TEMPERATURE DEPENDENCE OF ELASTIC PROPERTIES OF ZrB_2 -SiC COMPOSITES

M. Lugovy^{1,2}, V. Slyunyayev¹, N. Orlovskaya^{2*}, E. Mitrentsis^{3,4}, C.G. Aneziris³, T. Graule⁴,
J. Kuebler⁴

¹ Institute for Problems of Materials Science, 3 Krzhizhanivskii Str., 03142 Kyiv, Ukraine

² University of Central Florida, Orlando, 4000 Central Florida Blvd., Orlando, FL 32816, USA

³ TU Bergakademie Freiberg, D-09596 Freiberg, Germany

⁴ Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

* Corresponding Author

Abstract

Elastic properties (Young's modulus, shear modulus, bulk modulus and Poisson's ratio) of ZrB_2 , SiC ceramics and ZrB_2 -SiC ultra high temperature ceramic composites were measured by impulse excitation technique in the RT-1173 K temperature range. Two compositions of ZrB_2 with 17 vol% and 32 vol% of SiC strengthening phase were hot pressed to almost full density, followed by machining before the measurements took place. The temperature dependences of elastic properties have shown the expected softening behavior, where only small 4% and 5% linear reduction in Young's and shear moduli were detected, respectively, for ZrB_2 -17 vol% SiC and ZrB_2 -32 vol% SiC ceramic composites. The reported decrease in elastic moduli brings the respective linear increase of Poisson's ratio up to ~9% in the temperature of interest. Such high temperature behavior corresponds well to the upper and lower bounds of elastic moduli of two ZrB_2 -SiC ceramic composites calculated by Voigt and Reuss estimations using properties of pure ZrB_2 and pure SiC ceramics, as published in the literature.

Keywords: ZrB_2 -SiC ceramic composite, Young's modulus, shear modulus, Poisson's ratio, temperature dependence

Introduction

ZrB₂-based ultra high temperature ceramics (UHTC) caused a lot of interest in the past because of the unique combination of mechanical and physical properties, such as high melting points, high thermal conductivity, high stiffness, and relatively high oxidation resistance, which allowed for these materials to be used in different aerospace applications [1-7]. While ZrB₂-based ceramics are rather brittle, as is typical for most engineering ceramics, the prevalent covalent bonding in hexagonal ZrB₂ makes it very stiff with Young's modulus of pure ZrB₂ reported to be around ~500 GPa, shear modulus to be ~232 GPa, and bulk modulus of 240 GPa [8, 9]. Such stiff and hard materials have low Poisson's ratio and ZrB₂ has also very low Poisson's ratio of 0.14 at room temperature [10]. At high temperature, the ZrB₂ ceramics soften and elastic moduli are decreased in comparison with their respective room temperature values. However, the softening of ZrB₂ lattice is not significant, as the elastic moduli values decrease on the average by 8-9% with increasing temperature from RT to 1300 K. When SiC phase is added to ZrB₂, it provides a better oxidation resistance [11, 12], but as elastic properties of SiC ceramics are slightly lower than those of ZrB₂ [13], the ZrB₂-SiC ceramic composites are less stiff than pure ZrB₂.

Elastic properties of such high temperature materials are of high importance because they will determine the values of thermal residual stresses, which appear upon heating and cooling, define the lifetime of the materials, and play a major role in the reliability of the components as a whole. The knowledge of precise values of elastic moduli of the composites is also important for development of models targeting design of the leading edges of hypersonic vehicles or other industrial applications where ZrB₂-based or other UHTC composites are used as components of the design. Despite of the extensive amount of work published on ZrB₂-based UHTCs, the elastic properties of pure ZrB₂ and SiC are reported with a significant standard deviation even for room temperature measurements. The reported values of Young's modulus of ZrB₂ lie within 413 GPa to 555 GPa [8, 13-21]. The rather broad distribution of Young's modulus values of α -SiC provides

values in between 298-475 GPa depending on polytypes of SiC and the amount of residual porosity present in the material [8, 22-34]. Room temperature shear modulus of ZrB₂ and SiC is reported less seldom but it also has very different values reported for both materials [9, 25, 27, 29, 31, 34, 35]. The reported values of Young's modulus of ZrB₂-SiC composite are also very different in the literature and vary within 422-507 GPa for ZrB₂-10 vol% SiC [13, 36-39], 424-520 GPa for ZrB₂-20 vol% SiC [13, 36-38, 40-45], and 434-525 GPa for ZrB₂-30 vol% SiC [8, 13, 19, 36-38, 46, 47]. The shear modulus and Poisson's ratio of ZrB₂-SiC ceramic composites at room temperature are also rarely studied and the reported values are scarce [38, 42, 48, 49].

