

# Post-Deposition Treatment of Zirconia Thermal Barrier Coatings Using Sol-Gel Alumina

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This article addresses the problem of gas permeability of thermal sprayed yttria-stabilized zirconia thermal barrier coatings (TBC)s. The objective of this study was to decrease the open porosity of TBCs through deposition of dense alumina ceramic on the surface of the pores. A simple infiltration technique was used, beginning with aluminum isopropoxide as sol precursor, subsequently hydrated to aluminum hydroxide sol, which decomposed at relatively low temperatures to extra-fine, readily sinterable aluminum oxide. In some experiments, the sol-gel (SG) precursor was combined with fine grains of calcined alumina, constituting high solid-yield composite sol-gel (CSG) deposits within the pores of TBCs. Sinterability in the model systems, including aluminum hydroxide sol-calcined alumina and aluminum hydroxide sol-calcined alumina-zirconia, has been studied. A number of TBC specimens were impregnated with suspensions of alumina sols and CSG. It is shown that these ceramics effectively penetrated into the pores and cracks of TBCs and reduced the coating permeability to gases. The overall reduction of porosity was however small (from ~12 to ~11%), preserving the strain and thermal shock tolerance of the coatings. Burner rig tests showed an increase in sealed coating lifetime under thermomechanical fatigue conditions.

**Keywords** infiltration techniques, porosity modification, post treatment, thermal barrier coatings

## 1. Introduction

Thermal barrier coatings (TBCs) are frequently used in corrosive environments, even though their major purpose is to provide thermal resistance, rather than corrosion resistance (Ref 1). Porosity of TBCs is a desired feature to provide good thermal protection (through low thermal conductivity) and tolerance to differential strain and thermomechanical fatigue (through low stiffness). However, the interconnected (open) porosity allows the corrosive media to reach the coating-substrate interface, which eventually leads to delamination of the coatings. In the simplest case, the corrosive medium is hot oxygen that reacts with the bond coat to produce complex oxides at the TBC/bond coat interface.

The problem of interconnected porosity can be addressed by modifying the characteristics of the coating. Investigations have been carried out to explore the feasibility of using ion and laser beams to optimize the properties of plasma sprayed coatings by decreasing their porosity and improving the surface finish (Ref 1-6). Although substantial cracking usually accompanies these treatments, in some cases controlled cracking introduced to the coating can be beneficial. In particular, cracks perpendicular to the coating surface can help in accommodating the strains during thermal cycling (Ref 6-8). The successful use of high intensity arc lamp to sinter the surface of a sol-gel (SG) treated TBC was investigated to lower the overall costs of post-deposition treatments (Ref 9).

The method proposed in this study involves partial sealing of the pores and healing of the cracks of a zirconia TBC by infiltration with liquid precursors of alumina. Similar SG infiltration techniques have been used to fabricate multiphase ceramic bodies with improved properties (Ref 10-12). The principal objective of this work was to modify the surface and volume of thermal sprayed TBCs in an attempt to decrease their permeability to gases and therefore to increase the high temperature corrosion resistance of the coated substrates. The rationale to select alumina as a high-temperature sealant for porous zirconia was based on several factors. The alumina-zirconia system belongs to one of the best studied groups of composite ceramics. One of the toughest ceramics known (beyond fiber-reinforced composites) is zirconia-toughened alumina. The system exhibits no measurable solid solubility, promising long-term stability at elevated temperatures. It is also important that the alkoxide precursors to alumina and alumina hydroxide sols are readily available and one of the cheapest ceramics produced through the SG method.

The SG treatment of thermal sprayed coatings has been explored previously (Ref 12, 13). On heat treatment at relatively low temperatures and short times, the SG precursors of ceramics decompose to their respective oxides. The depth of penetration of the precursor in the coating is controlled by the immersion time in the sol and can be described by the Washburn model, which considers the porous medium as a constant cross-section capillary (Ref 14). If thermal sprayed coating can be assumed to be a porous body behaving as an assemblage of capillaries, the infiltrated depth  $l$ , is parabolic in time,  $t$ , and depends on fluid viscosity,  $\eta$ ; surface tension,  $\gamma$ ; pore radius,  $r$ ; and wetting angle,  $\theta$  (Ref 15):

$$l^2 = \frac{\gamma \cos \theta}{2\eta} r t \quad (\text{Eq 1})$$

Good penetration of the sealant into the porous coating is therefore ensured through its low viscosity high surface tension,

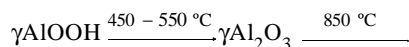
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and wetting of the coating material. The advantage of the SG route is that the starting precursor is usually a low viscosity fluid yielding a fine powder on decomposition (Ref 16, 17). Equation 1 has been shown to properly describe penetration of partially hydrated silica sols into thermal sprayed TBCs (Ref 9, 18).

