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Metal-Glass Based Composites for Application in TBC-Systems

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A new type of thermal barrier coating (TBC) based on metal-glass composite (MGC) consisting of an ordinary container glass and a NiCoCrAlY-alloy has been recently presented. This TBC material provides the possibility to easily adjust its thermal expansion coefficient to match the substrate by changing the metal to glass ratio of the composite. Vacuum plasma spraying (VPS) has been applied as a possible technologies for deposition of MGC coatings. Isothermal oxidation tests were carried out in air at temperatures of 950, 1000, and 1050 °C, respectively. Thermal cycling tests were carried out by applying a temperature gradient across the sample thickness by heating with an open flame of natural gas followed by removal of the burner and air cooling. Changes in the microstructure were examined by means of microscopy, microanalysis, and x-ray powder diffraction. For long-time annealing at high temperatures, a progressive degradation of the glass matrix as well as oxidation of the metal phases cannot be fully suppressed up to now. By lowering the effective temperature at the MGC layer when used as an intermediate layer, the degradation of the MGC can be reduced without losing its advanced features with respect to creeping and gas-tightness. Additional concepts for improved oxidation resistance of the MGC based on suitable heat treatments and on alternative glass compositions have been developed, and primary results are shown. Evaluation of results from isothermal oxidation experiments and from thermal cycling in burner-rig facilities validates a clear improvement of the lifetime of the coatings compared with earlier results.

Keywords coatings for engine components, coatings for gas turbine components, composite materials, heat treatment of coatings, high temperature oxidation, TBC topcoats

1. Introduction

Thermal barrier coatings (TBC) find an increasing number of applications to protect metallic turbine components from high temperature. Some basic requirements for the selection of TBC materials are low thermal conductivity, no phase transformation accompanied by volume change during heating, low sintering rate, chemical inertness, low thermal expansion mismatch with metallic substrates, and good adherence (Ref 1). The best compromise among these requirements is offered by partially stabilized zirconia as 7-8 wt.% Y_2O_3-ZrO_2 (YSZ) on top of a superalloy MCrAlY (M = Ni, Co) bondcoat (BC), deposited either by atmospheric plasma spraying (APS) or by electron beam physical vapor deposition (EB-PVD) (Ref 2).

However, application of YSZ-TBCs is limited by two factors. At temperatures above 1200 °C, phase transformations occur, giving rise to the formation of cracks in the coating (Ref 3). The other factor for failure is the insufficient oxidation resistance of the substrate, which has to be protected by the gas-tight MCrAlY bondcoat. This BC is forming a thermally grown oxide (TGO) layer (Ref 4). The stresses associated to the growth of this TGO layer, which is typically an Al_2O_3 layer, are presumed to induce spalling of the coating and are one of the most important sources of failure in TBC systems (Ref 5).

Recently a new type of TBC based on metal-glass composite (MGC) has been presented which provides the possibility to easily adjust its thermal expansion coefficient to match the substrate by changing the metal to glass ratio of the composite. Combined with the ductility of the glassy phase at elevated temperatures this leads to an improved adherence to the metallic substrate. Other advantages of the MGC material are the absence of open porosity, permitting the protection of the substrate material and the bondcoat from corrosive gases, and a rather low thermal conductivity of ~1.4 W m^{-1} K^{-1} due to the matrix out of glass (Ref 6-8).

However, because of its complex composition, the MGC coating is subjected to phase transformations and microstructural evolution during heat treatment. The hitherto proposed MGC consists of an ordinary container glass and a MCrAlY-alloy with high aluminum content. For long-time annealing at high temperatures, a progressive degradation of the glass matrix as well as oxidation of the metal phases cannot be fully suppressed up to now (Ref 9).

One solution is to use the MGC as an intermediate layer between the bondcoat and the ceramic TBC. Thus by lowering the effective temperature at the MGC layer the degradation of the MGC is reduced without loosing its advanced features with respect to creeping and gas-tightness. Additional concepts for an improved oxidation resistance of the MGC based on suitable

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Table 1 Composition data of MGC powders

1a			1b		
Alkali-silicate-MGC	NiCoCrAlY powder	Silicate glass powder	BaO-CaO-SiO$_2$-MGC	NiCoCrAlY powder	BaO-CaO-SiO$_2$ glass powder
Grain size, μm	25-40	<5	Grain size, μm	25-40	<5
Content, wt.%	63	37	Content, wt.%	53	47
Composition, wt.%	Ni 30	SiO$_2$ 71	Composition, wt.%	Ni 48	BaO 37
	Co 31	(Na$_2$O+K$_2$O) 14	…	Co 22	CaO 16
	Cr 30	CaO 10	…	Cr 17	SiO$_2$ 47
	Al 8	MgO 2	…	Al 12	…
	Si, Y < 1	Al$_2$O$_3$ 3	…	Si, Y, Pb < 1	…

heat treatments and on alternative glass compositions have been developed.