In addition, the uncertainties in the Poisson's ratio of pure ZrB₂ and pure SiC as well as of ZrB₂-SiC ceramic composites, calculated from known Young's and shear moduli, are also a problem. The standard deviation of Poisson's ratio is determined by the sum of the standard deviation of Young's and shear moduli as well as by an average value of the Poisson's ratio itself. For example, with standard deviations of Young's and shear moduli of 5% and an average value of Poisson's ratio equal to 0.2, the relative standard deviation of Poisson's ratio value will be equal to 60%. Thus, the analysis of the published Poisson's ratio results provides the values of 0.131 ± 0.013 for ZrB₂ [9, 10, 14, 17, 18, 35] and 0.188 ± 0.031 for α -SiC [17, 25-27, 29, 31, 33, 34]. For the case of SiC, the relative standard deviation of Poisson's ratio is equal to 16% because of the significant differences in reported values of Young's and shear moduli.

As the intended use of a ZrB₂ based composite is for high temperature application, the elastic properties of this class of ceramics are of high importance, not only for room temperature, but also mainly for high temperature. The high temperature dependencies of Young's, shear and bulk moduli of ZrB₂ were studied in [9, 14, 15, 20]. A very high temperature range up to 2373 K was used to measure Young's modulus behavior of pure ZrB₂ at high temperatures, where the measurements showed an expected decrease of Young's modulus of ZrB₂ with temperature increase [20]. While the detailed measurements at 1000-2373 K were performed in [20], the data in the lower temperature interval of RT-1300 K are practically absent in this publication. More detailed

results for Young's and shear moduli in the RT-1300 K temperature range were provided in [9, 14]. For pure α -SiC the high temperature Young's and shear moduli were measured in RT-1800 K and it was shown that elastic moduli decrease with temperature rise [24, 27]. The ZrB₂-20 vol% SiC Young's modulus behavior was studied in RT-1800 K temperature ranges [40, 43], and ZrB₂-30 vol% SiC in RT-1900 K [47]. In all publications the similar expected softening of pure ZrB₂ and SiC as well as ZrB₂-SiC composites were reported with increasing temperature in the experiments. Therefore, the analysis of the published data on elastic moduli provides various values that are difficult to interpret as a variety of different parameters, such as porosity, grain size, and impurities of materials are rather different for various experiments.

The goal of this work is to measure and analyze Young's modulus, shear modulus and Poisson's ratio of composites ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC in the temperature range from room temperature to 1173 K.

Experimental

ZrB₂-SiC ceramic composite processing steps included ball milling of ZrB₂ (Grade B, H.C. Starck, Germany; $d_{50}=2\text{ }\mu\text{m}$) and SiC (UF-10, H.C. Starck, Germany; $d_{50}=0.7\text{ }\mu\text{m}$) powders for 48 h in the required proportion in a plastic bottle using acetone and 7 mm yttria stabilized zirconia balls as milling media. Size of particles was reduced by approximately 1.5 times after milling. Then, the ZrB₂-10 wt% SiC and ZrB₂-20 wt% SiC powder mixtures were dried and sieved through 325 mesh sieves to remove large agglomerates. The powder was packed into a 35x55 mm graphite die coated with BN. The hot pressing of the powder was performed at 2150 °C and at a pressure of 30 MPa for 45 min, where 35x55x7 mm tiles were produced. The heating/cooling rate was 50 °C min⁻¹ during hot pressing. The hot pressed 35x50x7 mm ZrB₂-17vol% SiC and ZrB₂-32 vol% SiC ceramic tiles were further machined by PremaTech Advanced Ceramics, USA into 50x14x4 mm bars without chamfers for elastic moduli measurements.

The bulk densities of the sintered samples were determined using Archimedes' method in water using a precision scale (AG204 Delta Range® Mettler-Toledo, Switzerland) to minimize the measuring error. The theoretical densities were estimated by the rule of mixture, using theoretical densities of ZrB_2 (6.09 g/cm³) and SiC (3.21 g/cm³). The phase composition of the ZrB_2 -SiC ceramics were also confirmed by XRD analysis after densification. Only ZrB_2 and SiC were presented in the composites.

The determination of elastic moduli was carried out according to EN 843-2 standard [50] by Impulse Excitation technique using Grindo-Sonic Mk5 "Industrial" (J.W. Lemmens, Belgium). For the measurements at room temperature samples with known density were placed over the microphone lined up with the supporting cylinders. Then a test bar was struck lightly by a small hammer and the natural frequency of vibration was detected afterwards by a microphone placed beneath. Young's and shear moduli were then calculated using the mass of the bar, its dimensions, and the fundamental natural frequency of vibration. The Poisson's ratio was calculated according to the equation $\nu = E / 2G - 1$ using the measured Young's and shear moduli values. A total of 30 samples were tested to determine the Young's modulus of the material at room temperature.

