Development of Intermixed Zones of Alumina/Zirconia in Thermal Barrier Coating Systems

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The mechanisms whereby intermixed zones of alumina and zirconia are formed at the interface between the metallic bond coat and the ceramic top coat (yttria-stabilized zirconia) in thermal barrier coating systems have been investigated. The results lead to the following mechanism for the formation of the zones. The predominant mechanism for intermixed zone formation involves formation of a metastable alumina polymorph (θ or γ) during TBC deposition, with a significant amount of zirconia dissolved in it. The outward growth also begins to incorporate zirconia particles, which initiates the formation of the intermixed zone. Upon thermal exposure, the metastable TGO continues to grow outward, extending the intermixed zone, and eventually transforms to the equilibrium α-Al_2O_3. The transformation to α-Al_2O_3 results in an increase in the volume fraction of zirconia in the intermixed zone as it is rejected from solution. Once the α-Al_2O_3 appears, subsequent TGO growth produces a columnar zone of the TGO without a second phase. When α-alumina was preformed on the bond coat, prior to TBC deposition, no intermixed zone was formed for Pt-modified aluminide bond coats.

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I. INTRODUCTION

THE durability of thermal barrier coating (TBC) systems depends on the characteristics of the interfacial regions associated with the thermally grown oxide (TGO), which forms on the metallic bond coat during fabrication and service. In some cases, failures occur at the TGO/bond coat interface, in others at the TGO/TBC interface, and in some cases mixed failures are observed. The durability of the interfaces is determined by the interplay of a number of factors that include the microstructure of the as-deposited TBC, the composition and morphology of the TGO, the composition and strength of the bond coat, and the test conditions. This article describes the development of the interfacial structures at the TGO/TBC interface for bond coats for which the TGO consists primarily of alumina. Particular emphasis is placed on the conditions under which an intermixed layer of alumina and zirconia can develop.

Stiger *et al.*[1,2] first identified the intermixed zone on a platinum-modified aluminide bond coat on a René N5 substrate coated with standard 7 wt pct yttria-stabilized zirconia (7YSZ) (Figure 1). This coating, which was a commercially processed system with a grit-blasted bond coat and the TBC deposited by electron beam physical vapor deposition (EBPVD), was found to have a thin TGO (≈100-nm thick) in the as-processed condition. Cross-section transmission electron microscopy (XTEM) with selected area diffraction (SAD) indicated the TGO in the as-processed condition was α-Al_2O_3. The TGO, after an exposure of 10 hours at 1200 °C in air, developed a columnar inner zone and an intermixed outer zone (Figure 1(a)), which contained precipitates. The entire TGO was determined by SAD to be α-Al_2O_3 and the precipitates were found by scanning TEM to consist of Zr, Y, and O. Figure 1(b) presents an XTEM micrograph of the intermixed zone showing that, for these exposure conditions, it consists of a matrix of α-Al_2O_3 that contains particles of the oxides of Zr and Y. It was proposed that the alumina was growing partially outward into the YSZ during exposure and spherodizing entrapped YSZ particles.

Subsequently, Brickey and Lee[3] studied a commercially fabricated TBC presumably with a similar processing history to that studied by Stiger *et al.* It was found by TEM and SAD that the TGO on the as-processed coating was α-Al_2O_3 but that it already contained zirconia precipitates. However, the TGO thickness was already in excess of 500 nm, which indicates this coating underwent significantly more oxidation during TBC deposition. Cyclic exposure at 1135 °C caused this coating to evolve into a structure similar to that shown in Figure 1.

Murphy *et al.*[4] reported observations on a single-crystal superalloy substrate with a platinum-modified aluminide bond coat and EB-PVD TBC. The bond coat surface was media finished, rather than grit blasted,

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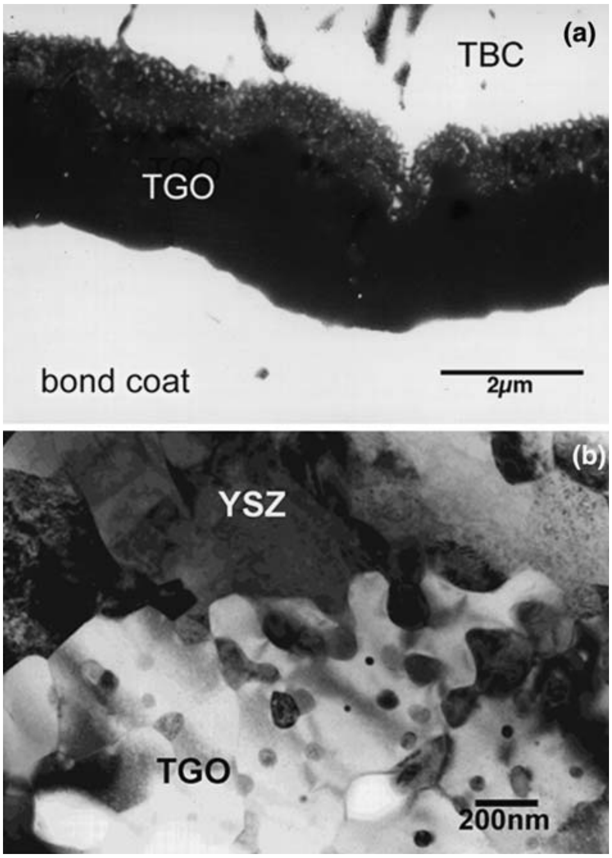

Fig. 1—Cross-sectional views of the intermixed zone formed on a commercial TBC with a Pt-modified aluminide bond coat after exposure at 1200 °C for 10 h: (*a*) SEM and (*b*) TEM.

