Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 28 (2008) 1105–1109

www.elsevier.com/locate/jeurceramsoc

Boron nitride (BN) and BN composites for high-temperature applications

Jens Eichler*, Christoph Lesniak

ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Straße 25, D-87437 Kempten, Germany

Abstract

Hexagonal boron nitride (h-BN) is a very versatile material that can be used in a number of applications due to its unique combination of properties. This paper reviews typical h-BN qualities and their applications. The use of h-BN as a composite material with zirconium oxide for side dams in thin-strip casting is looked at in particular detail. Recent results for corrosion, wear and high-temperature compressive stress of MYCROSINT® SO are presented here for the first time.

Keywords: Boron nitride; Composites; Refractories

1. Introduction

ESK Ceramics GmbH & Co. KG, a subsidiary of Ceradyne Inc., develops and manufactures pioneering products in the fields of advanced ceramics, ceramic powders and frictional coatings. One of the main products of ESK is hexagonal boron nitride (h-BN). BN can be used as powders, coatings or in its sintered form either as pure BN or as a composite. Although it was first synthesized by W.H. Balmain from boric acid and calcium cyanide in 1842, it took until the 1940s before it gained limited economical significance. Process improvements have led to more economical and higher quality BN qualities. This very versatile material is now used in a number of applications (e.g. metallization, the metal industry, cosmetics, the automotive industry, high-temperature furnaces, thermal management, etc.).[1,2] This paper concentrates on h-BN-sintered parts. A detailed description of the applications and properties of h-BN coatings has been reported elsewhere.[3]

The physical properties of BN are mostly governed by its atomic structure. BN is isoelectronic with carbon, and therefore h-BN is also known as “white graphite”. A high-pressure diamond-like modification with a cubic zinc-blende structure is also known,[1,2] but will not be further described here. h-BN consists of a layered structure comprising a network of $(BN)_3$ rings. Whereas graphite has metallic conductivity, boron nitride is an insulator. This is due to the covalent inter-layer bonding of the boron and nitrogen atoms, which localize the free electrons. This also explains the different colours of graphite (black) and boron nitride (white).

The hexagonal BN layers are bonded by weak van der Waals forces, which enables the layers to slide easily against each other. Therefore, h-BN is used as a solid lubricant or release agent either as a sintered body (e.g. side dams) or applied as suspensions or powders (e.g. aluminium extrusion or titanium shaping). The poor wettability by many glass and metal melts is another advantage of h-BN for these applications. Liquid aluminium does not wet h-BN up to 900 °C (contact angle ∼160°). BN-coatings (EKamold®) are therefore widely used in the aluminium casting industry due to their excellent release and lubrication properties.[3] Other important properties of boron nitride are its high-temperature resistance, thermal shock resistance, high-thermal conductivity, its chemical inertness, non-toxicity and environmental safety.[1,2,4] The weak inter-layer bonding also enables all sintered BN-materials to be easily machined to produce complex shapes from the hot-pressed billets.

BN-sintered parts are generally produced by pressure-assisted sintering (hot pressing or hot isostatic pressing). The densification mechanism can be described as vitreous sintering. Small amounts of boron oxide (B_2O_3) function as the liquid phase during sintering and as a binder for the BN platelets. In contrast to some other non-oxide ceramics, there is no solution

---

* Corresponding author. Tel.: +49 831 5618 508; fax: +49 831 5618 8508.
E-mail address: JEichler@esk.com (J. Eichler).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.09.005