## 2. Sinterability of Sol-Alumina/Calcined Alumina/Zirconia Systems

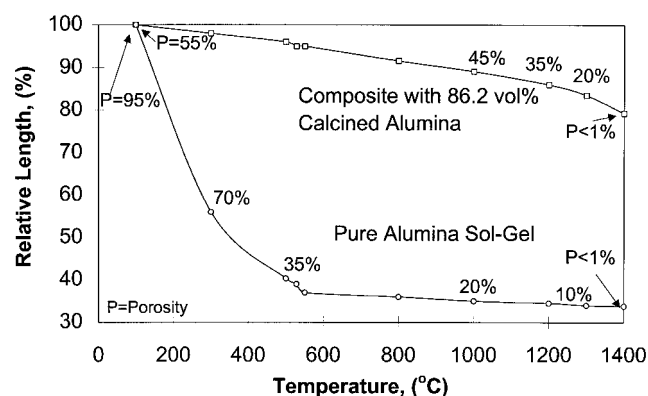
The starting precursor to prepare high purity alumina through SG is usually aluminum isopropoxide  $\text{Al}(\text{OC}_3\text{H}_7)_3$  dissolved in isopropyl alcohol. Aluminum isopropoxide is readily hydrolyzed to produce hydrated alumina sol particles. It is believed that the  $\sim 1$  nm large alumina sol particles of the formula  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{+7}$  are transformed during gelation into pseudobehmite ( $\text{AlOOH}$ ) because of the loss of the tetrahedrally coordinated aluminum (Ref 19). Gels form by step-wise linkage of  $\text{AlOOH}$  dimers into double chains to form a three-dimen-

sional network (Ref 19). The following phase transformations occur upon subsequent heat treatment of the result hydroxides:

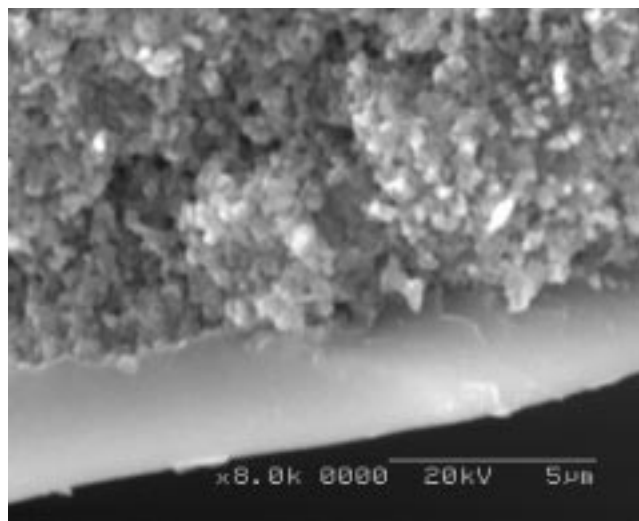


The inherent feature of SC processing is relatively low volumetric yield of a solid material out of a liquid precursor, leading to 60 to 70% shrinkage of gel upon transformation to a solid. The large strain can easily result in cracking of the component unless special precautions are undertaken to ensure uniform dehydration and pore collapse. One method to increase the yield and decrease densification strain of gel is to disperse secondary ceramic particles in the sol, which act as an inert filler in the composite sol-gel (CSG) (Ref 19, 20). A variety of solid phases, such as fine powders or fibers, can be dispersed into a sol before gelation, leading to a composite with good homogeneity and intimate contact between the components. The composite slurry is typically dried at 25 to 250 °C and sintered at temperatures several hundred degrees lower than the counterpart calcined ceramics. The respective shrinkage curves for heat-treated pure alumina SG phase and CSG with 86.2 vol% of calcined alumina (A16, Alcoa Chemicals) are shown in Fig. 1 (the vol% of total porosity,  $P$ , is shown at the various stages of heat treatment for both materials) (Ref 20). The pure alumina sol-gel phase shrinks linearly by about 66% upon reaching essentially full density ( $P < 1\%$  at 1400 °C in Fig. 1). This large shrinkage frequently results in cracking of SG derived ceramics. In contrast to this, CSG shrinks by about 20% upon reaching full density, a value more common to densification of calcined ceramics. The rationale to use CSG as a high temperature sealant for TBC is therefore in high solids yield and relatively small shrinkage during heat treatment.