prior to TBC deposition. The EB-PVD deposition process was carried out with three sets of (undisclosed) deposition parameters. The specimens were examined using SEM, XTEM, and photo-stimulated luminescence spectroscopy (PSLS). The TGO resulting from all three deposition conditions had a continuous inner layer of γ-Al_2O_3 and an outer intermixed zone of alumina and zirconia. The alumina in the intermixed zone was primarily γ for one deposition condition and was a mixture of γ, α, and θ for the other two conditions. Murphy *et al*. conclude that the intermixed zone is formed by irregular outward growth of γ-Al_2O_3 followed by YSZ filling in the gaps in the alumina as the TBC is deposited. These results could be consistent with those of Brickey and Lee[3] but are inconsistent with those of Stiger *et al*.,[1,2] where the intermixed zone was not observed in the as-deposited TBC but formed during subsequent high-temperature exposure.

Intermixed zones have also been observed on NiCoCrAlY bond coats. Schulz *et al*.[5] reported the zone formed during EB-PVD TBC deposition at about 1000 °C and comprised the entire TGO, which was about 800-nm thick. The zone continued to grow during subsequent exposure at 1050 °C until an inner, columnar layer of α-Al_2O_3 formed. At this stage, the intermixed zone (thickness of about 1500 nm) stopped growing.

Levi *et al*. studied the oxidation behavior of a bulk two-phase ($\beta + \gamma$) NiCrAl alloy with and without a TBC.[6] It was found that the two phases oxidized differently in the absence of a TBC. An intermixed zone in the TGO was observed on both phases under a TBC deposited at 1100 °C. However, if the alloy was preoxidized to form α-Al_2O_3 prior to TBC deposition, no intermixed zone formed. This was explained as resulting from the dissolution of zirconia in the transition θ-alumina, which has a significant solubility for zirconia,[7] and the reprecipitation of zirconia as the θ transformed to α. It was also argued that the dissolution of Zr (and Y) in θ further delays its transformation to α, enabling the mixed zone to grow to a thickness larger than that expected from the transient alumina growth on NiCrAlY absent the TBC.

The preceding results, some of which appear to be contradictory, provided the impetus for the current study. Here, the microstructures of a wide range of as-processed and exposed TBCs have been examined with a particular emphasis on the mechanism(s) and kinetics of the development of the intermixed zone. Also, a set of carefully controlled TBC deposition experiments has been conducted to further elucidate the mechanism(s).

II. EXPERIMENTAL

Disks (2.5-cm diameter) of René N5 were coated with Pt-modified aluminide and NiCoCrAlY bond coats using commercial processes. The Pt-modified aluminides were prepared by electroplating a thin (~5 to 7 μm) layer of Pt on the superalloy, heat treating, and then aluminizing in a chemical vapor deposition reactor under "low aluminum activity" conditions. The Pt-modified aluminide coatings were single phase (B2) with composition Ni, 40–45Al, 8 to 10 Pt, 5Cr, and 5Co (at. pct) plus traces of other substrate elements (Ta, Hf). The NiCoCrAlY bond coats were deposited by argon-shrouded plasma spraying. The NiCoCrAlY bond coats had composition Ni-24Al-19Co-15Cr-0.1Y (at. pct) and were two phase (B2, fcc). Most of the bond coats were grit blasted prior to TBC deposition ($R_a \approx 2$ μm). However, selected specimens were TBC coated in the as-bond-coated condition or had their surfaces polished. Some specimens were also preoxidized prior to TBC deposition. The TBC was 7YSZ deposited by EBPVD using commercial processing parameters. This involved deposition at elevated temperatures (≈1000 °C) with a low oxygen partial pressure in the coater. Exact details of the deposition conditions are proprietary. The same TBC was also deposited onto sapphire crystals.

The specimens were exposed in air under both isothermal and cyclic conditions at temperatures of 1100 °C, 1121 °C, and 1200 °C. Most exposures were performed in laboratory air using a bottom-loading furnace. The heating and cooling rates were approximately 2 °C/s. As-processed and exposed specimens were examined in a cross section by SEM, and selected specimens were examined by TEM.

A. *Controlled TBC Deposition*

A separate group of specimens was prepared under laboratory conditions so that all of the TBC deposition parameters were known and controlled. Four slabs of René N5 (2.5 cm × 2.5 cm) had perpendicular grooves machined through the center of one face of each slab (to facilitate subsequent sectioning into four coupons) and were coated with the commercial Pt-modified aluminide, described previously. Two slabs (set A) were left in the as-aluminized condition and two (set B) were pre-oxidized for 2 hours in dry air at 1100 °C. The preoxidation conditions were based on previous results,[8] which indicated they would result in the formation of α-alumina scales. The presence of only α on the preoxidized surfaces was confirmed by PSLS.

The TBC deposition was carried out using the EBPVD system at UCSB in two separate runs. The system is equipped with a 20 kW electron gun operating at 40 kV. In each deposition, one as-aluminized (A) and one pre-oxidized (B) substrate were mounted diametrically opposite to each other on a cylindrical alumina substrate holder that was rotated at 8 rpm. The substrates were actively heated to 1000 °C using a SiC heater coaxial with the holder. The electron beam was focused onto a 7YSZ ingot of 2.5-cm diameter to obtain stable evaporation while the temperature was ramped up. The substrates were exposed to the vapor after reaching 1000 °C by opening the vapor shutter. The summary of conditions used for the different specimens is given in Table I.