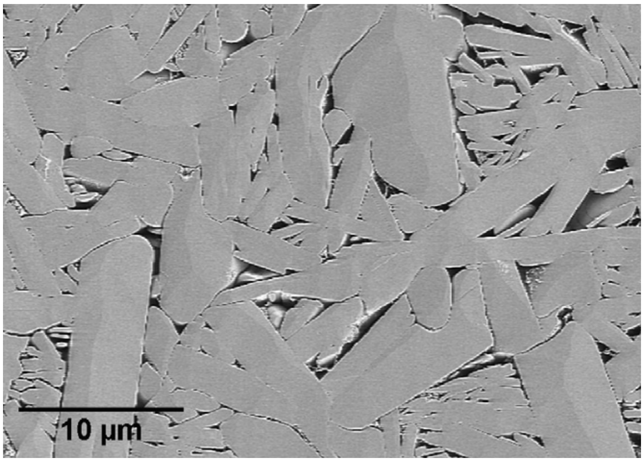

Fig. 1. SEM micrograph of hot-pressed h-BN (MYCROSINT® S) with >94% relative density by ion polishing showing h-BN crystallites. Boric oxide was removed during polishing, forming the voids visible in the micrograph.

and precipitation process known for the sintering of BN. Fig. 1 shows a SEM micrograph of a hot-pressed BN material. The procedure has previously been described elsewhere.[5] The B_2O_3 binder phase was removed during the sample preparation process which explains the porous appearance of the material, while in fact it has a density of >94% compared to the theoretical density. The BN grains are well defined and limited contacts are visible between the grains.

2. BN qualities and their applications

MYCROSINT® S with boron oxide as the binder phase for BN is used as a sealing element in oxygen sensors (lambda sensors) for the automotive industry. For modern engine control the exact composition of the exhaust gases has to be known. Lambda sensors measure the oxygen content in the exhaust gas compared to a reference concentration.[6] A difference between the two oxygen concentrations leads to a change in voltage of the sensing element. This signal is transferred to the engine control, which adjusts the fuel/air mixture accordingly. In order to measure the concentration difference, the exhaust and reference chambers have to be separated by a sealing element.[7] The material for the sealing element also has to be an electrical insulator, high-temperature stable and suitable for the lambda sensor fabrication process. One of the two components of the gas seal is h-BN ring made of MYCROSINT® S.

In order to reduce the moisture sensitivity of the binder phase, calcium oxide is added to form a calcium borate binding phase (MYCROSINT® CD).[8] Both materials are stable at temperatures up to 1500 °C in an inert atmosphere. MYCROSINT® CD is used as spanker plates for the production of TV tubes and

Table 1
Typical properties of MYCROSINT® materials

			Boron Nitride										
Material properties	Norm	Symbol/Unit	MYCROSINT® HD	MYCROSINT® S		MYCROSINT® CD		MYCROSINT® SO20		MYCROSINT® SO43		MYCROSINT® O40	
Crystalline phases			hex. BN	hex. BN		hex. BN		$BN+ZrO_2+SiC$		$BN+ZrO_2+SiC$		$BN+ZrO_2$	
Binder phase/Binder type			< 1 % B_2O_3	4 % B_2O_3		$B_2O_3 + CaO$						2 % B_2O_3	
Orientation dependency			Isotropic	Anisotropic		Anisotropic		Anisotropic		Anisotropic		Anisotropic	
				⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥
Density (typical)	DIN EN 623-2	ρ [g/cm³]	1,96	2,07	2,07	1,97	1,97	2,3	2,3	2,92	2,92	2,82	2,82
Total porosity (calculated using theoretical density)	DIN EN 623-2	P [%]	< 13	< 7	< 7	< 12	< 12	10	10	< 6	< 6	< 6	< 6
Brinell hardness	DIN EN ISO 6506-1	HBW2,5/ 31,25	10	30	30	13	13	30	30	85	85	63	63
Young's modulus	DIN EN 843-2	E [GPa]	23	35	30	30	25	35	20	45	30	45	25
Flexural strength	DIN EN 843-1	σ_B [MPa]	19	95	85	40	35	70	40	120	80	120	80
Weibull modulus	DIN EN 843-1												
Compressive strength	AAW/ AC-R-302-03	σ_D [MPa]	36	105	125	50	55	85	100	175	175	185	185
Coefficient of thermal expansion	DIN EN 821-1			Thermal expansion behavior: nonlinear, residual elonation after cooling; CTE given indication only									
20 °C - 500 °C		α [10^{-6}/K]	-1	1	2	-1	-1	0,5	4,6	2	8	2	6
500 °C - 1000 °C		α [10^{-6}/K]	0,5	1	2	1,5	2	1,9	6,6	4	9	3,5	9
1000 °C - 1500 °C		α [10^{-6}/K]	2,5	1	5	3	4	0,5	2,2	1,4	4,5	1,5	8
Specific heatm at 20 °C	DIN EN 821-3	C_p [J/g K]	0,61	0,6	0,6	0,58	0,58	0,6	0,6	0,5	0,5	0,5	0,5
Thermal conductivity at 20 °C	DIN EN 821-2	λ [W/m K]	25	40	25	35	35	45	25	40	30	30	20
Maximum temperature of use (oxidizing/inert atmosphere)		[°C]	900/1800	1000/ 1500	1000/ 1500	1100/ 1500	1100/ 1500	1100/ 1800	1100/ 1800	1100/ 1800	1100/ 1800	1100/ 1800	1100/ 1800
Specific electrical resistance at 20 °C	DIN EN 50359	ρ [Ω cm]	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$	$>10^{12}$