The same Impulse Excitation technique was used for measurements of elastic moduli at high temperatures. The measurements were performed in air using an electrical furnace. The ZrB_2 -SiC samples were placed on a sample holder and fixed with weights, and the microphone for the detection of vibration was placed beneath. Instead of the hammer used for room temperature experiments, either ZrO_2 or stainless steel balls with 4 mm in diameter were used for excitation. The measurements were performed with 50 °C step in temperature range between room temperature and 1173 K. Before the measurements, the samples were dwelled for 30 min at the temperature of interest to allow the temperature to equilibrate. Every measurement was repeated 5 times at each temperature to provide high data accuracy.

The equations used for the calculation of elastic moduli using the natural frequency of the specimen vibrations include the dimensions of the sample, which change as a function of temperature upon heating. Young's modulus is calculated using [50]

$$E = 0.946 \frac{m f_f^2 l^3}{b h^3} A_f, \quad (1)$$

where m is the specimen mass, b is the specimen width, h is the specimen height, l is the specimen length, f_f is the frequency of flexural vibration, and $A_f = 1 + 6.585(h/l)^2$. Shear modulus is calculated using [50]

$$G = \frac{4m f_t^2 l}{b h} A_t, \quad (2)$$

where f_t is the frequency of torsional vibration and

$$A_t = \frac{h/b + b/h}{4h/b - 2.52(h/b)^2 + 0.21(h/b)^6}.$$

To account for the changes due to thermal expansion, the correction coefficient

$$k = \frac{1}{1 + \alpha(T - T_0)}, \quad (3)$$

where T and T_0 are the current and room temperature, respectively, α is the average coefficient of thermal expansion (CTE) in T_0 to T temperature range, was introduced into the equations (1) and (2) to account for the dimensional changes as temperature of the tests increased. The temperature dependences of CTE was approximated as $\alpha(T) = 1.66 \cdot 10^{-9} T + 6.09 \cdot 10^{-6}$ and $\alpha(T) = 1.78 \cdot 10^{-9} T + 5.72 \cdot 10^{-6}$ for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC, respectively, based on the CTE data published in [51], where T is in °C and $\alpha = (\alpha(T_0) + \alpha(T))/2$ is an average coefficient of thermal expansion. Therefore, the values of the elastic moduli measured at high temperature were calculated using the corrected dimensions of the samples.

Results and Discussion

The ZrB₂-SiC ceramics used in this study had a very low level of residual porosity, where ZrB₂-17 vol% SiC ceramic composite had 1% of porosity, and ZrB₂-32 vol% SiC ceramic composite had 0.82% of porosity. The presence of porosity reduce the values of elastic moduli [52, 53], and is one of the reasons for the large reported scatter of both Young's and shear moduli as well as the Poisson's ratio of the composite materials. The porosity of ZrB₂-SiC composite ceramics typically vary significantly over the reported data [13, 36-46], thus the values from the literature cannot be compared directly. However, for ceramics with a porosity lower than 10%, a linear dependence of elastic moduli on porosity is known [54]. Therefore, a recalculation of elastic properties of real ceramics with a residual level of porosity to estimate the elastic moduli of the fully dense ceramic composites was performed using the following procedure. The Young's and the shear moduli of porous and fully dense ceramic composites are related by the following equations [53]:

$$E = E_0(1 - \alpha_E P), \quad (4a)$$

$$G = G_0(1 - \alpha_G P), \quad (4b)$$

where E and G are Young's modulus and shear modulus, respectively, of the porous specimens, E_0 and G_0 represent the moduli of the nonporous material, α_E and α_G are constants, and P is the volume fraction of porosity. The α_E and α_G constants are determined using the following equations:

$$\alpha_E = \frac{3(9 + 5\nu_0)(1 - \nu_0)}{2(7 - 5\nu_0)}, \quad (5a)$$

$$\alpha_G = \frac{15(1 - \nu_0)}{7 - 5\nu_0}, \quad (5b)$$

where ν_0 is the Poisson's ratio of the nonporous material. Taking into account the reported 0.12 to 0.2 values of Poisson's ratios ZrB₂-SiC composites, the calculated values of α_E and α_G vary within 1.98-2 and 2-2.06, respectively. Taking into account the low sensitivity of α_E and α_G values to the variation of the Poisson's ratio of the fully dense material, one can safely use the average 1.99 and

2.03 α_E and α_G values, respectively. Therefore the following equations for the calculation of E_0 and G_0 of fully dense ceramic composites were used:

$$E_0 = E / (1 - 1.99P), \quad (6a)$$

$$G_0 = G / (1 - 2.03P). \quad (6b).$$

The E and G values of both, the ones experimentally measured in this experiments and the ones taken from published papers were all recalculated by using Eq. (6a) and (6b) in order to be able to compare the results adequately for the non-porous materials.