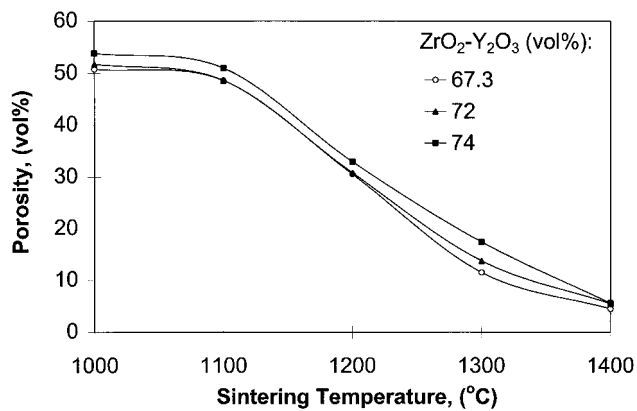
The compatibility between the CSG sealant and the pure SG phase is further illustrated in Fig. 2. In this figure, the CSG base (86.2 vol% of calcined alumina, the “grainy” structure in the top of the figure) sintered at 550 °C has been coated with pure alumina sol (the “smooth,”  $\sim 4$   $\mu\text{m}$  thick layer in the bottom of the figure) and sintered repeatedly at 550 °C. While both the CSG and sol-derived coating still have substantial porosity after sintering at this low temperature, the porosity of the sol-derived coating appears to be closed and well below 0.1  $\mu\text{m}$  in size (the pores are not resolved in the smooth SG derived coating in the bottom of Fig. 3). This system offers a combined ceramic sealant that can be applied to TBCs at moderately high temperatures (e.g., 550 °C). If the temperature of heat treatment is further increased, the alumina sealant sinters completely, especially in the presence of a MgO additive (Fig. 4). Thus the process of sealant densification is expected to continue during service of TBCs. Figure 3 illustrates the results of investigation of another model ceramic-ceramic system with the CSG ceramic sealant. The zirconia-yttria ceramic was impregnated with alumina precursor to result in 67.3, 72, and 74% of zirconia-yttria component after calcination. Likewise, substantial sinterability in this model system was observed only about 1100 °C.



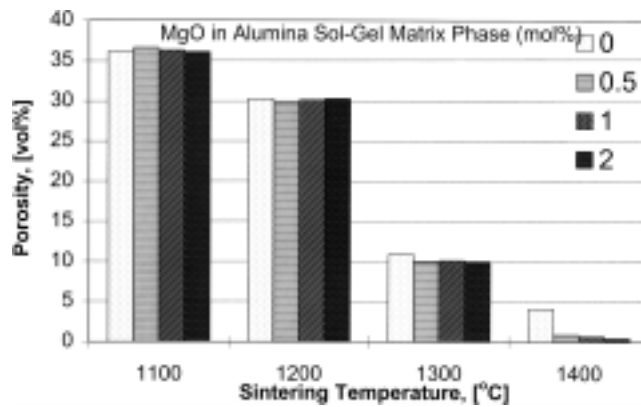
**Fig. 1** Linear shrinkage and porosity ( $P$ , vol%) versus heat treatment temperature for pure sol-gel derived alumina sealant for TBCs and for the composite sol-gel (CSG) alumina sealant containing 86.2 vol% calcined alumina.