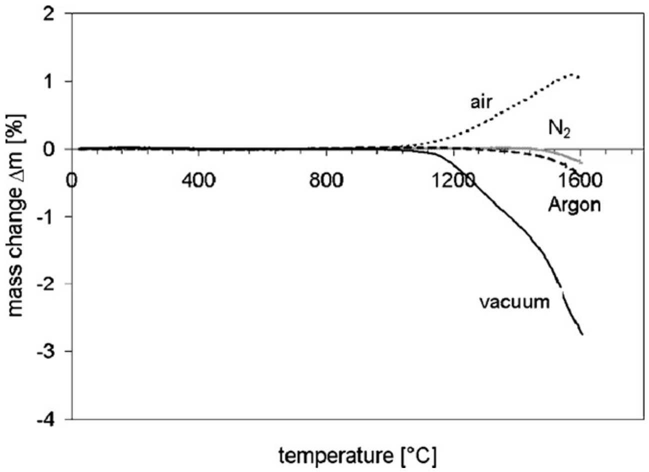

Fig. 2. Thermogravimetric analysis of MYCROSINT® CD up to 1600 °C under different atmospheric conditions.

as components for the glass industry. If produced by hot isostatic pressing (MYCROSINT® HD) the boron oxide content can be reduced for conditions in which high-temperature stability (up to 1800 °C) or high purity is required (e.g. insulators for HT furnaces). Electrical insulators for high-temperature applications (e.g. furnaces) and crucibles for molten glass or metals are made from this material. Table 1 gives an overview of the properties of the MYCROSINT® materials.

Fig. 2 shows a thermogravimetric measurement (Netzsch STA 429) of MYCROSINT® CD up to 1600 °C as an example of the degradation of BN. At about 1100 °C h-BN oxidizes to form boric oxide. Around 1500 °C, degradation starts in an inert atmosphere. In order to further investigate the degradation process in an inert atmosphere, samples heat treated at 1800 °C in argon were subsequently analysed by electro paramagnetic resonance (Fig. 3). An EPR spectrometer (Bruker ESP 300 E) with an X-band microwave frequency of 9.4 GHz, microwave power of 1 mW, modulation frequency of 100 kHz and modulation amplitude of 0.5 mTorr was used at room temperature and 10 °C. From Fig. 3, the spin concentration was calculated and increased from $\sim 10^{16}$ spins/mg for the as-sintered specimen to 5.2×10^{18} spins/mg for the heat-treated specimen. Katzir et al.[9] showed that the spin concentration is a measure of the nitrogen vacancy concentration of h-BN. The spin concentration measurement by EPR can therefore be used to quantify the degradation of the BN lattice in an inert atmosphere. The change in optical appearance from white for the as-hot-pressed h-BN to yellowish for the heat-treated h-BN specimen can therefore be related to the formation of nitrogen vacancies.

