Hot-pressed laminated composites consisting of ZrB_2 -SiC ceramic and Cf/ ZrB_2 -SiC composites

Shuqi GUO[†]

Hybrid Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

In this study, laminated composites consisting of ZrB_2 -SiC (ZS) ceramic and carbon fiber (Cf) reinforced- ZrB_2 -SiC matrix composites (Cf/ ZrB_2 -SiC, hereafter denoted by CfZS) were fabricated by hot-pressing. The effects of the layer thickness ratio of ZS to CfZS (ZS/CfZS) and the fiber concentration on the flexural strength were investigated. The flexural strength of the laminated composites was improved compared to that of the single-composites and the improvement was enhanced with increase of the ZS/CfZS ratio. However, the flexural strength decreased with increasing the fiber concentration of CfZS. In addition, the crack propagation behavior of the laminated composites was examined under indent cracking. The results showed that the crack propagation behavior related to the fiber concentration of CfZS, irrespective of the layer thickness. The cracks induced by the indenter rapidly propagated through the CfZS layer when the fiber volume fraction was 10%. However, the cracks were arrested ahead the CfZS layers for the fiber volume fraction equal to or greater than 30%.

©2016 The Ceramic Society of Japan. All rights reserved.

Key-words : Zirconium diboride, Carbon fiber, Laminate composites, Flexural strength, Crack propagation behavior

[Received August 24, 2015; Accepted December 16, 2015]

1. Introduction

Zirconium diborides (ZrB_2)-based ceramics with SiC particles have high melting points, high thermal and electrical conductivities, high fracture strength, better oxidation, thermal shock and ablation resistance.¹⁾⁻⁹⁾ As a result, the unique combinations of mechanical and physical properties make them attractive candidates for a variety of high-temperature thermomechanical structural applications.^{10),11)} However, the use of those ceramics materials for high temperature structural applications is limited by their poor fracture resistance and high density as well as by degradation of strength at high-temperature.

To improve fracture resistance as well as to reduce weight of ZrB_2 -based ceramics with SiC, several ceramic fiber-reinforced ZrB_2 -SiC matrix composites are developed. The improved fracture toughness and lowered density due to addition of fibers are demonstrated in the short PAN-based carbon and/or SiC fibers-reinforced ZrB_2 matrix composites,¹²⁾⁻¹⁵⁾ resulting from the crack bowing, and crack deflection or bridging of fiber and low density of fiber. However, neither PAN-based carbon fiber nor SiC fiber is suitable for the thermomechanical structural applications above 1600°C due to their strength degradation. On the other hand, author showed that the flexural strength of the HfB₂- or ZrB_2 -SiC-based composites with pitch-based carbon fiber was significantly higher at 1600°C than at room temperature.^{16),17)} Unfortunately, the room-temperature flexural strength is significantly lower for the composites than for the monolithic ceramics. Hence, it is required for obtaining the composite material with high performance to improve the flexural strength. One of the most promising solutions is to fabricate a laminated composite.^{18),19)} The laminated approach has been successfully applied for ZrB_2 -SiC ceramics. For example, Zhou et al.²⁰⁾ showed that the fracture strength and toughness could be improved for the

laminated ZrB_2 -SiC ceramics prepared by alternately stacking compressive layers and tensile layers. However, improvement in the fracture strength of the laminated composites consisting of ZS ceramic and CfZS composite is not well-known.

In this study, laminated composites consisting of ZS and CfZS, having various distinct fiber concentrations and layer thickness ratios, were fabricated by hot pressing. The room-temperature flexural strengths of the resulting laminated composites were measured and the crack propagation behavior was examined. Also, the effects of the fiber concentration and the ZS/CfZS ratio on the flexural strength and crack propagation behavior were discussed.

2. Experimental procedure

The starting powders used in this study were: ZrB_2 (Grade O, Japan New Metals, Osaka), average particle size $\approx 2.12 \mu\text{m}$, α -SiC (UF-15, H.C. Starck, Berlin, Germany), average particle size $\approx 0.5 \mu\text{m}$, and pitch-based carbon fiber (XNG-90, Nippon Graphite Fiber Co., Himeji, Hyogo, Japan), average fiber length $\approx 0.5 \text{ mm}$. The ZrB_2 -20 vol % SiC mixture powder (ZS) and the short pitch-based carbon fiber-containing ZrB_2 -20 vol % SiC composites (CfZS) were prepared, respectively. The detailed fabrication procedure was previously reported elsewhere.²¹⁾ To examine the effects of fiber concentration of CfZS layer on the flexural strength and cracking behavior of the laminated composites, 10, 30 and 50 vol % carbon fibers-containing CfZS materials were used.