Following TBC deposition, each slab was sectioned along the previously machined grooves to yield four coupons (12 × 12 mm) for each combination of pretreatment and TBC deposition conditions. One specimen from each slab was examined by PSLS with the laser beam directed through the TBC. This confirmed that, as expected, the TGO on the two preoxidized coupons consisted only of α-alumina. The PSLS spectra from the coupons that were TBC coated in the as-aluminized condition produced a weak α-alumina signal and another weak peak that could not be conclusively identified. It is possible that this weak peak corresponds to a metastable polymorph of alumina. Another specimen from each slab was cross sectioned and examined by SEM. One additional specimen from each slab was exposed isothermally for 10 hours at 1200 °C in air (the conditions used to produce the intermixed zone in Figure 1) and cross sectioned.

B. *Transmission Electron Microscopy*

The TEM specimens were obtained using a focused ion beam (FIB, FEI Strada DB235) both from the as-deposited and exposed TBCs from coupons of A1 (non-preoxidized with minimal oxidation in the coater). The TEM cross sections were normal to the TBC/TGO interface. Electron diffraction and imaging were carried out on an FEI Tecnai T20 transmission electron microscope operated at 200 kV. Energy dispersive X-ray spectrometry was performed using a JEOL*-2010 TEM fitted with an Oxford Instruments spectrometer.

III. RESULTS

A. *Baseline Scenario*

To provide context, it is useful to examine first the possibilities of diffusional interaction between YSZ and α-Al_2O_3 when in contact at high temperatures. Figure 2(a) depicts the interface of a 7YSZ TBC deposited on a sapphire crystal, and Figure 2(b) presents the same interface after exposure for 10 hours in air at 1200 °C, the conditions used to produce the intermixed zone in Figure 1. This micrograph shows that there has been substantial coarsening and rearrangement of the porosity within the TBC, but no evidence of reaction or even significant morphological evolution at the YSZ/sapphire interface, *e.g.*, no grooving of the YSZ grain boundaries. This result indicates that an intermixed zone cannot form by interaction between YSZ and α-alumina that is not growing.

B. *Controlled TBC Deposition Study*

Figure 3 shows a comparison of SEM cross sections for the TGOs generated in the four different specimens investigated (A1, B1, A2, B2), both after deposition (a, c, e, g) and after oxidation in air for 10 hours at 1200 °C (b, d, f, h), respectively. (The vertical arrows indicate total TGO thickness including any intermixed zone.) It is first noted that the deposition conditions have no effect on the development of the TGO for the preoxidized specimens (B1, B2). The TGO is approximately 0.3-μm thick after deposition (Figures 3(c) and (g)) and grows to ~1 μm after the prescribed exposure, with no

Table I. Summary of Conditions Used for the Different Specimens in the Controlled Deposition Study of Intermixed Zone Formation

			Ramp-Up		Deposition	
Specimen	Preoxidation	Oxidation in Coater	Time (min)	Pressure (torr)	Time (min)	Pressure (torr)
A1	no	minimal	60	5×10^{-7}	30	1.5×10^{-3}
B1	yes					
A2	no	maximal	60	5×10^{-3}	60	5×10^{-3}
B2	yes					

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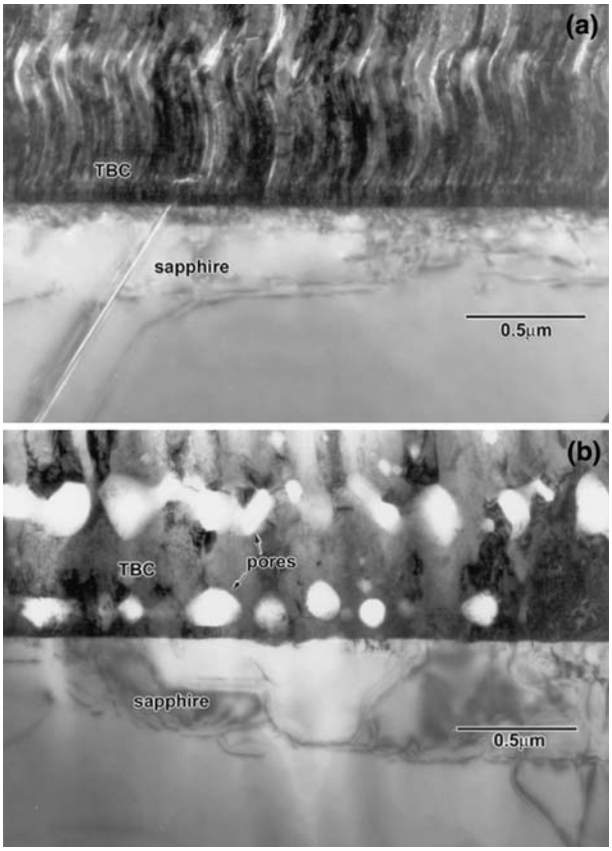

Fig. 2—Cross-sectional micrograph (TEM) of the interface between a sapphire crystal and an EBPVD YSZ TBC (*a*) in the as-processed condition and (*b*) after a 10-h exposure at 1200 °C in air.

evidence of mixed zone formation (Figures 3(d) and (h)). The TGO prior to deposition was identified as α-Al_2O_3 by PSLS and continues to develop as such during the subsequent stages.