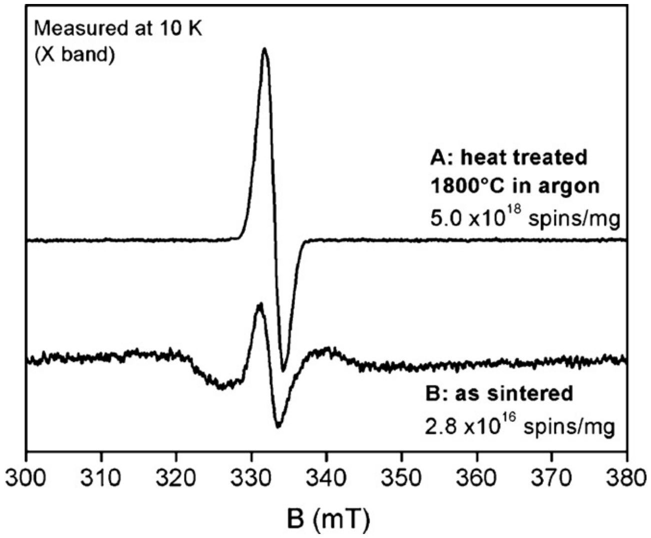

Fig. 3. Electro paramagnetic resonance measurement of (A) a specimen heat-treated at 1800 °C in argon and (B) a hot-pressed specimen of h-BN.

3. BN composite for the steel industry

Due to its unique combination of properties BN is an excellent material for applications in the steel and non-ferrous metals industry. As a composite with monoclinic zirconia, BN-based materials are used in steel production as a side-dam material for thin-strip casting as well as a break ring for horizontal continuous casting (MYCROSINT® O and MYCROSINT® SO). It is known that pure monoclinic zirconia (m-ZrO_2) undergoes a phase transition during heating from tetragonal to monoclinic at about 1170 °C which leads to catastrophic failure of the m-ZrO_2 body.[10] The combination with h-BN enables crack free production of the composite, which underscores the thermal shock resistance of h-BN.

Production of hot strip by the conventional continuous casting route requires reheating and roughing of continuously cast slabs (150–250 mm) by two high roughing mills into sheet bar (30–60 mm) followed by hot rolling of the sheet bar by a tandem strip mill or steckel mill into a strip of the target thickness. Recent thin-strip casting technology has made it possible to eliminate the roughing mills and reduce the number of roll stands in the tandem strip mill. Once perfected, this process will offer huge energy savings up to 85%, reduction of emissions by over 70% and capital cost savings over conventional casting and rolling processes for producing steel sheet products.

The process of thin-strip casting was first developed by Sir Henry Bessemer in 1856. Since process technology and suitable refractory materials were not available at the time, realization on an industrial scale was not possible. At the beginning of the 1980s, the process was reinvented and has been developed for market introduction in recent years. Steel sheets of less than 2 mm in thickness are now possible with this new process.

Fig. 4 shows a schematic of the thin-strip caster with the side dams attached. Common to all thin-strip casters is a reservoir of molten steel which is formed by two counter-rotating water-cooled metal rollers and two boron nitride composite side dams. The solidification of the steel melt first takes place at the two cooled rollers. The two separate sheets are transported by the two rollers and joined. The advantages over the process of slab casting, which is currently used, are energy savings and a decrease in the overall length of the facility from 400 m to 800 m for the current process down to 60 m for thin-strip casting.