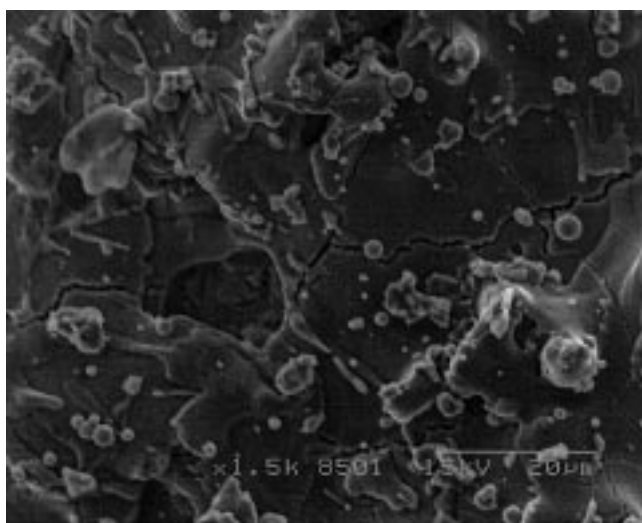
**Fig. 2** Sol-derived alumina sealant coating (bottom) on the composite sol-gel alumina sealant (top), sintered at 550 °C



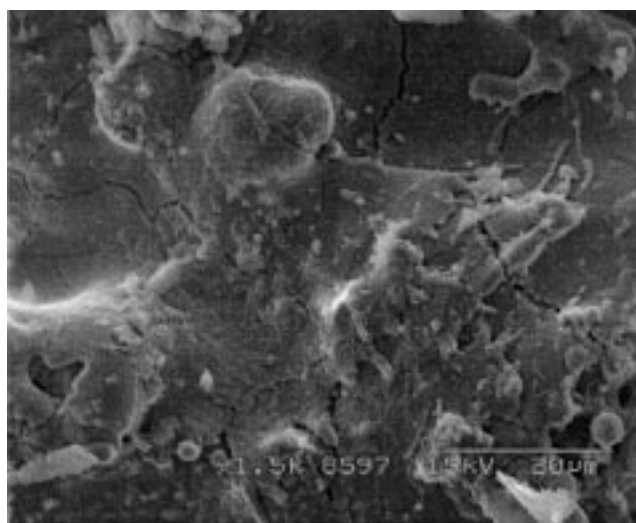
**Fig. 3** Densification in the system containing composite sol-gel alumina sealant (86.2 vol% calcined alumina in sol-gel alumina matrix) plus various contents of zirconia-yttria powder as a function of sintering temperature



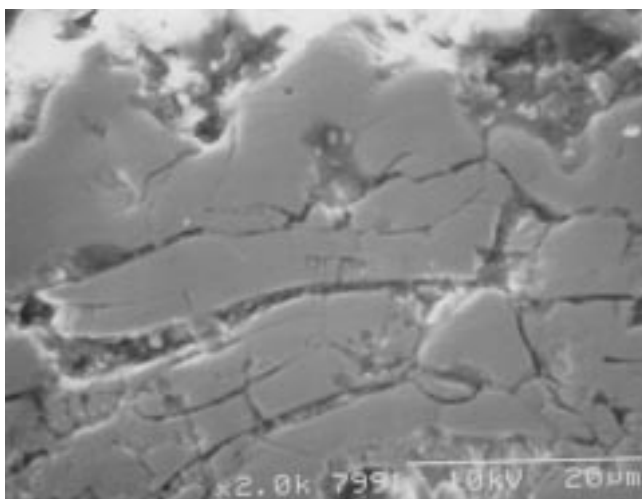
**Fig. 4** Densification of composite sol-gel (CSG) alumina sealant containing 86.2 vol% calcined alumina in sol-gel alumina matrix as a function of temperature and MgO content



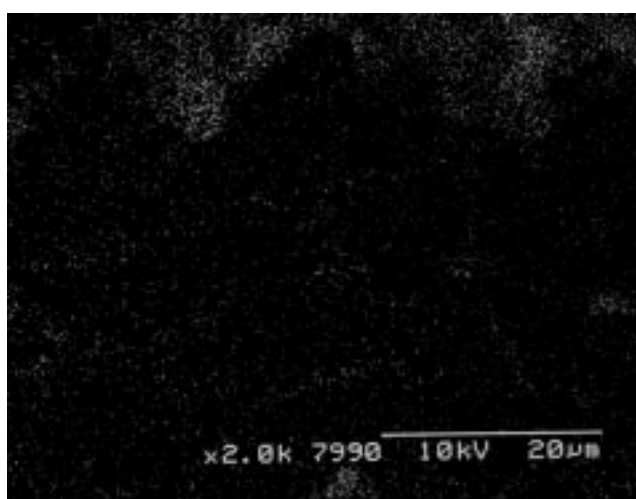
(a)