The dependences of Young's and shear moduli of ZrB₂-SiC ceramics measured at RT as a function of volume fraction of SiC strengthening phase are shown in Fig. 1. Both measurements performed in this work and the results published in the literature [8, 9, 13, 16, 19, 20, 23, 25, 27-31, 34-46, 48] are shown, where the open symbols present data published in the literature and the closed symbols present data obtained in this work. The values of the Young's modulus of the composites ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC obtained in this work are 497±1 and 485±1 GPa, respectively. The values of the shear modulus of the composites ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC obtained in this work are 218±1 and 212±1 GPa, respectively. Note that the experimental error bars are smaller than the symbol sizes. As one can see from Fig. 1, excellent correlation is found between the measurements taken from the literature sources and the ones obtained in the present work. The Young's modulus values of pure ZrB₂ (520 ± 10 GPa) and pure SiC (410 ± 54 GPa) ceramics were averaged using the data taken from [8, 9, 13, 16, 19, 20] and [23, 25, 27-31, 34], respectively. The shear modulus values of pure ZrB₂ (231 ± 1 GPa) and pure SiC (171 ± 26 GPa) were averaged using the data from [9, 49] and [25, 27, 29, 31, 34], respectively. The Young's and shear moduli values published in the literature of ZrB₂-10 vol% SiC ceramic composites were taken from [13, 35, 38] and [35, 38]; ZrB₂-20 vol% SiC ceramic composites from [13, 19, 36-44] and [38, 42]; ZrB₂-30 vol% SiC ceramic composites from [8, 13, 19, 36-38, 45, 46, 48] and [38, 45, 48], respectively. Young's modulus of ZrB₂-45 vol% SiC ceramic composites is presented in [55].

The upper and lower bounds of theoretical values of elastic moduli of ZrB₂-SiC ceramic composites are usually determined using Voigt equations [56]:

$$E_V = E_{ZrB_2}(1 - f_{SiC}) + E_{SiC}f_{SiC} , \quad (7a)$$

$$G_V = G_{ZrB_2}(1 - f_{SiC}) + G_{SiC}f_{SiC} , \quad (7b)$$

where E_V and G_V are the Young modulus and the shear modulus of a composite according to Voigt, respectively; E_{ZrB_2} and E_{SiC} are the Young moduli of ZrB₂ and SiC, respectively; G_{ZrB_2} and G_{SiC} are the shear moduli of ZrB₂ and SiC, respectively; f_{SiC} is the SiC volume fraction, and Reuss equations [57]:

$$E_R = \frac{E_{ZrB_2}E_{SiC}}{E_{ZrB_2}f_{SiC} + E_{SiC}(1 - f_{SiC})} , \quad (8a)$$

$$G_R = \frac{G_{ZrB_2}G_{SiC}}{G_{ZrB_2}f_{SiC} + G_{SiC}(1 - f_{SiC})} , \quad (8b)$$

where E_R and G_R are the Young modulus and the shear modulus of a composite according to Reuss, respectively. Such upper and lower bounds are presented in Fig. 1 for both the Young's and the shear moduli of the ZrB₂-SiC ceramic composites and show that both E and G moduli obtained in this study fit very well within the area limited by the upper (Voigt) and lower (Reuss) boundaries.

As both E and G moduli were analyzed as a function of composition, the Poisson's ratio has also been calculated using average values of corresponding Young's and shear moduli and the dependence of the Poisson's ratio of ZrB₂-SiC ceramic composites as a function of volume fraction of SiC is presented in Fig. 2. As one can see, the Poisson's ratio is increasing in an almost linear manner with increasing SiC phase content in the composite. The Poisson's ratio values were equal to 0.142 and 0.146 for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC, respectively. Note that the averaged data collected from literature probably represent many different types of SiC ceramics with various properties, impurity content, and other factors.