The two side dams are stressed mechanically (pressed against the rollers), by corrosion (due to contact with liquid steel), by wear (contact with copper rollers and steel strip) and by thermal

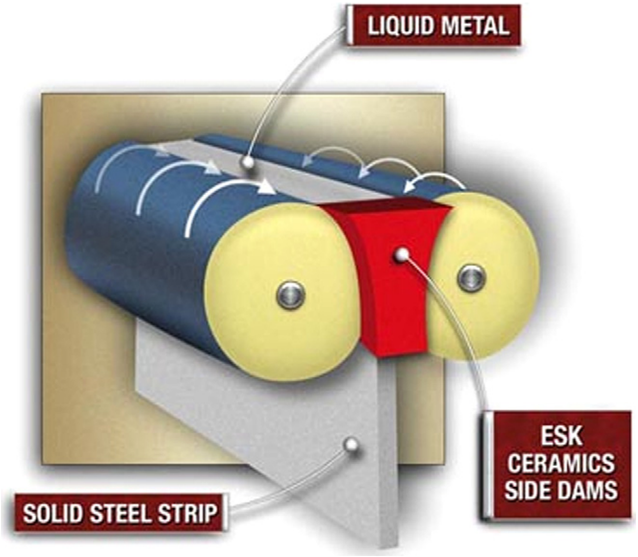

Fig. 4. Schematic of thin-strip caster with ESK side dam.

shock (initial contact with liquid steel). The side dams also have to seal the sides of the rollers with respect to the molten steel. Currently the material best suited for this very demanding combination of properties is MYCROSINT® SO (see Table 1). This composite contains boron nitride, monoclinic zirconia and silicon carbide. Fig. 5 shows an SEM micrograph of this material prepared by ion polishing.

Corrosion resistance was tested by melting steel 1.4308 in a crucible made of MYCROSINT® SO at 1600 °C in an argon atmosphere. The micrograph in Fig. 6 shows that no slag penetrated the surface of MYCROSINT® SO and no sticking occurred during the test. No corrosion was found at the grain boundaries. Corrosion is not a limiting factor in the use of MYCROSINT® SO for thin-strip casting.

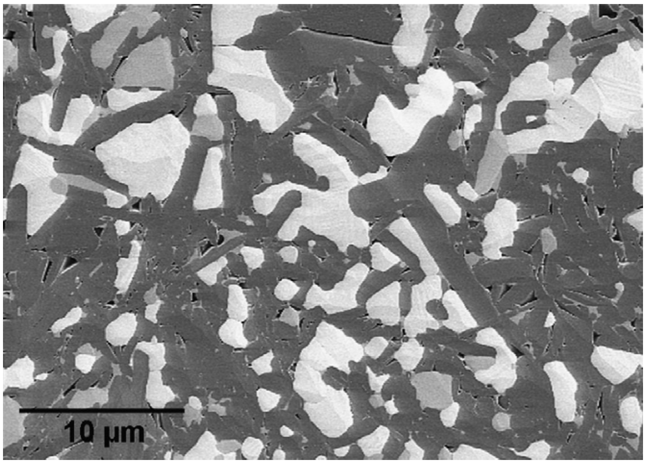

Fig. 5. SEM micrograph of MYCROSINT® SO showing the three composite phases hexagonal boron nitride (dark), monoclinic zirconia (white) and silicon carbide (grey).

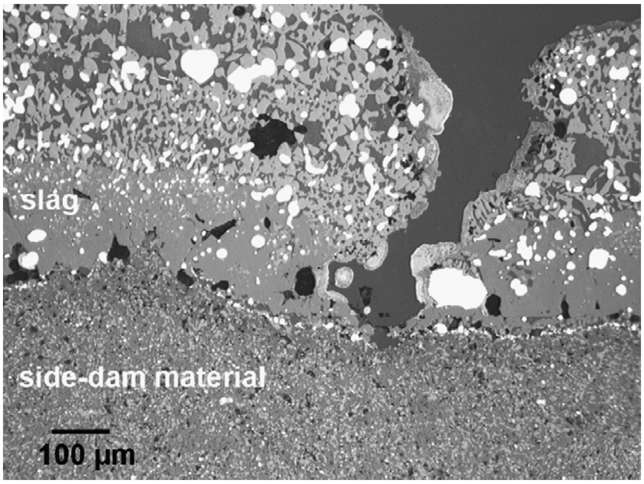

Fig. 6. Micrograph of corrosion test with 1.4308 steel (upper part) on h-BN (lower part). No penetration of the slag into the h-BN material is observed.