2. Experimental

2.1 Sample Manufacturing

2.1.1 Powders. Compositions of raw materials for the preparation of metal glass powder mixtures are compiled in Table 1. The MGC composition (Table 1a) is based on an alkali-silicate container glass, while that of composition (Table 1b) is glass-ceramic based. The preparation of the powder starts with ball milling of glass and metal powder with zirconia balls for 24 h in ethanol. After the powder had been dried, it was homogenized by ball milling with steel balls. It was then annealed for 2 h under an H$_2$/Ar-atmosphere at 700 or 900 °C. Afterward, the slightly densified and agglomerated powder was then dry coarse-mortared, and finally a powder fraction of 40-90 μm was sieved for thermal spraying.

2.1.2 Coatings. The MGC layers were deposited on Inconel 738 substrates with an MCrAlY bondcoat of 100-150 μm thickness sprayed by vacuum plasma spraying (VPS). The same bondcoat powder with respect to the particular composite was used. A SMA 3000 apparatus (Sulzer Metco, Wohlen, Switzerland) with a F4 gun was used. For some samples, the bondcoat has been oxidized at 1050 °C for 18 h in air to produce a dense aluminum layer ~2 μm thick on top of the BC. VPS has been applied as a possible technologies for deposition of MGC coatings using the following conditions:

- Chamber atmosphere, Ar, 60 mbar
- Plasma gas, Ar/H$_2$, 50/5 SLPM
- Gun power, 55 kW
- Gun current, 580 A
- Powder feed rate, ~1 g s^{-1}
- Stand-off distance, 275 mm
- Substrate temperature, 800 °C

The thickness of the MGC layer varied from 150 μm in the multilayer system to 500 μm for the single-layer TBC. Microstructural investigation of the as sprayed coatings showed only closed porosity below 5%.

Prior to deposition of the YSZ topcoat in the multilayer TBC system, appropriate heat treatment of the MGC layers of different composition had to be applied: The MGC based on silicate container glass was exposed to air at 950 °C for 24 h. The surface near the oxidized layer of about 70 μm thickness has been removed by grit blasting with coarse glass particles. The MGC based on BaO-CaO-SiO$_2$ glass was heated up to 950 °C under an H$_2$/Ar atmosphere to achieve the crystallization of the glass ceramic.

The multilayer-TBC samples were equipped with a 300 μm standard ceramic topcoat of Y$_2$O$_3$-stabilized ZrO$_2$ (Metco 204NS powder, Sulzer Metco, Wohlen, Switzerland), which where deposited by APS using a triplex gun (Sulzer Metco, Wohlen, Switzerland).

2.2 Reliability Tests and Evolution of Microstructure

2.2.1 Isothermal Oxidation. Isothermal oxidation tests were carried out in air at temperatures of 950, 1000, and 1050 °C, respectively. The exposure time was varied from 10 min to 72 h.

2.2.2 Thermal Cycling. Thermal cycling tests were carried out by applying a temperature gradient across the sample thickness: direct heating of TBC for 5 min by an oxygen-methane flame with simultaneous air cooling from the back of the substrate (TBC surface temperature, ~1250 °C; substrate temperature, ~980 °C), followed by removing of the burner and air cooling for 2 min; this cycle was repeated for up to 2000 cycles or until spallation of the TBC in the central part of the sample occurred. Details of the experimental setup are described in Ref 10.

2.2.3 Evolution of Microstructure. The changes in the microstructure were examined by means of optical and scanning electron microscopy (SEM), energy dispersive x-ray microanalysis (EDX), and x-ray powder diffraction.

3. Results and Discussion

3.1 Oxidation Mechanism of Alkali-Silicate Based MGC

TBCs made of the metal-glass composite based on cost-effective alkali-silicate glasses have already been proven to perform well at moderate temperatures competitive to standard YSZ coatings (Ref 7). During annealing at temperatures above 800 °C, a complex transformation of the microstructure of the composite is observed, which is shown in Fig. 1.