The results of the high temperature measurements of elastic moduli for ZrB₂ with 17vol% and 32 vol% SiC ceramic composites are shown in Fig. 3. As one would expect, both Young's and

shear moduli exhibit softening behavior with an increase in the temperature. The open and solid circles represent the experimental data obtained in the current work for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC, respectively, while solid lines represent the calculated high temperature behavior of elastic moduli of pure ZrB₂ and pure SiC ceramics. The high temperature behavior of pure compounds was approximated by analyzing experimental results published in the literature. Thus, it was established that the equation $E_{ZrB_2}(T) = 530 - 0.033T$ provides a good approximation of high temperature behavior of Young's modulus of pure ZrB₂ in RT-1300 K temperature range, as published in [9, 14, 15, 20] and that the equation $G_{ZrB_2}(T) = 239 - 0.024T$ can be used to describe shear modulus of pure ZrB₂ in RT-1300 K temperature range based on the results published in [9, 14]. The temperature dependencies of elastic moduli of SiC can be described by $E_{SiC}(T) = 417 - 0.0244T$ and $G_{SiC}(T) = 174 - 0.0099T$ for Young's and shear moduli, respectively in RT-1300 K temperature range based on the experimentally measured E and G values of pure SiC [22, 24, 27, 31]. Once the elastic moduli behavior of pure ZrB₂ and SiC ceramics was established, the upper and lower bounds of E and G moduli of the ZrB₂-17vol% and ZrB₂-32 vol% SiC were established according to the Voigt and the Reuss estimations, which are presented as dashed lines in Fig. 3. As one can see, the E and G values experimentally measured in this work fit very well into the upper and lower bounds, showing almost linear dependence as a function of temperature. Such a good agreement between the experimental data and the theoretical estimates proves a reliability of the obtained results.

The Poisson's ratio of ZrB₂-17vol% and ZrB₂-32 vol% SiC was calculated using the obtained results of Young's and shear moduli and its high temperature dependence is presented in Fig. 4. As one would expect, the value of Poisson's ratio is increasing with temperature increase, as ZrB₂-SiC ceramics became more ductile upon temperature raise. For ZrB₂-17vol% ceramic composite there is a 10% increase in Poisson's ratio when temperature increases from RT to 1173 K. A similar increase of 9% exists for Poisson's ratio of ZrB₂-32 vol% SiC, when temperature

increases from RT to 973 K. Such an increase is rather substantial and has to be accounted into the calculations and estimations of high temperature ceramics behavior.

Conclusions

Both Young's and shear moduli of ZrB₂-SiC based ceramic composites have been measured by Impulse Excitation technique up to 1000 °C in air. Poisson's ratio has been calculated using obtained values of both elastic moduli. The obtained results were compared with the values published in the literature. It was concluded that the measured values of elastic properties of ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC ceramic composites aligned well with the results published in the literature and the high temperature elastic properties of the composites corresponded well to theoretically calculated Voigt and Reuss upper and lower limits of the moduli. Despite of the fact that high temperature testing was done in air, the measured high temperature Young's modulus showed very little deviation from theoretically predicted values for ZrB₂-17 vol% SiC ceramic composites, while both Young's modulus of ZrB₂-32 vol% SiC and shear modulus values of ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC lied almost perfectly within the theoretically predicted bounds. It is expected that the obtained results could be further utilized in the predictive modeling of these ultra high temperature ceramic composites.

Acknowledgements

This work was supported by the National Science Foundation, the Division of Materials Research, project #0748364 in the Ceramics program. Dr. Slyunyayev's work at Empa was supported by the Swiss National Science Foundation via the International Short Visit fellowship (Decision IZK0Z2_147715). Dr. Lugovy's work at Empa was supported by the Swiss National Science Foundation via the International Short Visit fellowship (Decision IZK0Z2_134265). Ms. E.

Mitrentsis was supported by Empa via the Lab for High Performance Ceramics internal grant for MSc student research.

References

1. D. Debnath, S. Chakraborty, A.R. Mallick, R.K. Gupta, A. Ranjan, P.K. Das, Mechanical, tribological and thermal properties of hot pressed ZrB_2 – SiC composite with SiC of different morphology, *Adv. Appl. Ceram.* 114 (2015) 45–54.
2. N. Fist, J. Dinan, R. Stadelmann, N. Orlovskaya, In situ three point bending device for measurements of vibrational response of ceramics under stress by microRaman spectroscopy, *Adv. Appl. Ceram.* 111 (2012) 433–439.
3. E. Padovano, C. Badini, S. Biamino, M. Pavese, W.S. Yang, P. Fino, Pressureless sintering of ZrB_2 – SiC composite laminates using boron and carbon as sintering aids, *Adv. Appl. Ceram.* 112 (2013) 478–486.
4. J.K. Sonber, A.K. Suri, Synthesis and consolidation of zirconium diboride: review, *Adv. Appl. Ceram.* 110 (2011) 321–334.
5. R.S. Dohedoe, G.D. West, M.H. Lewis, Spark plasma sintering of ceramics: understanding temperature distribution enables more realistic comparison with conventional processing, *Adv. Appl. Ceram.* 104 (2005) 110–116.
6. M. Lugovy, N. Orlovskaya, M. Neubert, C.G. Aneziris, T. Graule, J. Kuebler, Time dependent mechanical properties of ZrB_2 – SiC ceramic composites: Room temperature fatigue parameters, *Sci. Adv. Mater.* 6 (2014) 844–852.
7. M. Lugovy, N. Orlovskaya, V. Subbotin, M. Neubert, C.G. Aneziris, T. Graule, J. Kubler, Room temperature fatigue of ZrB_2 – SiC ceramic composites, *Ceram. Int.* 39 (2013) 9187–9194.
8. S.-Q. Guo, Densification of ZrB_2 -based composites and their mechanical and physical properties: a review, *J. Eur. Ceram. Soc.* 29 (2009) 995–1011.
9. N.L. Okamoto, M. Kusakari, K. Tanaka, H. Inui, S. Otani, Anisotropic elastic constants and thermal expansivities in monocrystal CrB_2 , TiB_2 , and ZrB_2 , *Acta Mater.* 58 (2010) 76–84.
10. H.Y. Wang, F.Y. Xue, N.H. Zhao, D.J. Li, First-principles calculation of elastic properties of TiB_2 and ZrB_2 , *Adv. Mat. Res.* 150–151 (2010) 40–43.