A hot-pressing apparatus with high-frequency heating was used herein to consolidate the laminated composites. The laminated composite green bodies were formed by sandwiching ZS and CfZS layers. Early study in the CfZS composites having various fiber concentrations showed that highly dense composite could be obtained at 2000°C and 20 MPa for 1 h.²¹⁾ Hence, to obtain highly dense samples, the laminated composite green bodies were heated to 2000°C under a pressure of 20 MPa in a flowing Ar atmosphere with a heating rate of $\sim 20^\circ\text{C}/\text{min}$. After

[†] Corresponding author: S. Q. Guo; E-mail: GUO.Shuqi@nims.go.jp

Table 1. Constituent composition, thickness of layer, number of layer and flexural strength of the laminated composites

Samples	Constituent composition (vol %)		Thickness of layer, h (mm)		Number of layer, n		Flexural strength σ_{fs} (MPa)
	ZS	CfZS	ZS	CfZS	ZS	CfZS	
L10ZSCF11	ZrB ₂ -20SiC	10CF-90(ZrB ₂ -20SiC)	0.2	0.2	6	5	466.3 ± 58.8
L10ZSCF21	ZrB ₂ -20SiC	10CF-90(ZrB ₂ -20SiC)	0.2	0.1	7	6	492.5 ± 40.7
L10ZSCF31	ZrB ₂ -20SiC	10CF-90(ZrB ₂ -20SiC)	0.3	0.1	5	4	522.4 ± 87.3
L30ZSCF21	ZrB ₂ -20SiC	30CF-70(ZrB ₂ -20SiC)	0.2	0.1	7	6	224.9 ± 19.9
L30ZSCF31	ZrB ₂ -20SiC	30CF-70(ZrB ₂ -20SiC)	0.3	0.1	5	4	290.7 ± 13.5
L50ZSCF21	ZrB ₂ -20SiC	50CF-50(ZrB ₂ -20SiC)	0.2	0.1	7	6	163.8 ± 28.4
L50ZSCF31	ZrB ₂ -20SiC	50CF-50(ZrB ₂ -20SiC)	0.3	0.1	5	4	210.2 ± 21.2

Fig. 1. FE-SEM micrographs of the microstructure for (a) L50ZSCF21, (b) L50ZSCF31, (c) ZS layer in L50ZSCF21, and (d) CfZS layer in L50ZSCF21.

the hot press was held at 2000°C for 60 min, the load was removed and the sample was cooled to 500°C with ~15°C/min, and the electric powder was then shut off. In order to examine the effect of the ZS/CfZS ratio on the flexural strength, the laminated composites with three distinct ratios were fabricated, as listed in Table 1. The microstructure of the resulting laminated composites was observed by field emission scanning electron microscopy (FE-SEM).

Specimens averaging 25 mm × 2.5 mm × 2 mm in size were cut from the hot-pressed plates, with the tensile surface perpendicular to the hot-pressing direction, by using a diamond grinding wheel. The flexural strength of the specimens was measured using a four-point bending test fixture (inner span 10 mm and outer span 20 mm) at room temperature. The bending tests were performed using an Autograph testing system (AG-X/R, AG-100KND, Shimadzu, Kyoto, Japan) with a crosshead speed of 0.5 mm/min. The loading direction used for the bend test is parallel to the hot-pressing direction, i.e. perpendicular to the aligned layers of the laminated composites. At least 5 specimens were used for each measurement. After the bending tests, the fracture surfaces of the samples were observed by FE-SEM. Additionally, in order to examine crack propagation behavior,

Vickers indentations were performed by indenting the polished surface of the specimens for 15 s under a load of 98 N (AVK-A, Akashi, Co., Ltd., Yokohama, Japan).