At the surface of the coating, an oxidation layer is formed within minutes to a few hours. In this layer, an outermost nickel-cobalt oxide scale is followed first by a depletion zone containing only traces of the main constituents of the bondcoat alloy and then by a fine-grained mixture of chromium oxide and partly crystallized glass oxides.

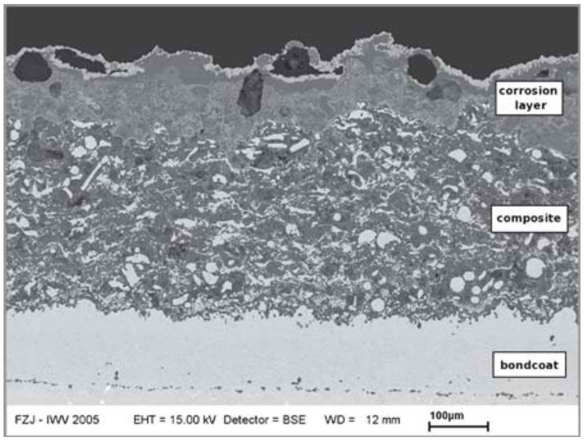

Fig. 1 Microstructure of plasma-sprayed MGC-TBC from white container glass after annealing at 1000 °C for 72 h

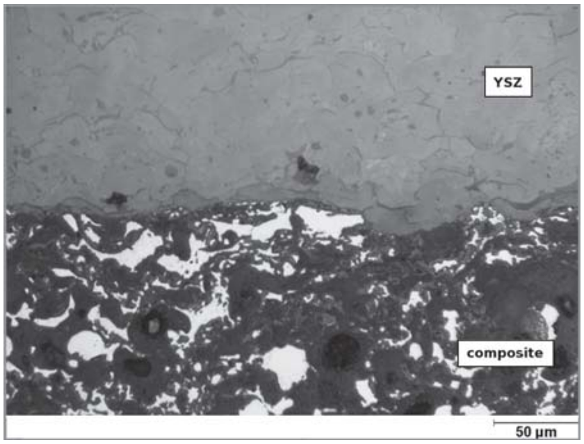

Fig. 2 Interface region between YSZ and MGC based on container glass after annealing at 1000 °C for 72 h. A surface corrosion layer has been removed by grit blasting prior to the coating with YSZ.

On a larger time scale, aluminum diffuses from the metal particles within the composite and from the bondcoat into the glass matrix where it is found in oxidized form. In parallel, a partly crystallization of the glassy phase occurs. Evaluation of the diffraction patterns and EDX analysis indicates the formation of alumina, diopside, and nephelite, where alumina is enriched close to the metal particles. However, detailed phase analysis is complicated due to the fine dispersion within the aged composite matrix.

Crystallization and coarsening of the composite matrix at moderate temperatures are not accompanied by the formation of cracks or spallation. Long-term annealing tests of 1000 h at 1000 °C have shown that the adherence of the aged composite remains stable (Ref 9), and both thermal and oxidizing impacts to the substrate are effectively reduced. Unfortunately, at temperatures above 1200 °C, the kinetics of degradation of the composites matrix increases and the stability of the composite is drastically reduced.

3.2 Multilayer Alkali-Silicate MGC/YSZ System

A simple method to overcome this limited temperature of the MGC barrier coatings is to protect it by an additional porous ceramic TBC layer. The degradation of the MGC should be slowed down and the advanced properties with respect to adhesion, creeping, and gas-tightness could still be used. In this study, conventional layers of YSZ have been deposited by APS onto MGC coatings of reduced thickness to check this approach.

The first set of experiments reveals that adhesion of a YSZ top layer on a MGC is very poor if it is deposited onto an untreated MGC layer. In isothermal oxidation tests as well as in thermal cycling tests, spallation of the coating occurs after a short time within the upper part of the MGC layer. This behavior is due to the brittle morphology of the outermost oxidation layer of the MGC. The open porosity of the APS-YSZ coating does not prevent underlying layers from oxidation. An oxidation layer is also formed beneath the YSZ topcoat.

From previous works, it is known that the growth of the oxidation layer stops after a few hours at a thickness of ~30-70 µm (Ref 7). This is synchronous with the occurrence of a basic crystallization of the MGC glass matrix and is therefore presumably caused by decreased ion mobility within the crystallized oxide phases compared with the amorphous glassy phases. Taking this empirical finding into account, an appropriate procedure to improve the adhesion of the ceramic top layer includes two steps: first, the coated sample is annealed to achieve the partially crystallization of the glass matrix; and second, a potentially formed corrosion layer is subsequently removed.