(b)



(c)



(d)

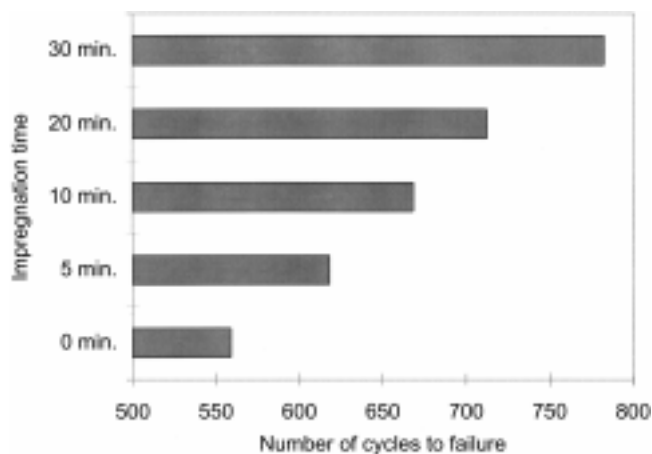
**Fig. 5** Scanning electron micrograph of the yttria-stabilized zirconia TBC: (a) As sprayed, top surface. (b) Infiltrated with alumina precursor for 10 min and heat treated at 600 °C for 15 min, top surface. (c) Cross section, secondary electron image. (d) Cross section, x-ray map of aluminum

### 3. TBC Impregnation Experiments

The yttria-stabilized zirconia thermal sprayed TBCs studied in this work were supplied by Northwest Mettech, British Columbia, Canada (sprayed directly on steel or nickel) and Pratt & Whitney, Quebec, Canada (deposited on nickel-base alloy with an intermediate MoCrAlY alloy bond coat). The precursors for infiltration were prepared through the alkoxide route, as described previously. The specimens were infiltrated by immersion in the precursor solutions for various lengths of time (4 min to 1 h). The infiltrated specimens were dried at 65 °C for 12 h, and furnace or flame heat treated at 600 or 700 °C for times between 15 s and 15 min. The heat treatment temperature was chosen based on thermogravimetric analysis and x-ray diffraction results. According to the previous discussion, the principal form of alumina achieved in this process is  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which transforms to the final form of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> during the burner rig tests at 1270 °C.

The effectiveness of the sealing process was verified in this work using potentiodynamic polarization, gas permeability, and thermogravimetric tests. The full set of results of these tests has been published elsewhere (Ref 18). The durability and thermomechanical fatigue resistance of infiltrated TBC was comparatively assessed in a simple burner rig using natural gas/oxygen flame and air cooling. The burner rig test samples were 0.38 mm thick 18Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> TBC on 0.22 mm MoNi-CrAlY alloy, on nickel-alloy substrate. A turntable held six specimens, with adjustable residence time at the heating or cooling station. Severe heat treatment schedules were selected to accelerate the test, that is, heating in a flame to 1270 °C ± 20 °C for 56 s and then quenching to room temperature with a jet of cold air, in approximately 20 s. The test temperature was measured continuously using a thermocouple, positioned just below the surface (in the coating) and verified by intermittent pyrometric measurements.

The definition of coating failure in burner rig tests is rather arbitrary. In some investigations failure was considered to have occurred when the ceramic coating spalled from 50% or more of the test zone, whereas in other investigations complete spalla-



**Fig. 6** The number of burner rig cycles to failure tests (i.e., heating in a flame to 1270 ± 20 °C for 56 s and then quenching to room temperature with a jet of cold air, in approximately 20 s) for TBC specimens impregnated with alumina sealant for various periods of time

tion was used as the criterion (Ref 7). Appearance of cracks was used in some investigations as a sign of failure (Ref 7). In the setup for this study, failure was considered to have occurred when 75% or more of the test zone (area of the coating exposed) spalled. This criterion for failure was set based on previous reports (Ref 3).