11. W.G. Fahrenholtz, Thermodynamic analysis of ZrB_2 -SiC oxidation: formation of a SiC-depleted region, *J. Am. Ceram. Soc.* 90 (2007) 143–148.
12. F. Monteverde, Plasma wind tunnel testing of ultra-high temperature ZrB_2 -SiC composites under hypersonic re-entry conditions, *J. Eur. Ceram. Soc.* 30 (2010) 2313–2321.
13. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, D.T. Ellerby, High-strength zirconium diboride-based ceramics, *J. Am. Ceram. Soc.* 87 (2004) 1170–1172.
14. D.E. Wiley, W.R. Manning, O.J. Hunter, Elastic properties of polycrystalline TiB_2 , ZrB_2 and HfB_2 from room temperature to 1300 °K, *J. Less-Common Metals* 18 (1969) 149–157.
15. W.H. Rhodes, E.V. Clougherty, D. Kalish, Research and development of refractory oxidation-resistant diborides, Technical Report AFML-TR-68-190, Part II, Vol. IV, ManLabs Incorporated and Avco Corporation, Wright Patterson Air Force Base, OH, 1970.
16. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, Pressureless sintering of zirconium diboride, *J. Am. Ceram. Soc.* 89 (2006) 450–456.
17. X. Zhang, X. Luo, J. Han, J. Li, W. Han, Electronic structure, elasticity and hardness of diborides of zirconium and hafnium: first principles calculations, *Comput. Mater. Sci.* 44 (2008) 411–421.
18. H. Li, L. Zhang, Q. Zeng, J. Wang, L. Cheng, H. Ren, K. Guan, Crystal structure and elastic properties of ZrB compared with ZrB_2 : a first-principles study, *Comput. Mater. Sci.* 49 (2010) 814–819.
19. Z. Lue, D. Jiang, J. Zhang, Q. Lin, Processing and properties of ZrB_2 -SiC composites obtained by aqueous tape casting and hot pressing, *Ceram. Int.* 37 (2011) 293–301.
20. E.W. Neuman, G.E. Hilmas, W.G. Fahrenholtz, Strength of zirconium diboride to 2300°C. *J. Am. Ceram. Soc.* 96 (2013) 47–50.
21. F. Monteverde, S. Guicciardi, A. Bellosi, Advances in microstructure and mechanical properties of zirconium diboride based ceramics, *Mater. Sci. Eng. A* 346 (2003) 310–319.