Conversely, the TGO in the specimens coated in the as-aluminized condition (A1, A2) are not only significantly different from their B counterparts, but also exhibit notable differences between themselves. For the specimen wherein efforts were made to minimize oxidation during deposition (A1, Figure 3(a)), the TGO is not markedly different in thickness from its preoxidized counterpart (*cf.* Figures 3(a) and (c)) but appears slightly less convoluted and, more importantly, shows weak peaks in PSLS, which were definitely not α-Al_2O_3 but could not be conclusively identified. After the 1200 °C/10 h oxidation in air, the TGO has clearly evolved into two distinct layers: an intermixed zone ~1 μm thick on top, with a dense layer consisting only of alumina, presumably columnar and ~1.2-μm thick (Figure 3(b)). By comparison, the total thickness of the TGO for the preoxidized specimen was only ~1 μm, as noted previously (Figure 3(d)).

For the specimen wherein oxidation was promoted during deposition (A2), the TGO was noticeably thicker (~0.5 μm) than the others after deposition and showed the presence of small second phases (Figure 3(e)). Again, the polymorph of alumina could not be conclusively identified, but PSLS spectra were inconsistent with α or θ. Exposure at 1200 °C/10 h also resulted in the formation of an intermixed zone over a dense inner layer (Figure 3(f)), but the former was much thinner than that developed on the A1 specimen (Figure 3(b)). Both the intermixed zones showed the formation of some needlelike alumina extending into the TBC after the 1200 °C exposure.

The bright-field TEM images in Figure 4 show the microstructure of the TGO for specimen A1 in the as-deposited condition, with the neighboring TBC and bond coat layers (Figure 4(a)) and in the nanocrystalline oxide in more detail (Figure 4(b)). The EDS showed the presence of ~3.7 at. pct Zr on a cation (Zr + Al) basis or 7.14 mol pct ZrO_2 on an oxide basis. Selected area electron diffraction (inset in Figure 4(a)) showed that the TGO is most likely a distorted θ-Al_2O_3 and possibly contains some γ-Al_2O_3 but no evidence of ZrO_2 or any other second phase. Analysis of bright-field and dark-field images indicates that the contrast in Figure 4(b) is from differences in grain orientation rather than atomic mass. The TEM evidence strongly suggests that the TGO is made up of metastable alumina solid solution, with no ZrO_2 phase or α-Al_2O_3 being present. The TBC/TGO interface is not significantly convoluted, as noted previously in Figure 3(a), suggesting that the θ-Al_2O_3 did not grow in the typical needlelike morphology prior to 7YSZ deposition.

The bright-field TEM image from an exposed specimen of A1 (Figure 5) shows the mixed zone consisting of fine equiaxed grains and precipitates between the TBC (above) and the columnar TGO free of precipitates (below). A few pores were seen at the interface between the precipitate zone and columnar zone in the TGO. The EDS from the entire precipitate zone showed ~3.6 pct Zr on a Zr + Al basis, consistent with the analysis of the TGO in the as-deposited condition. Figure 5 also shows SAD patterns from the locations indicated in the BF image.** The SAD I corresponds to a columnar α-Al_2O_3 grain (ZAP = 211), free of precipitates. The SAD III is taken from a large α-Al_2O_3 grain (ZAP = 100) with precipitate inclusions, traversing much of the mixed zone. The SAD II shows a mixture of α-Al_2O_3 and tetragonal ZrO_2 randomly oriented grains in the location indicated in the BF image. Comparison with the as-deposited condition indicates that the intermixed zone formed by the precipitation of dissolved ZrO_2 in the θ-Al_2O_3 as the latter transformed to α-Al_2O_3 upon thermal exposure.

C. *Deposition of TBC on Preoxidized Specimens with Alumina Needles*

Figure 6(a) shows the surface of a Pt-modified aluminide bond coat, which was media finished and then preoxidized for 2 hours at 1100 °C in a mixture of Ar-4 pct H_2, *i.e.*, where the O_2 content was very low

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**Different *X* and *Y* tilts were used for recording the BF image and each of the three diffraction patterns in Fig. 5, so the areas do not necessarily appear in contrast in the image as expected from the ZA patterns.