Grit blasting is a suitable tool to additionally ensure the necessary surface roughness for a good adherence of the plasma sprayed YSZ layer. Figure 2 shows the interface region between MGC and YSZ of a sample that has been heat treated in air for 72 h at 1000 °C. Neither reoccurrence of an oxidation layer nor a spallation is found. In thermal cycling experiments, up to 2000 cycles are performed without spallation of the ceramic coating in the central region of the disc-shaped sample. The number of cycles attained is lower if compared with a number of >4000, which can be achieved for standard TBCs made of YSZ under same conditions (Ref 10, 11). Nevertheless, improvement of cycling numbers from the order of 1000, which have been achieved with single-layer MGC-based TBCs (Ref 7-9), by a factor of 2 gives reason enough to further pursue the multilayer concept for MGC with optimized composition and microstructure.

3.3 BaO-CaO-SiO$_2$ Glass-Ceramic Based MGC

In addition to a general reduction in the temperature of the MGC layer, an alternative starting point to enhance the durability of MGC coatings is to improve the oxidation resistance of the metal particles of the composite.

From analysis of the aging mechanism of the MGC, it can be assumed that the oxidation and finally the decomposition of the metal particles within the MGC is promoted by the continued dissolution of aluminum into the glass matrix. Looking at the general chemistry of glasses for high-temperature sealing applications (Ref 12), it seems difficult to find a glass in its amorphous state that has a much lower solubility for aluminum than the hitherto used alkali-silicate glass. This estimation is based on the fact that aluminum is able to act as a glass-forming agent and thus will be able to fit in nearly any glassy structure.

Based on the hypothesis that crystallization of the glass matrix hinders any transport within the MGC, it is proposed to use an easily crystallizing glass-ceramic as component of the MGC to improve the stability of the MGC against oxidation. Once crystallized, the oxide components of the glass ceramic are expected not to react with the metal ions and thus to prevent a decomposition of the metal particles.

For the use of the MGC barrier coatings for turbine application, a BaO-CaO-SiO_2-based glass ceramic has been chosen that is proven successfully as sealing material in the development of solid oxide fuel cells (Ref 13). This specialized glass-ceramic is suitable for application temperatures of more than 800 °C and shows a relative high coefficient of thermal expansion [$(9\text{-}12) \times 10^{-6}$ K^{-1}] comparable to or better than the properties of the previously used container glass. An additional benefit can be expected from the fact that this glass-ceramic does not contain sodium or potassium, which would potentially promote hot corrosion in sulfur atmospheres.

Identical parameters and procedures were used for the preparation and VPS deposition of the MGC powder and coating, except for the calcination temperature of the MGC powder that has to be increased to 900 °C due to the properties of the glass-ceramic. A fundamental difference is to be recognized at the stage of post-deposition treatment of the MGC layer. To ensure the crystallization of the glass ceramic up to a large extent and to prevent a coarse structure, the samples were heated up slowly to the desired temperature of crystallization and were held at that temperature for some hours. To prevent oxidation of the metal particles by occasionally open pores, the process was performed under a Ar/H_2 atmosphere.

The upper part of Fig. 3 shows a cross-sectional micrograph of a pressed and sintered pellet of glass-ceramic based MGC powder after crystallization in an Ar/H_2 atmosphere. The glass-ceramic has been crystallized with a fine, needlelike structure, whereas the metal particles still show a pattern of β- and γ-phase, which are typical for the MCrAlY alloys. The glass-ceramic consists mainly of the crystalline phases of walstromite and sanbornite, which are expected for this oxide system. By means of EDX and x-ray diffraction (XRD) analysis, no indication is found for a dissolution of aluminum into the glass-ceramic or any reaction between the glass-ceramic and the metal. An ultrathin scale of alumina is found on some metal particles.