3. Results and discussion

Figure 1 shows the FE-SEM micrographs of the microstructures for the laminated composites. It is found that the ZS layers and CfZS layers are well-alternately presented in the resulting laminated composites [Figs. 1(a) and 1(b)]. Very good bond is observed in the ZS layer and at the ZS/CfZS boundary for all the samples, in absence of cracks. Under higher-magnification FE-SEM observations, the ZS layer shows a homogeneous and fine grain microstructure in which the equiaxed ZrB₂ (brighter contrast) and SiC (dark contrast) grains were uniformly dispersed [Fig. 1(c)]. For the CfZS layer, in the case of 10 vol % fibers, no defects are observed. However, some pores were observed in the clumps of fibers [indicated by arrows in Fig. 1(d)] when the fiber volume fraction was equal to or greater than 30%. Early study in the CfZS materials showed that the pores existed in the samples with equal to or greater than 30 vol % fibers,²¹⁾ as a result of the hindering effect of fibers on the densification of matrix. Similar cause is expected for the laminated composites investigated in

this study.

Figure 2 shows the four-point flexural strengths of the laminated composites and the CfZS samples. It is found that the flexural strength of the CfZS strongly depended on the fiber concentration and it significantly decreased with increase of the fiber concentration. Approximate 48, 66 and 74% reductions in the flexural strength were obtained for 10, 30 and 50 vol% carbon fiber-containing CfZS, compared to that of the monolithic ZS. Similar effect of the fiber concentration on the flexural strength was previously reported in the pitch-based carbon fiber-reinforced HfB₂-20 vol% SiC matrix composites.¹⁶⁾ The reduction in the strength due to addition of fibers was associated with the presence of defects (pores and clumps of fibers) and the residual tensile internal stress induced in the matrix by the thermal expansion misfit between the fiber and the matrix as well.¹⁶⁾

On the other hand, the flexural strength of the laminated composite is always larger than that of the CfZS, but it is lower than that of the ZS, in carbon fiber concentration ranging from 10 to 50 vol%. In addition, the magnitude of the flexural strength is not only related to the fiber concentration, but also to the ZS/CfZS ratio. In the case of 10 vol% fibers, the flexural strength of the laminated composites was significantly improved compared to that of the CfZS, corresponding increase of approximate 62% for ZS/CfZS = 3, 52% for ZS/CfZS = 2 and 44% for ZS/CfZS = 1. It is evident that the improvement of the strength was enhanced with increasing the ZS/CfZS ratio. The magnitude of the strength is close to the level of the ZS. For the laminated composites with the CfZS equal to or greater than 30 vol% fibers, on the other hand, the flexural strength is close to the level of the

CfZS materials. Significant improvement of the strength is observed for the laminated composites with ZS/CfZS = 3. In the case of ZS/CfZS = 2, however, only slight improvement of the strength is detectable and the magnitude of the strength is very close to the level of the CfZS.

It is well-known that residual internal stresses in the laminated composites develop during cooling from the sintering temperature to room temperature because of the difference in thermal expansions between layers of different compositions. In the present study, because thermal expansion coefficient of the pitch-based carbon fiber is approximately equal to zero, thus the thermal expansion coefficient is lower for the CfZS than for the ZS. This suggests that the residual tensile stresses and compressive stresses are produced in the ZS layer and the CfZS layer, respectively, upon cooling. Because there is perfectly rigid bonding between the ZS layers and the CfZS layers and the symmetrical and periodic structure for the studied laminated composites [Figs. 1(a) and 1(b)], in the case of an in-plane stress state with the stress normal to the surface equal to zero, thus the residual internal stress induced in each layer of the laminated composite is given by the following equations,²²⁾

$$\sigma_{rs1} = -\frac{nE_1E_2h_2(\alpha_2 - \alpha_1)\Delta T}{n(1 - \nu_1)E_2h_2 + (n + 1)(1 - \nu_2)E_1h_1} \quad (\text{In ZS layer}) \quad (1)$$

$$\sigma_{rs2} = \frac{(n + 1)E_1E_2h_1(\alpha_2 - \alpha_1)\Delta T}{n(1 - \nu_1)E_2h_2 + (n + 1)(1 - \nu_2)E_1h_1} \quad (\text{In CfZS layer}) \quad (2)$$