22. J.B. Wachtman Jr., D.G. Lam Jr., Young's modulus of various refractory materials as a function of temperature, *J. Am. Ceram. Soc.* 42 (1959) 254–260.
23. G.D. Swanson, Fracture energies of ceramics, *J. Am. Ceram. Soc.* 55 (1972) 48–49.
24. M. Fukuhara, Y. Abe, High-temperature elastic moduli and internal frictions of α -SiC ceramic, *J. Mater. Sci. Lett.* 12 (1993) 681–683.
25. C.A. Tracy, G.D. Quinn, Fracture toughness by the surface crack in flexure (SCF) method, *Ceram. Eng. Sci. Proc.* 15 (1994) 837–845.
26. G.J. Zhang, X.M. Yue, Z.Z. Jin, J.Y. Dai, In-situ synthesized TiB_2 toughened SiC, *J. Eur. Ceram. Soc.* 16 (1996) 409–412.
27. R.G. Munro, Material properties of a sintered α -SiC. *J. Phys. Chem. Ref. Data* 26 (1997) 1195–1203.
28. K. Wang, R.R. Reeber, *MRS Internet J. Nitride Semicond. Res.* 4S1 (1999) G3.18.
29. C.L. Hsieh, W.H. Tuan, Elastic properties of ceramic–metal particulate composites, *Mater. Sci. Eng. A* 393 (2005) 133–139.
30. X. Sun, J.-G. Li, S. Guo, Z. Xiu, K. Duan, X.Z. Hu, Intragranular particle residual stress strengthening of Al_2O_3 –SiC nanocomposites, *J. Am. Ceram. Soc.* 88 (2005) 1536–1543.
31. L.L. Snead, T. Nozawa, Y. Katoh, T.-S. Byun, S. Kondo, D.A. Petti, Handbook of SiC properties for fuel performance modeling, *J. Nucl. Mater.* 371 (2007) 329–377.
32. G. Zhang, Q. Guo, K. Wang, H. Zhang, Y. Song, J. Shi, L. Liu, Finite element design of SiC/C functionally graded materials for ablation resistance application, *Mater. Sci. Eng. A* 488 (2008) 45–49.
33. Y. Tan, D. Yang, Y. Sheng, Discrete element method (DEM) modeling of fracture and damage in the machining process of polycrystalline SiC, *J. Eur. Ceram. Soc.* 29 (2009) 1029–1037.
34. E. Sanchez-Gonzalez, P. Miranda, F. Guiberteau, A. Pajares, Effect of microstructure on the mechanical properties of liquid-phase-sintered silicon carbide at pre-creep temperatures, *J. Eur. Ceram. Soc.* 31 (2011) 1131–1139.

35. S.-Q. Guo, Y. Kagawa, T. Nishimura, Mechanical behavior of two-step hot-pressed ZrB_2 -based composites with ZrSi_2 , *J. Eur. Ceram. Soc.* 29 (2009) 787–794.
36. F. Monteverde, Beneficial effects of an ultra-fine α -SiC incorporation on the sinterability and mechanical properties of ZrB_2 , *Appl. Phys. A* 82 (2006) 329–337.
37. C. Hu, Y. Sakka, B. Jang, H. Tanaka, T. Nishimura, S. Guo, S. Grasso, Microstructure and properties of ZrB_2 -SiC and HfB_2 -SiC composites fabricated by spark plasma sintering (SPS) using TaSi_2 as sintering aid, *J. Ceram. Soc. Jpn.* 118 (2010) 997–1001.
38. S.C. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Mechanical properties of sintered ZrB_2 -SiC ceramics, *J. Eur. Ceram. Soc.* 31 (2011) 893–901.
39. M. Mallik, S. Roy, K.K. Ray, R. Mitra, Effect of SiC content, additives and process parameters on densification and structure–property relations of pressureless sintered ZrB_2 -SiC composites, *Ceram. Int.* 39 (2013) 2915–2932.
40. L. Kaufman, E.V. Clougherty, H. Nesor, Report NASA-CR-124732. Investigation of the fracture mechanics of boride composites. 19720005842. Manlabs, Inc. 21 Erie Street, Cambridge, Massachusetts 02139. Jul. 1971, 106 p.
41. S. Ran, Van der Biest O., J. Vleugels, ZrB_2 -SiC composites prepared by reactive pulsed electric current sintering, *J. Eur. Ceram. Soc.* 30 (2010) 2633–2642.
42. M.W. Bird, R.P. Aune, A.F. Thomas, P.F. Becher, K.W. White, Temperature-dependent mechanical and long crack behavior of zirconium diboride–silicon carbide composite, *J. Eur. Ceram. Soc.* 32 (2012) 3453–3462.
43. J. Zou, G.-J. Zhang, C.-F. Hu, T. Nishimura, Y. Sakka, H. Tanaka, J. Vleugels, Van der Biest O., High-temperature bending strength, internal friction and stiffness of ZrB_2 -20 vol% SiC ceramics, *J. Eur. Ceram. Soc.* 32 (2012) 2519–2527.
44. C. Yue, W. Liu, L. Zhang, T. Zhang, Y. Chen, Fracture toughness and toughening mechanisms in a (ZrB_2 -SiC) composite reinforced with boron nitride nanotubes and boron nitride nanoplatelets, *Scr. Mater.* 68 (2013) 579–582.