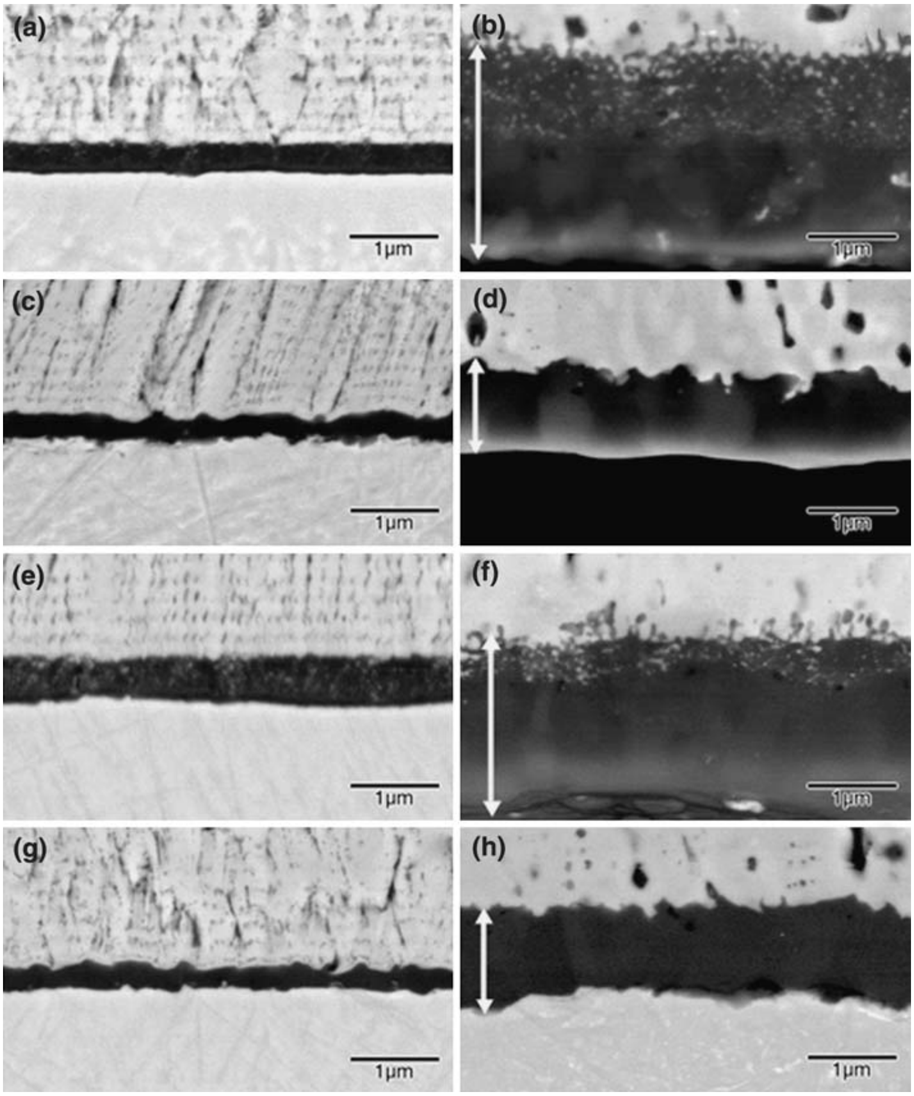

Fig. 3—Cross-sectional micrographs (SEM) of controlled deposition specimens in the as-deposited state (left) and after 10 h at 1200 °C in air (right): (*a*) and (*b*) A1, (*c*) and (*d*) B1, (*e*) and (*f*) A2, and (*g*) and (*h*) B2. The TGO appears dark with the TBC on top and the bond coat underneath. The arrows denote the thickness of the TGO after exposure. Specimen A was not preoxidized prior to deposition, whereas specimen B was preoxidized. (It is also noted that the BC/TGO interface delaminated on cooling from the 1200 °C oxidation temperature.).

($pO_2 < 10^{-6}$atm). This treatment resulted in an oxide that consisted of θ-alumina, as identified by PSLS, which grew outward with a needlelike morphology. A TBC was then deposited onto such a surface and subsequently exposed for 260 cycles at 1121 °C. This specimen exhibits a 1-μm-thick intermixed zone (Figure 6(b)), which appears to have formed, at least partially, by the deposition of the YSZ into the needlelike θ-alumina region. The structure of the needles was not determined following cyclic oxidation, but the literature[9] suggests they would have transformed to α after relatively short exposure times.

D. *Intermixed Zone Formation on a Variety of Commercially Processed Coatings*

Table II summarizes the observations of mixed zone formation on commercially produced bond coats with various surface treatments. All specimens had YSZ topcoats deposited by EBPVD in a commercial coater. Systems with NiCoCrAlY bond coats tended to form discontinuous regions of intermixed alumina and YSZ except when a thin layer of Pt was applied prior to TBC deposition. These specimens were produced by electroplating a thin layer of Pt (5 to 7 μm) on a NiCoCrAlY bond coat. The specimens were annealed for 4 hours in vacuum at 1025 °C prior to TBC deposition. This resulted in the development of a layer of a Pt-Al compound under the TBC, which formed a layer of pure alumina during TBC deposition. Details of these specimens are given in References 10 and 11. In this case, very extensive intermixed zones were formed, as illustrated in Figure 7. The crystal structure of the alumina within the intermixed zone was not determined, but the dense alumina layer beneath the zone was concluded to be α based on its thickening kinetics. In the case of Pt-