where E_1 , E_2 , α_1 , α_2 , ν_1 , ν_2 , h_1 , and h_2 are the Young's modulus, thermal expansion coefficient, Poisson's ratio and thickness of the ZS layer and the CfZS layer, respectively. The Young's modulus and Poisson's ratio of the ZS ceramic and the CfZS composite are measured by using an ultrasonic technique which was reported elsewhere.²³⁾ The thermal expansion coefficient of the ZS is $7.18 \times 10^{-6}/\text{K}$.²⁴⁾ In addition, the thermal expansion coefficient of the CfZS is calculated according to rule of mixture where the thermal expansion coefficient of pitch-based carbon fiber is approximately equal to zero. ΔT and n are the difference of temperature between room temperature and the hot-pressing temperature ($\Delta T = 1975^\circ\text{C}$) and the number of CfZS layer (Table 1), respectively. The Young's modulus, Poisson's ratio, thermal expansion coefficient of constituting materials and the calculated residual internal stresses in each layer for the laminated composites are summarized in **Table 2**. It is evident that the magnitude of the residual internal stresses depends on the ZS/CfZS ratio and on the fiber content as well. The compressive stress in the CfZS layer increases when the ZS/CfZS ratio increases, whereas the tensile stress in the ZS layer decreases. In

Fig. 2. A comparison of flexural strengths of the laminated composites with different fiber volume fractions and the thickness ratios of ZS layer to CfZS layer.

Table 2. Young's modulus, Poisson's ratio, thermal expansion coefficient of constituting materials and the residual internal stresses calculated in ZS layer and CfZS layer for the laminated composites

Samples	Young's modulus, E (GPa)		Poisson's ratio, ν		Thermal expansion coefficient, α ($10^{-6}/\text{K}$)		Residual internal stress, σ_{rs} (MPa)	
	ZS	CfZS	ZS	CfZS	ZS	CfZS	ZS	CfZS
L10ZSCF11	510	384	0.144	0.134	7.18	6.46	324	-389
L10ZSCF21	510	384	0.144	0.134	7.18	6.46	204	-478
L10ZSCF31	510	384	0.144	0.134	7.18	6.46	140	-526
L30ZSCF21	510	194	0.144	0.126	7.18	5.02	349	-816
L30ZSCF31	510	194	0.144	0.126	7.18	5.02	229	-861
L50ZSCF21	510	94	0.144	0.041	7.18	3.59	278	-649
L50ZSCF31	510	94	0.144	0.041	7.18	3.59	177	-665

Fig. 3. Typical FE-SEM micrographs of the fracture surfaces for the laminated composites-containing CfZS layers with different fiber volume fractions; (a) L10ZSCF21, (b) L30ZSCF21, (c) and (d) L50ZSCF21.

addition, these stresses increase with increasing the fiber content of CfZS layer. One exception is the decreases of the residual internal stresses for the laminated composite with CfZS of 50 vol % fibers due to very low Poisson's ratio (Table 2).

The effect of internal stresses which developed within the individual layers upon cooling on the rupture strength is well documented in the literature. Chartier et al.²²⁾ showed the tensile internal stress overlaps the applied stress, leading to a strength lower than the strengths of the constitutive materials of the laminar ceramic composites when the rupture is initiated from internal defects located in the outer layer in tension. Wang et al.²⁵⁾ examined the effects of the residual internal stresses on the flexural strength of laminar ceramic composites composing of ZrB_2 outer layer and SiC interlayer by means of change interlayer composition. They concluded that the combination of low tensile stress in the ZrB_2 layer and high compressive stress in the SiC interlayer led to a relative high strength and the presence of pores in the SiC layer led to reduction of the strength. In the present study, for the laminated composites with CfZS layers of 10 vol % fibers, the superposition of the measured strengths and the internal stress in the ZS layer is approximately close to the level of the strength of the ZS ceramic (Tables 1, 2 and Fig. 2). Presumably, the tensile internal stress in the ZS layer overlaps the applied stress, leading to the rupture strength lower than the strength of the ZS ceramic of the laminated composites (Fig. 2). For the laminated composites with CfZS layers equal to or greater than 30 vol % fibers, however, the superposition of the measured strengths and the internal stress in the ZS layer is lower than the strengths of the ZS ceramic. In particular, for the laminated composites with $\text{ZS/CfZS} = 2$, the superposition of the measured strengths and the internal stress in the ZS layer is significantly lower than the strength of the ZS ceramic. The discrepancy seems to be associated with the remarkable low strength of the CfZS (Fig. 2) and the presence of defects in the CfZS layer

[Fig. 1(d)]. Early study in laminar material consisting of stronger outer layers and weaker interlayers with symmetrical and periodic structure showed that the weaker component is always facing stresses on the level which is very close to the level of maximal stress applied.²⁶⁾ As a result, the flexural strength of the laminar material keeps the level of strength of the weaker component and only small improvement is detectable with increasing level of compressive stresses increase. Similar behavior is observed in the present laminated composites with the CfZS layers equal to or greater than 30 vol % fibers.

