitrides, Noyes Publications, Westwood, New Jersey, U.S.A., 1996.

[15] C.L. Yeh, E.W. Liu, Combustion synthesis of tantalum carbides TaC and Ta_2C, Journal of Alloys and Compounds 415 (1–2) (2006) 66–72.

[16] C.B. Bargeron, R.C. Benson, A.N. Jette, T.E. Phillips, Oxidation of hafnium carbide in the temperature-range 1400-degrees to 2060-degrees-C, Journal of the American Ceramic Society 76 (4) (1993) 1040–1046.

[17] M.M. Opeka, I.G. Talmy, J.A. Zaykoski, Oxidation-based materials selection for 2000 degrees C plus hypersonic aerosurfaces: theoretical considerations and historical experience, Journal of Materials Science Letters. 39 (19) (2004) 5887–5904.

[18] V.A. Lavrenko, V.N. Talash, M. Desmaison-Brut, Y.B. Rudenko, Protective oxide layers formed during electrochemical oxidation of hafnium carbide, Powder Metallurgy and Metal Ceramics 48 (9–10) (2009) 595–599.

[19] M. DesmaisonBrut, N. Alexandre, J. Desmaison, Comparison of the oxidation behaviour of two dense hot isostatically pressed tantalum carbide (TaC and Ta2C) materials, Journal of the European Ceramic Society 17 (11) (1997) 1325–1334.

[20] E.L. Courtright, J.T. Prater, G.R. Holcomb, G.R. Stpierre, R.A. Rapp, Oxidation of hafnium carbide and hafnium carbide with additions of tantalum and praseodymium, Oxidation of Metals 36 (5–6) (1991) 423–437.