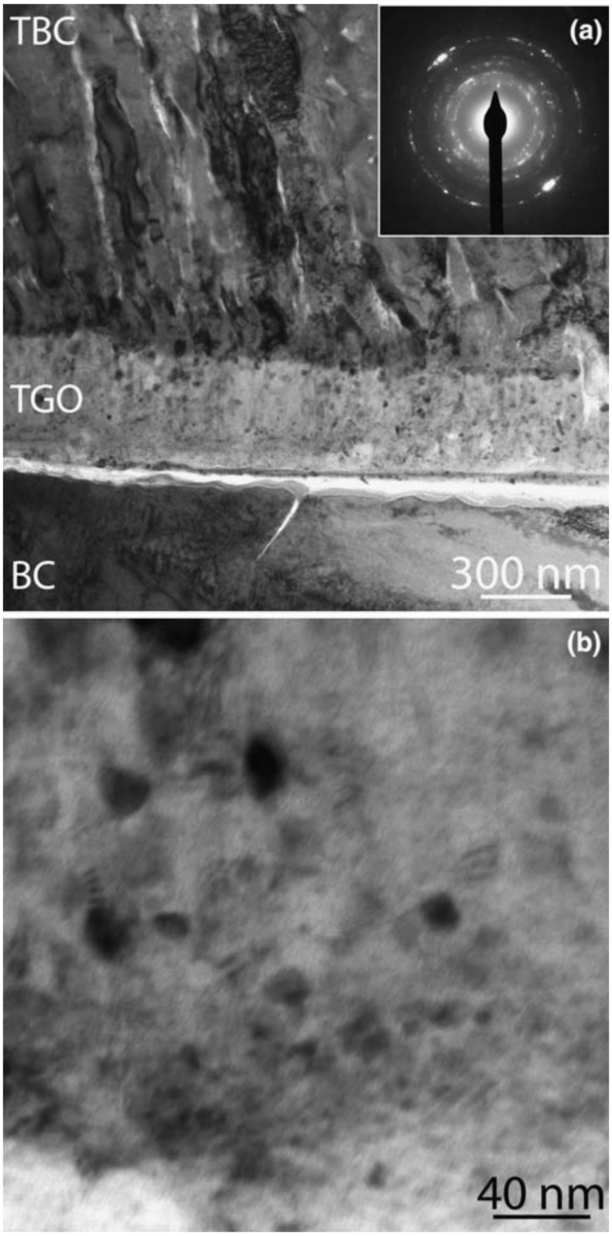

Fig. 4—Bright-field images of a TBC as deposited on a substrate as aluminized (A1). (*a*) The TGO after deposition and the neighboring TBC and bond coat. (b) A detail of the nanocrystalline TGO. The inset SAD pattern in (a) reveals the presence of θ-Al_2O_3. The bright contrast near the BC/TGO interface is a crack introduced during FIB sectioning.

modified aluminide bond coats, continuous intermixed zones were formed on specimens wherein the TBC was deposited on an as-aluminized bond coat. Preoxidation prevented the formation of an intermixed zone, in agreement with the controlled deposition experiments.

Figure 7 presents results for the formation kinetics of the intermixed zone. There was no intermixed zone observed in the TGO on the as-coated specimen at the level of resolution of the SEM. Figure 7 shows cross sections of identical specimens exposed in air for 10, 60, 100, and 880 cycles where one cycle included 45 minutes at 1100 °C. After 10 cycles, there was an intermixed zone approximately 1-μm thick over a thin layer of pure alumina. After 60 cycles, the thickness of the intermixed zone had increased to about 2 μm but did not thicken further after exposures of 100 and 880 cycles. (Note that the magnification of Figure 7(d) is different from that of Figures 7(a) through (c).) This indicates that between 10 (7.5 hours of hot time) and 60 cycles (45 hours of hot time), the intermixed zone stopped growing. The dense layer of alumina continued to thicken throughout the duration of the experiment.

Figure 8 presents cross-sectional micrographs of a TBC with a NiCoCrAlY bond coat, which was hand polished using 3-μm diamond prior to TBC deposition. The as-deposited coating exhibits a thin TGO with no intermixed zone (Figure 8(a)). After 220 cycles, a substantial intermixed zone had developed (Figures 8(b) and (c)). The intermixed zone was the same thickness after 1520 cycles (Figure 8(d)) as after 220 cycles. This specimen had not yet failed after 1520 cycles, but cracks and buckle-type delaminations formed between the intermixed zone and the dense TGO even after 220 cycles (Figure 8(c)). The light phases in the dense alumina in Figures 8(c) and (d) are reactive element (Y, Hf) oxides formed by internal oxidation and subsequent incorporation into the inward-growing alumina.[11]

IV. DISCUSSION

The cumulative evidence indicates that intermixed zones may form in a variety of circumstances and exhibit somewhat diverse characteristics, including content, size, and morphology of the zirconia and "host" thermally grown oxide. Hence, it appears unlikely that a single mechanism may account for all the different observations. It is helpful, however, to consider first which mechanisms are unlikely to operate so they can be eliminated from the subsequent discussion.

There has been some conjecture that the intermixed zone may form by vapor transport of an Al-containing species from the TGO into the TBC. Figure 9 presents a vapor species diagram for the Al-O system calculated for a temperature of 1200 °C. This diagram was calculated using data from Barin[12] using the method described in Reference 13. The solid lines pertain to pure Al, while the dashed lines were calculated for Al at an activity of 10^{-2}, *i.e.*, a value that might be expected at a TGO/bond coat interface. However, the activity of Al only affects the diagram at low partial pressures of oxygen. The YSZ TBC is transparent to oxygen so that the oxygen partial pressure at the TGO/TBC interface is essentially that in the ambient atmosphere. The intersections of the various vapor species lines with the vertical line corresponding to air, at the right of the diagram, indicate the species with the highest vapor pressure is AlO_2. However, the pressure of this species is on the order of 10^{-20} atm, which is much too low to result in measurable vapor phase transport (it corresponds to one molecule in a volume of about 20 cm^3).

A mechanism based on the dissolution of YSZ in α-Al_2O_3 at elevated temperatures followed by subsequent precipitation upon cooling is also not supported