### 4. Results and Discussion

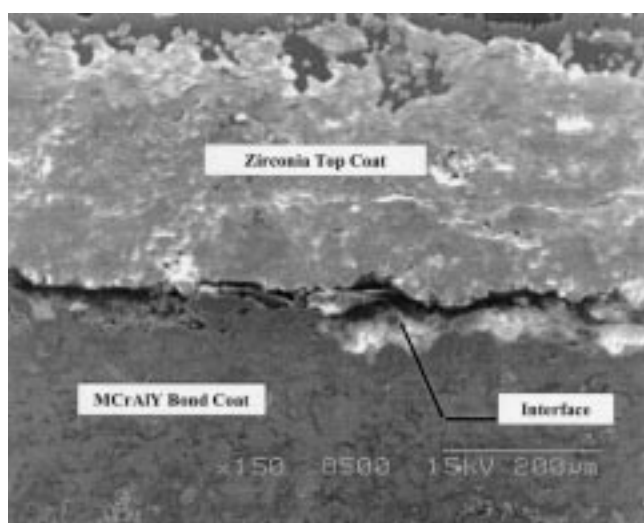
Figure 5(a) shows highly microcracked surface of a typical unsealed plasma sprayed TBC and Fig. 5(b) shows the surface of a coating that was infiltrated with alumina precursor for 10 min and heat treated at 600 °C for 15 min. The bright regions in Fig. 5(b) are representative of alumina as determined by energy dispersive x-ray analysis. However, it is difficult to observe the distribution of the sealant material inside the pores and microcracks of the coating in a scanning electron micrograph because of absorption of x-rays inside the pores by the surrounding material. The distribution of the sealant material (alumina) in the coating was also studied by mapping the element (aluminum) in the precursor across the cross section of the coating. Figure 5(c) shows a scanning electron micrograph of the cross section of the zirconia-yttria TBC infiltrated with alumina precursor for 10 min. This figure presents the top ~40 μm of the coating, with the coating surface seen on top of the figure. Figure 5(d) also shows the x-ray map of aluminum for the same sample and the same region as in Fig. 5(c). The high concentration of aluminum on the surface and in the pores of the coating shows that the precursor is effective in sealing the surface and penetrating the pores of the coating.

Weight gain measurements were carried out to evaluate the amount of two-molar (2M) alumina infiltrant deposited in the coatings, before and after the heat treatment. The open porosity of these coatings, measured by Archimedes water displacement method, was ~12%. For example, typically the weight gained, that is, the weight of dry infiltrant (gel) in the coating, with 10 min of infiltration was 5.5 mg. When heat treated at 600 °C for 15 min, the surface exhibited the weight of the precursor decomposing to oxide ( $\gamma$ -alumina) in the coating at 4.2 mg. This corresponded to a yield of 76% and was in good agreement with thermogravimetric analysis results, which showed a decomposition yield of 78% from the dry alumina gel (Ref 18). The volume yield of the 2M alumina precursor was 4.5%. Assuming that the liquid precursor fills up all the pores in the coating, the maximum decrease in porosity would also be 4%, for example, porosity would decrease from 12 to ~11.5%. Therefore a single infiltration process does not substantially change the overall porosity content of the coatings. Further tests indicate however that the type of porosity and the microcrack morphology was modified to result in decreased permeability and increased resistance to thermomechanical fatigue.

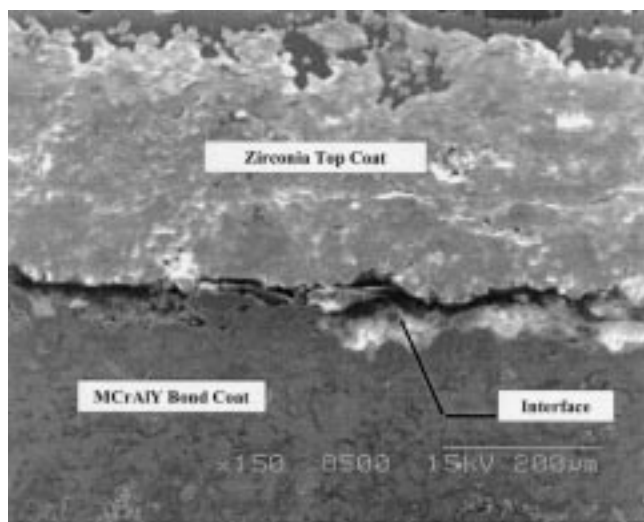
Figure 6 summarizes the results obtained in the cyclic burner rig tests. Four of the five specimens tested were infiltrated with alumina precursor (2M) for 5, 10, 20, and 30 min. The infiltrated specimens were dried and subsequently heat treated at 600 °C in a flame for 15 s. During the test, the cracking behavior of the coatings was visually examined and recorded in terms of the total area exposed. There was a significant increase in the cyclic life, from approximately 560 cycles in the untreated coating to

approximately 780 cycles in the coating treated with 30 min of infiltration. The bond coat coating interface of the untreated sample after 500 cycles shows evidence of delamination prior to spallation (Fig. 7(a)), compared with the as-received coating in Fig. 7(b)).