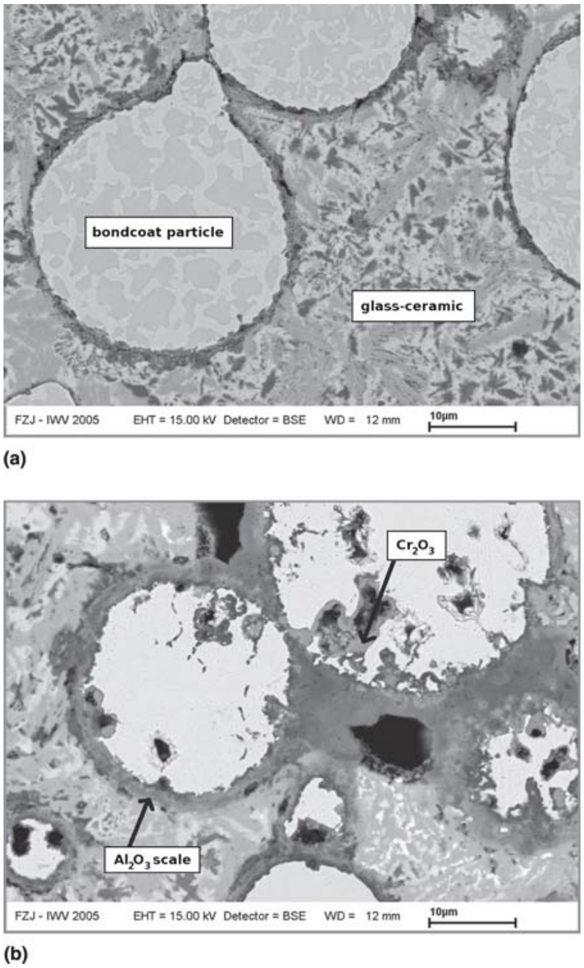

Fig. 3 SEM micrographs of pressed and sintered pellets of glass-ceramic based MGC powder: (a) calcined and crystallized, (b) after additional isothermal oxidation for 72 h at 1000 °C in air

The lower part of Fig. 3 shows a pellet after an additional isothermal oxidation for 72 h at 1000 °C in air. Analysis reveals an enhanced oxidation of the metal particles with nearly all aluminum removed from the alloy. In contrast to the alkali-silicate-glass based MGC, a dense aluminum scale has been formed around the particles, but no reaction with the glass-ceramic is evident in this case.

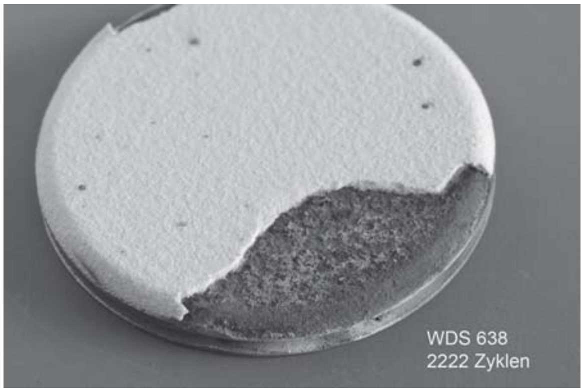

Fig. 4 Photography of MGC/YSZ multilayer system based on glass-ceramic after thermal cycling on a burner rig for 2222 cycles

Figure 4 and 5 show respectively a photograph and a cross section of a MGC/YSZ multilayer system based on glass-ceramic after thermal cycling in a burner rig for 2222 cycles. It can be seen that the spallation occurs within the YSZ top layer close to the YSZ/MGC interface. First failures have been located at the curved edges of the disc-shaped sample, thus indicating a critical mismatch of the coefficient of thermal expansion between MGC and YSZ. The cross section of the central zone of the sample (as shown in Fig. 5) indicates an almost intact microstructure of the multilayer system in this area of reduced stress. Only a few cracks or local delaminations are observed in the inner region.

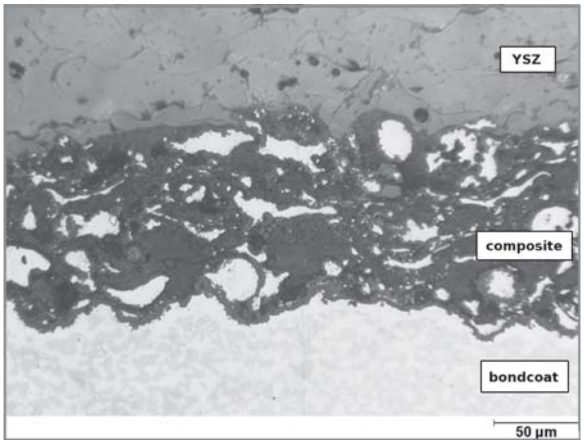

Fig. 5 Cross-sectional micrograph of the glass-ceramic based MGC/YSZ multilayer sample after 2222 thermal cycles

4. Conclusions

Starting from a thorough analysis of the oxidation and the degradation mechanisms in the alkali-silicate based metal-glass composite thermal barrier coatings, two concepts have been developed. First, a multilayer system is described that includes an additional YSZ top layer. To ensure a sufficient adhesion of the ceramic top layer, suitable heat treatment and mechanical surface treatment had to be applied. Second, an alternative MGC based on a glass-ceramic with improved oxidation resistance has been introduced.