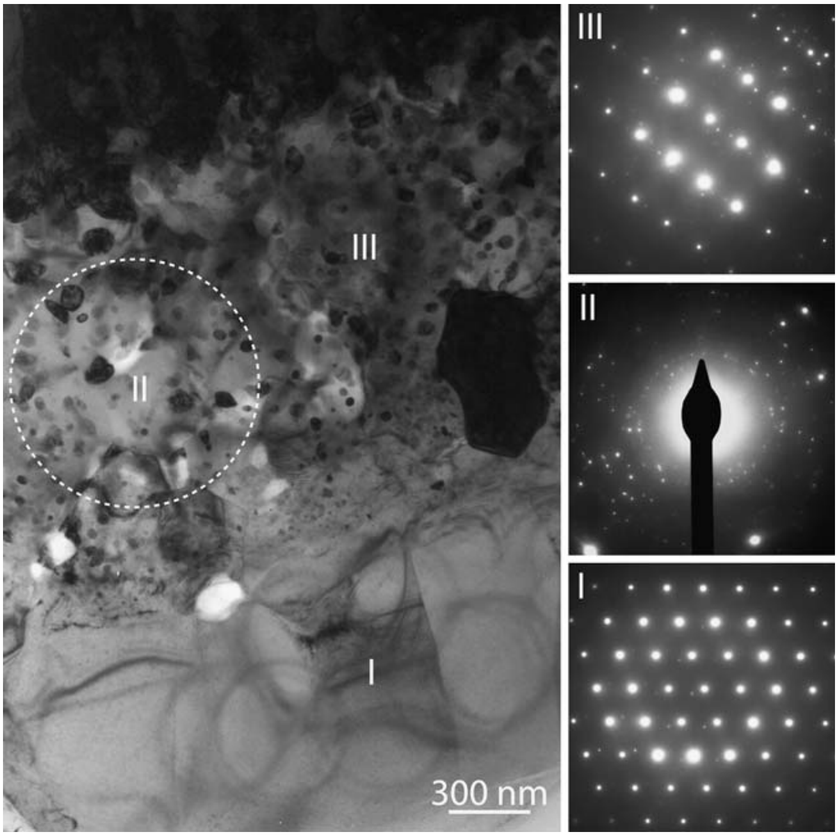

Fig. 5—Bright-field image of the TGO after 10 h at 1200 °C. The diffraction patterns are taken from the marked regions. I: 211 zone axis of α-Al_2O_3; II: 100 zone axis of α-Al_2O_3; and III: ring patterns from tetragonal ZrO_2 and α-Al_2O_3.

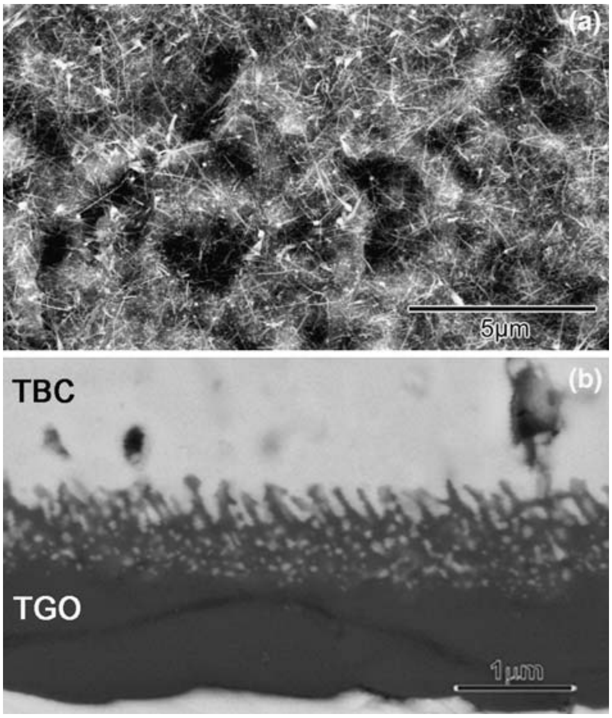

Fig. 6—(*a*) Surface micrograph (SEM) of a Pt-modified aluminide bond coat, which was media finished and preoxidized in Ar-4 pct H_2 for 2 h at 1100 °C. (*b*) Cross-sectional SEM view of a specimen prepared in the same manner as that in (a) but coated subsequently with an EBPVD TBC and then exposed in air for 260 cycles at 1121 °C.

by the evidence or what is known about the phase equilibria.[14] The YSZ and α-Al_2O_3 are in thermochemical equilibrium at the temperatures of interest (≤1200 °C), and thus, there is no driving force for any chemical reaction (apparently the activity of yttria in the YSZ is too low for the formation of ternary Al-Y-O compounds). Moreover, the equilibrium solubility of YSZ in α-alumina is negligible, and that of Al_2O_3 in YSZ is only about 2 mol pct. Hence, no mixed zone of any significance is expected by simple contact between YSZ and α-Al_2O_3, in agreement with Figure 2 and the absence of mixed zones in specimens preoxidized to establish α-Al_2O_3 before TBC deposition (*e.g.*, Figures 3(d) and (h)).

The formation of the intermixed zone appears to require an outward growing alumina scale (*e.g.*, γ or θ) and intimate contact between the YSZ and the alumina. The straightforward way that this can occur is the mechanism proposed by Murphy *et al.*[4] and illustrated in Figure 6. If there is substantial needle growth of θ- or γ-alumina prior to TBC deposition, clearly, an intermixed zone will develop as the YSZ deposits among the needles. A zone formed in this manner has a distinct elongated morphology of the alumina in the intermixed zone (Figure 6(b)). However, all of the other zones were formed on specimens that had little or no intermixed zone present immediately after TBC deposition, at least within the resolution of the SEM. Moreover, the TBC in Figures 3(b) and (f) had no apparent needles present in

Table II. Summary of Intermixed Zone Observations on TBCs Deposited in a Commercial EBPVD Coater

Bond Coat	Preparation*	Continuous	Discontinuous	None/trace
NiCoCrAlY	HGB		√	
	MF		√	
	VF		√	
	PtU		√	
	Al		√	
	HP	√		
	HP + PO			√
	PtO	√		
	MF + PtO	√		
	MF + PtO + MF	√		
	MF + PtO + MF + PO	√		
Ni(Pt)Al	AA	√		√
	HGB		√	
	HP			√
	LGB + PO			√

*Key to preparation: AA = as aluminized, Al = aluminized, HGB = heavy grit blast, HP = hand polished, LGB = light grit blast, MF = media finish, PO = preoxidized, PtO = Pt overlayer, PtU = Pt underlayer, and VF = vibratory finish.