Moreover, it is known that the flexural strength of materials generally is lower at high temperature than at room temperature. Early studies in ZrB_2 -SiC ceramics showed that the flexural strength decreased with increasing temperature.^{1),2)} Differing with the ZrB_2 -SiC ceramics, previous studies in ZrB_2 - and/or HfB_2 -20 vol % SiC based-composites with 10–50 vol % pitch-based carbon fibers showed that the flexural strengths at 1600°C increased by a factor of ~ 2 compared to room-temperature strength.^{16),17)} In addition, recent study in ZrB_2 -20 vol % SiC ceramics demonstrated that the high-temperature flexural strength was improved up to 1600°C by adding 5 vol % WC, compared to room-temperature flexural strength.²⁷⁾ Furthermore, previous study in the laminated ceramic composite consisting of stronger outer layers and weaker interlayers showed that the flexural strength and fracture toughness are close to the properties of the weaker layer.²⁶⁾ In the present study, the room-temperature strength of the laminated composites is close to or greater than that of the weaker layer (CfZS). Although, not well-known, it could be expected that the laminated composites should have an improved high-temperature flexural strength compared to room-temperature flexural strength by designing the stronger ZS outer layer at high temperature, and further detailed investigation is needed.

The fracture surfaces of the laminated composites were examined under FE-SEM; typical micrographs are shown in

Fig. 4. Indentation cracks in the laminated composites show crack propagation across CfZS layer for (a) L10ZSCF21, cracks arrested ahead CfZS layer for (b) L30ZSCF21 and (c) L50ZSCF21, and (d) crack deflection and fiber bridging in CfZS layer for L30ZSCF21 where cracks indicated by arrows.

Figure 3. The fracture surface is stepped across the thickness. In particular, for the samples with the CfZS layers equal to or greater than 30 vol% fibers, a more stepped fracture surface is observed [Figs. 3(b) and 3(c)]. The occurrence of the stepped fracture surface suggests that the fracture behavior of the CfZS layer differed with that of the ZS layer. Under higher-magnification [Fig. 3(d)], the CfZS layer shows the jagged fracture surface with fiber pullout, as a result of the crack deflection and the interface debonding. For comparison, the ZS layer shows the flat fracture surface with the typical intragranular fracture.

The crack propagation behavior in the laminated composites was examined by FE-SEM observations of the indents induced by the Berkovich indenter under a load of 98 N; typical micrographs are shown in **Figure 4**. It is found that the crack propagation behavior depended on the fiber concentration. For the sample with the CfZS of 10 vol% fibers, the cracks induced in the ZS layer directly entered the neighbor ZS layer through the CfZS layer [Fig. 4(a)], in absence of crack deflection. This suggests that the CfZS layer with 10 vol% fibers is inefficient for hindering crack propagation. This crack propagation behavior led to the relative flat fracture surface of the laminated composite [Fig. 3(a)]. For comparison, for the samples with CfZS layers equal to or greater than 30 vol% fibers, the cracks were arrested ahead the CfZS layers [Figs. 4(b) and 4(c)] and did not enter the neighbor ZS layer. This behavior indicated that the presence of the CfZS layers is effective for hindering crack propagation in the laminated composites. Further observations exhibited the crack deflection behavior at the fiber/matrix interface and the fiber bridging behavior [Fig. 4(d)].

4. Summaries

Laminated composites consisting of ZS ceramic layers and CfZS composite layers were fabricated by hot-pressing. The

flexural strength of the laminated composites was investigated and compared to that of the CfZS composites. The strength was higher for the laminated composites than for the single CfZS composites. The strength of the laminated composites increased with increasing the ZS/CfZS ratio, however, the strength decreased with increase of the fiber concentration of the CfZS layer. On the other hand, the crack propagation behavior in the laminated composites depended on fiber concentration of the CfZS layer, irrespective of the layer thickness. The CfZS layer containing 10 vol% fibers was ineffective for hindering crack propagation. In contrast, the cracks were arrested ahead the CfZS layers for the laminated composites containing CfZS layers equal to or greater than 30 vol% fibers.