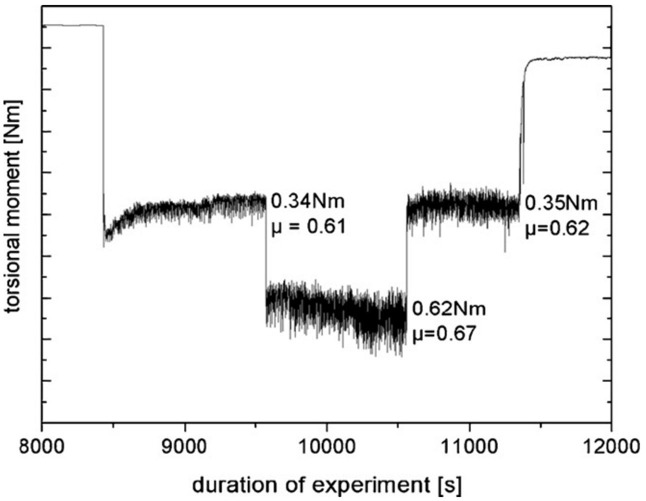

Fig. 7. Tribological testing of MYCROSINT® SO for two different loads. Results by DIFK (Deutsches Institut für Feuerfestkeramik).

In order to test the wear resistance of MYCROSINT® SO under conditions comparable to the thin-strip casting process, a setup at the DIFK (Deutsches Institut für Feuerfestkeramik, Bonn) was used. A metal body was rotated against a MYCROSINT® SO part while both were heated to 300 °C in a furnace attached to the wear-tester. Fig. 7 shows initial results comparing the friction parameters μ (0.61 and 0.67) and wear rates for two different loads. The wear surface shows textured grooves brittle fracture and microplastic deformation.

Reliable mechanical properties at the operating temperature are an important factor in the use of MYCROSINT® SO for thin-strip casting. Compressive fracture strength tests at 1500 °C were performed at the Technical University of Darmstadt. The compressive stress at this temperature is around 60 MPa, which is about half the compressive stress at room temperature.

4. BN composite for the metallizing industry

For the metallizing industry BN/titanium diboride (TiB_2) and aluminium nitride (AlN) composites (Fig. 8) are used as evaporation boats for aluminium (LaserMet®, EllipsoMet®, DiMet® and TriMet®). h-BN has been used for this application now for

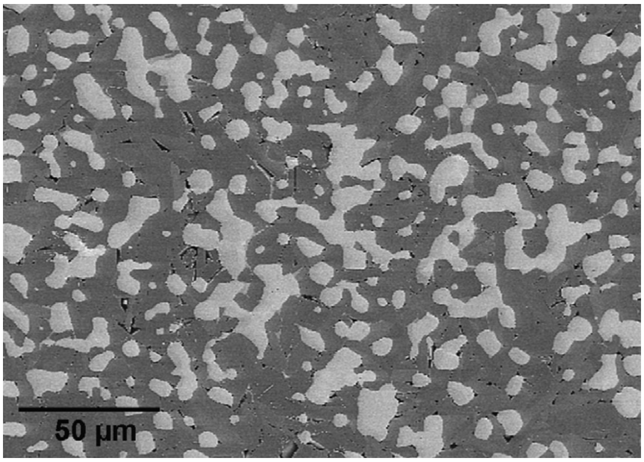

Fig. 8. SEM micrograph of evaporation boat material showing the two composite phases hexagonal boron nitride (dark) and titanium diboride (white).

more than 30 years, making this the oldest commercial application of h-BN. Despite continuing research to find a replacement for h-BN, due to its high materials costs and low sinterability, no alternative has been found, yet. The good thermal conductivity, thermal shock resistance and corrosion resistance of boron nitride are the key properties for this application.