45. J. Zou, G.-J. Zhang, H. Zhang, Z.-R. Huang, J. Vleugels, Van der Biest O., Improving high temperature properties of hot pressed ZrB_2 -20 vol% SiC ceramic using high purity powders, *Ceram. Int.* 39 (2013) 871–876.
46. S. Henderson, W.G. Fahrenholtz, G.E. Hilmas, High-velocity impact resistance of ZrB_2 -SiC, *Ceram. Eng. Sci. Proc.* 27 (2007) 3–10.
47. E.W. Neuman, G.E. Hilmas, W.G. Fahrenholtz, Mechanical behavior of zirconium diboride–silicon carbide ceramics at elevated temperature in air, *J. Eur. Ceram. Soc.* 33 (2013) 2889–2899.
48. F. Monteverde, L. Scatteia, Resistance to thermal shock and to oxidation of metal diborides–SiC ceramics for aerospace application, *J. Am. Ceram. Soc.* 90 (2007) 1130–1138.
49. S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, Influence of silicon carbide particle size on the microstructure and mechanical properties of zirconium diboride–silicon carbide ceramics, *J. Eur. Ceram. Soc.* 27 (2007) 2077–2083.
50. EN843-2, Advanced technical ceramics - Mechanical properties of monolithic ceramics at room temperature. Part 2: Determination of Young's modulus, shear modulus and Poisson's ratio (2006).
51. R.E. Loehman, E.L. Corral, H.P. Dumm, P. Kotula, P. Gabriel, R. Tandon, Ultra-high temperature ceramics for hypersonic vehicle applications. SANDIA Report SAND 2006-2925. Sandia National Laboratories, Albuquerque, NM, Department of Energy, Washington DC, June 2006, 50 p.
52. A.R. Boccaccini, Z. Fan, A new approach for the Young's modulus-porosity correlation of ceramic materials, *Ceram. Int.* 23 (1997) 239–245.
53. W. Pabst, E. Gregorova, G. Ticha, Elasticity of porous ceramics—A critical study of modulus–porosity relations, *J. Eur. Ceram. Soc.* 26 (2006) 1085–1097.
54. D.P.H. Hasselman, R.M. Fulrath, Effect of small fraction of spherical porosity on elastic moduli of glass, *J. Am. Ceram. Soc.* 47 (1964) 52–53.

55. N. Orlovskaya, R. Stadelmann, M. Lugovy, V. Subbotin, G. Subhash, M. Neubert, C.G. Aneziris, T. Graule, J. Kuebler, Mechanical properties of ZrB_2 -SiC ceramic composites: room temperature instantaneous behavior, *Adv. Appl. Ceram.* 112 (2013) 9–16.
56. W. Voigt, Über die Beziehung zwischen den beiden Elastizitätskonstanten isotroper Körper, *Wied. Ann.* 38 (1889) 573–587.
57. A. Reuss, Berechnung der Fließgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle, *Z. Angew. Math. Mech.* 9 (1929) 49–58.

Figure captions

Fig. 1. Dependence of Young's modulus (A) and shear modulus (B) of ZrB₂-SiC composite on SiC volume fraction. Open squares are experimental data from literature: 1 - ZrB₂ according to [8, 9, 20, 35]; 2 - ZrB₂-10 vol% SiC according to [13, 36, 39]; 3 - ZrB₂-20 vol% SiC according to [13, 19, 37-45]; 4 - ZrB₂-30 vol% SiC according to [8, 13, 19, 37-39, 46, 47, 49]; 5 - ZrB₂-45 vol% SiC according to [55]; 6 - SiC according to [25, 27-29, 31, 34]; 7 - ZrB₂ according to [9, 35]; 8 - ZrB₂-10 vol% SiC according to [36, 39]; 9 - ZrB₂-20 vol% SiC according to [39, 43]; 10 - ZrB₂-30 vol% SiC according to [39, 46, 49]; 11 - SiC according to [25, 27, 29, 31, 34]. Solid circles are experimental data from this work. Dashed lines are upper and lower bounds of elastic moduli of composite according to Voigt and Reuss estimations respectively.

Fig. 2. Dependence of Poisson ratio of ZrB₂-SiC composite on SiC volume fraction. Open squares are the values calculated using E and G from literature: 1 - ZrB₂ according to [9, 35]; 2 - ZrB₂-10 vol% SiC according to [36, 39]; 3 - ZrB₂-20 vol% SiC according to [39, 43]; 4 - ZrB₂-30 vol% SiC according to [39, 46, 49]; 5 - SiC according to [25, 27, 29, 31, 34]. Solid circles are data from this work.

Fig. 3. Dependencies of Young modulus (A) and shear modulus (B) of ZrB₂, SiC, ZrB₂-17 vol% SiC, and ZrB₂-32 vol% SiC composites on temperature. Open and solid circles are experimental data from this work for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC respectively. Dashed lines are upper and lower bounds of elastic moduli of composites according to Voigt and Reuss estimations for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC.

Fig. 4. Dependencies of Poisson's ratio of ZrB₂-SiC composites on temperature. Open and solid circles are experimental data from this work for ZrB₂-17 vol% SiC and ZrB₂-32 vol% SiC respectively.

Figure 1

Figure 2

Figure 3

Figure 4