Figure 8 presents the results of another series of the burner rig tests (that is, heating in a flame to  $1270 \pm 20$  °C for 56 s and then quenching to room temperature with a jet of cold air, in approximately 20 s). As in the previous tests, six specimens were analyzed simultaneously, but some samples were additionally infiltrated with the precursors for 30 min after 300 cycles in the burner rig. This intermittent infiltration treatment was carried to establish the feasibility and usefulness of the sealing technique to improve the life of coatings already in service. Out of the two untreated coatings at the start of the test (i.e., No. 1 and 2 in Fig. 8), one was infiltrated after 300 cycles with alumina precursor



(a)



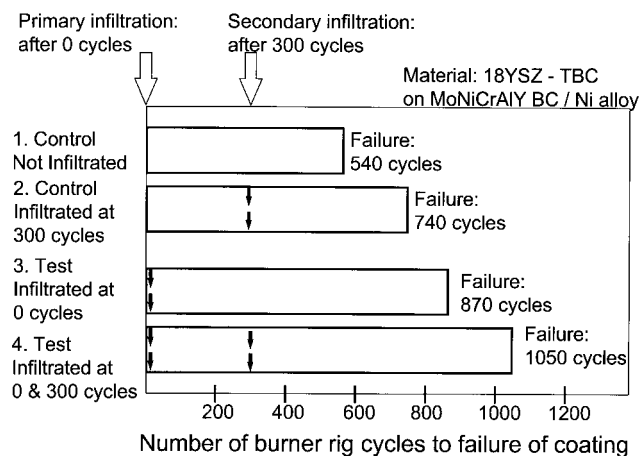
(b)

**Fig. 7** Scanning electron micrograph of the cross section of yttria-stabilized zirconia TBC after 500 cycles in (a) the burner rig and (b) as sprayed

for 30 min. Out of the two coatings infiltrated with alumina precursor for 30 min at the start of the test (i.e., No. 3 and 4 in Fig. 8), one was treated again after 300 cycles. Figure 8 summarizes the results obtained from this test, in terms of the number of cycles to failure. The cyclic life of the coating untreated at start of the test increased from 540 cycles to 740 cycles with 30 minutes of infiltration (after 300 cycles) with the 2M alumina precursor. The life of the initially infiltrated coatings further increased from 870 to 1050 cycles with 30 min of infiltration (after 300 cycles) with the alumina precursor.

## 5. Conclusions

Sol-gel alumina sealing treatments were carried out to improve the protective characteristics of porous plasma sprayed, yttria-stabilized zirconia TBCs. Sinterability of the sealant in the system, alumina sol-calcined alumina-zirconia, has been studied. The effects of such a sealing treatment on the permeability and mechanical properties of the parent coating were characterized. An x-ray map of the sealant material in the parent coating shows that the infiltrant is effective in penetrating into the pores and capillaries of the coating. Porosity of the modified coatings is decreased minimally (~12 to ~11%), and thus it is believed that this sealing technique preserves the overall strain tolerance of the porous coatings, as evidenced through the subsequent thermal cycling tests. Burner rig cyclic tests (i.e., heating in flame to  $1270 \pm 20$  °C for 56 s and then quenching to room temperature with a jet of cold air, in approximately 20 s) show an improvement in the cyclic life of the coating from 560 to 780 cycles with alumina infiltration. The burner rig tests on coatings additionally sealed after 300 cycles show a further improvement in the cyclic life of these treated coatings to 1050 cycles. It appears therefore that this technique is equally suited for sealing fresh coatings as well as enhancing the life expectancy of coatings already in service. The results of the investigations on post-treated coating permeability and durability indicate a potential for the application of this method for high temperature environments subject to corrosive gaseous attack.



**Fig. 8** The burner rig tests results for TBC specimens impregnated with alumina sealant of various stages of damage. Refer to text for explanations.

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