Evaporation boats are heated by direct electrical continuity with TiB_2 as the electrical conductor. The electrical resistance is adjusted by the h-BN/TiB_2 composition. In a vacuum chamber the aluminium on the boat surface melts and evaporates at about 1600 °C. Aluminium deposits onto a plastic film, which is guided through the aluminium vapour. Typical applications for these aluminium-coated films are film capacitors for electronic devices and the food packaging industry.

5. Conclusions

Hexagonal boron nitride, either in its pure form or as a composite, is an extremely suitable material for special applications at high temperatures. Gas seals for oxygen sensors, parts for high-temperature furnaces, crucibles for molten glasses and metals, side dams for thin-strip casting and evaporation boats for aluminium are the most common applications.

New results are presented on the high-temperature properties of h-BN. Electro paramagnetic resonance is used as a measure of the degradation in an inert atmosphere. MYCROSINT® SO, a BN/m-ZrO_2-composite was analysed for its corrosion resistance with liquid steel, wear behaviour at elevated temperatures and high-temperature compressive strength. All results showed, that MYCROSINT® SO is suitable for use as a side dam for thin-strip casting.

Acknowledgments

The authors would like to thank Dr. Sören Höhn of IKTS Dresden, Germany for the ion sample preparation and for providing SEM micrographs of all the boron nitride materials and composites presented in this paper. The electro paramagnetic resonance (EPR) measurements were provided by Dr. R.-A. Eichel, Physical Chemistry II at the Technical University of Darmstadt, Germany. Wear resistance was tested by Dr. Ralf Simmat at Deutsches Insitut für Feuerfest und Keramik GmbH (DIFK), Bonn, Germany. Finally we would like to thank Dr. Ludwig Weiler of the Materials Science Dept. at the Technical University of Darmstadt, Germany, for providing the compressive-strength measurements at elevated temperatures.

References

1. Lipp, A., Schwetz, K. A. and Hunold, K., Hexagonal boron nitride: fabrication, properties and applications. *Journal of the European Ceramics Society*, 1989, **5**, 3–9.
2. Schwetz, K. A., *Boron Carbide, Boron Nitride, and Metal Borides Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH, 1999.
3. Hahn, C., New boron nitride hard coatings open up attractive prospects in non-ferrous metallurgy. *Giesserei*, 2003, **9**.
4. Damasch, R., Talk at meeting of “Keramverband”, January 30, 2006.
5. Höhn, S. and Obenaus, P., Ionenpräparation von keramischen pulvern und grünkörpern für die hochauflösende rasterlektronenmikroskopie. *Praktische Metallographie*, 2004, **36**, 299–301, Special Volume.
6. Moos, R., Brief overview on automotive exhaust gas sensors based on electroceramics. *International Journal of Applied Ceramics Technology*, 2005, **2**(5), 401–413.
7. Weyl, H. and Diehl, L., Elektrochemischer Messfühler und Verfahren zu dessen Herstellung, German Patent 100 09 597 B4; February 29, 2000.
8. Carlson, E. T., The system CaO–B_2O_3. *Bureau of Standards Journal of Research*, 1932, **9**, 825–832.
9. Katzir, A., Suss, J. T., Zunger, A. and Halperin, A., Point defects in hexagonal boron nitride. I. EPR, thermoluminescence, and thermally stimulated-current measurements. *Physical Review B*, 1975, **11**(6), 2370–2377.
10. Eichler, J., Eisele, U. and Rödel, J., Mechanical properties of monoclinic zirconia. *Journal of American Ceramics Society*, 2004, **87**(7), 1401–1403.