References

- 1) W. G. Fahrenholtz, G. E. Hilmas, I. G. Talmy and J. A. Zaykoski, *J. Am. Ceram. Soc.*, **90**, 1347–1364 (2007).
- 2) S. Q. Guo, *J. Eur. Ceram. Soc.*, **29**, 995–1011 (2009).
- 3) W. C. Tripp, H. H. Davis and H. C. Graham, *Am. Ceram. Soc. Bull.*, **52**, 612–616 (1973).
- 4) F. Monteverde, *Appl. Phys. A: Mater. Sci. Process.*, **82**, 329–337 (2006).
- 5) F. Monteverde and A. Bellosi, *Solid State Sci.*, **7**, 622–630 (2005).
- 6) A. L. Chamberlain, W. G. Fahrenholtz and G. E. Hilmas, *J. Am. Ceram. Soc.*, **87**, 1170–1172 (2004).
- 7) A. Rezaie, W. G. Fahrenholtz and G. E. Hilmas, *J. Mater. Sci.*, **42**, 2735–2744 (2007).
- 8) S. Zhu, W. G. Fahrenholtz and G. E. Hilmas, *J. Eur. Ceram. Soc.*, **27**, 2077–2083 (2007).
- 9) S. Q. Guo, J.-M. Yang, H. Tanaka and Y. Kagawa, *Compos. Sci. Technol.*, **68**, 3033–3040 (2008).
- 10) E. Wuchina, E. Opila, M. Opeka, W. Fahrenholtz and I. Talmy, *Interface*, **16**, 30–36 (2007).

- 11) A. Paul, D. D. Jayaseelan, S. Venugopal, E. Zapata-Solvas, J. Binner, B. Vaidhyanathan, A. Heaton, P. Brown and W. E. Lee, *Am. Ceram. Soc. Bull.*, **91**, 22–29 (2012).
- 12) F. Yang, X. Zhang, J. Han and S. Du, *Mater. Des.*, **29**, 1817–1820 (2008).
- 13) F. Yang, X. Zhang, J. Han and S. Du, *J. Alloys Compd.*, **472**, 395–399 (2009).
- 14) H. Hu, Q. Wang, Z. Chen, C. Zhang, Y. Zhang and J. Wang, *Ceram. Int.*, **36**, 1011–1016 (2010).
- 15) D. Sciti, S. Guicciardi and L. Silvestroni, *Scr. Mater.*, **64**, 769–772 (2011).
- 16) S. Q. Guo, K. Naito and Y. Kagawa, *Ceram. Int.*, **39**, 1567–1574 (2013).
- 17) Y. Kagawa and S. Q. Guo, Ultrahigh Temperature Ceramic-Based Composites. In: N. P. Bansal and L. Lamon, editor. *Ceramic Matrix Composites: Materials, Modeling and Technology*, The American Ceramic Society, John Wiley & Sons, Inc., III River Street, Hoboken, NJ07030, USA (2014) pp. 273–292.
- 18) R. Lakshminarayanan, D. K. Shetty and R. A. Cutler, *J. Am. Ceram. Soc.*, **79**, 79–87 (1996).
- 19) M. P. Rao, A. J. Sanchez-Herencia, G. E. Beltz, R. M. McMeeking and F. F. Lange, *Science*, **286**, 102–105 (1999).
- 20) P. Zhou, P. Hu, X. H. Zhang and W. B. Han, *Scr. Mater.*, **64**, 276–279 (2011).
- 21) S. Q. Guo, *Ceram. Int.*, **39**, 5733–5740 (2013).
- 22) T. Chartier, D. Merle and J. L. Besson, *J. Eur. Ceram. Soc.*, **15**, 101–107 (1995).
- 23) S. Q. Guo, N. Hirotsaki, Y. Yamamoto, T. Nishimura and M. Mitomo, *J. Eur. Ceram. Soc.*, **23**, 537–545 (2003).
- 24) R. Loehman, E. Corral, H. P. Dumm, P. Kotula and R. Tandon, Ultra high temperature ceramics for hypersonic vehicle applications. Sandia report: 2006. Sand 2006-2925.
- 25) H. Wang, B. Fan, L. Feng, D. Chen, H. Lu, H. Xu, C.-A. Wang and R. Zhang, *Ceram. Int.*, **38**, 5015–5022 (2012).
- 26) Z. Chlup, H. Hadraba, L. Slabakova, D. Drdlik and I. Dlouhy, *J. Eur. Ceram. Soc.*, **32**, 2057–2061 (2012).
- 27) J. Zou, G.-J. Zhang, C.-F. Hu, T. Nishimura, Y. Sakka, J. Vleugels and O. Van der Biest, *J. Am. Ceram. Soc.*, **95**, 874–878 (2012).