The evaluation of results from isothermal oxidation experiments and from thermal cycling in burner rig facilities validates a clear improvement of the lifetime of the coatings compared with the earlier results. Further improvement is expected from optimization of the thermal expansion of the MGC for use in multilayer systems.

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References

1. V. Arnault, R. Mévrel, S. Alpérine, and Y. Jaslier, Thermal Barrier Coating for Aircraft Turbine Airfoils: Thermal Challenge and Materials, *Rev. Metall.–CIT/Sci. Genie Mater.,* **96**(5), 1999, p 585-597
2. S. Stecura, Optimization of the Ni-Cr-Al-Y/ZrO_2-Y_2O_3 Thermal Barrier System, *Adv. Ceram. Mater.,* 1986, **1**(1), p 68-76
3. R.A. Miller, J.L. Smialek, and R.G. Garlick, Phase Stability in Plasma Sprayed Partially Stabilized Zirconia-Yttria: Science and Technology of Zirconia, *Advances in Ceramics,* A.H. Heuer and L.W. Hobbs, Ed., American Ceramic Society, 1981, Vol 3, p 241-251
4. R. Miller, Oxidation-Based Model for Thermal Barrier Coating Life, *J. Am. Ceram. Soc.,* 1984, **67**(8), p 517-521
5. A.G. Evans, D.R. Mumm, J.W. Hutchinson, G.H. Meier, and F.S. Pettit, Mechanisms Controlling the Durability of Thermal Barrier Coatings, *Prog. Mater. Sci.,* 2001, **46**(5), p 505-553
6. V. Verlotski, D. Stöver, H.P. Buchkremer, and R. Vaßen, Wärmedämmende Glas-Metall/Keramik-Schichten, German Patent 198 52 285, 2000
7. M. Dietrich, V. Verlotski, R. Vaßen, and D. Stöver, Metal-Glass Based Composites for Novel TBC-Systems, *Materialwiss. Werkstofftech.,* 2001, **8,** p 669-672
8. D. Stöver, G. Pracht, H. Lehmann, M. Dietrich, J.-E. Döring, and R. Vaßen, New Material Concepts for the Next Generation of Plasma-Sprayed Thermal Barrier Coatings, *J. Therm. Spray Tech.,* 2004, **13**(1), p 76-83
9. M. Dietrich, V. Verlotski, R. Vaßen, and D. Stöver, “Microstructure and Performance of New Metal Glass Composite TBC,” Presented at the 26th Annual Conference (Cocoa Beach), *Ceramic Engineering and Science Proceedings,* H.-T. Lin and M. Singh, Ed., American Ceramic Society, 2002, **23**(4), p 449-456
10. F. Traeger, R. Vaßen, K.-H. Rauwald, and D. Stöver, A Thermal Cycling Setup for Thermal Barrier Coatings, *Adv. Eng. Mater.,* 2003, **5**(6), p 429-432
11. R. Vaßen, F. Traeger, and D. Stöver, New Thermal Barrier Coatings Based on Pyrochlore/YSZ Double-Layer Systems, *Int. J. Appl. Ceram. Technol.,* 2004, **1**(4), p 351-361
12. I.W. Donald, Preparation, Properties and Chemistry of Glass- and Glass-Ceramic-to-Metal Seals and Coatings, *J. Mat. Science,* 1993, **28,** p 2841-2886
13. S.M. Gross, T. Koppitz, J. Remmel, and U. Reisgen, Glass-Ceramic Materials of the System BaO-CaO-SiO_2 as Sealants for SOFC Applications, *Advances in Solid Oxide Fuel Cells: A Collection of Papers Presented at the 29th International Conference on Advanced Ceramics and Composites,* January 23-28, 2005 (Cocoa Beach, FL), *Ceramic Engineering and Science Proceedings,* N.P. Bansal, D. Zhu, and W.M. Kriven, Ed., 2005, **26**(4), p 239-245