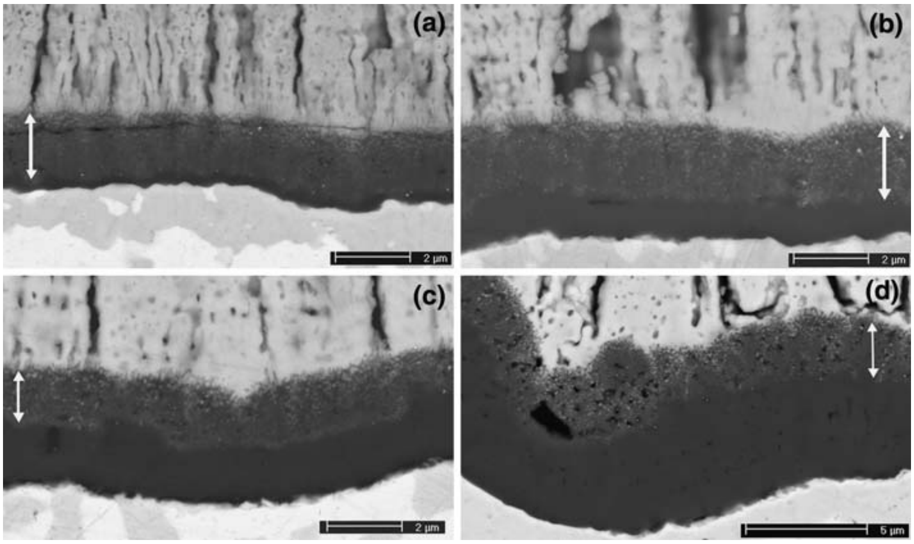

Fig. 7—Cross-sectional micrographs (SEM) of the intermixed zone developed between an EBPVD TBC and a NiCoCrAlY bond coat with a Pt overlayer after (*a*) 10, (*b*) 60, (*c*) 100, and (*d*) 880 cycles at 1100 °C in air.

the as-deposited coating, but developed needlelike alumina growth into the intercolumnar gaps during subsequent exposure.

The results of the controlled deposition study, especially the TEM analysis, strongly suggest the following mechanism for the formation of the majority of the zones. The TGO in the as-deposited condition, for specimens that were not preoxidized, appears to be a solid solution of ZrO_2 in θ-Al_2O_3, because no ZrO_2 phase was detected. Upon heat treatment at 1200 °C, the TGO grew outward and eventually transformed to the stable α-Al_2O_3. Because the solubility of ZrO_2 in α-Al_2O_3 is negligible,[9,14] precipitation of ZrO_2 in the tetragonal form accompanied this transformation. The appearance of a few pores in the precipitate zone as well as at the interface with the columnar zone is consistent with the difference in molar volume between θ-Al_2O_3 and α-Al_2O_3. (Laxman *et al.*[15] reported similar void formation in a system where γ was the dominant transient Al_2O_3, also with a large difference in molar volume relative to α.) However, the intermixed zone can also form as the result of the outward growth of the metastable alumina concurrent with dissolution of ZrO_2 and subsequent reprecipitation upon transformation to α. This is suggested by the results in Figure 7, where a 1-μm-thick intermixed zone had formed after 10 cycles and the zone continued to grow until at least 60 cycles had been reached. Presumably, the transformation from θ to α occurred between 10 and 60 cycles, stopping the further growth of the zone.

The overall results suggest that the intermixed zone formation in the majority of present systems involves formation of a metastable alumina polymorph during TBC deposition, with a significant amount of zirconia

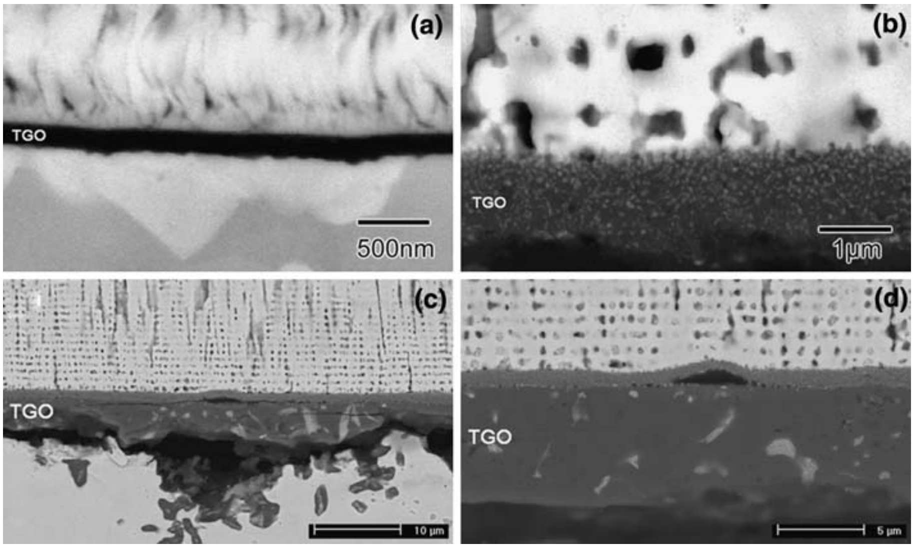

Fig. 8—Cross-sectional micrographs (SEM) of the (a) as-deposited coating and the intermixed zone developed between an EBPVD TBC and a hand-polished NiCoCrAlY bond coat after (*b*) and (*c*) 220 cycles and (*d*) 1520 cycles at 1100 °C in air.

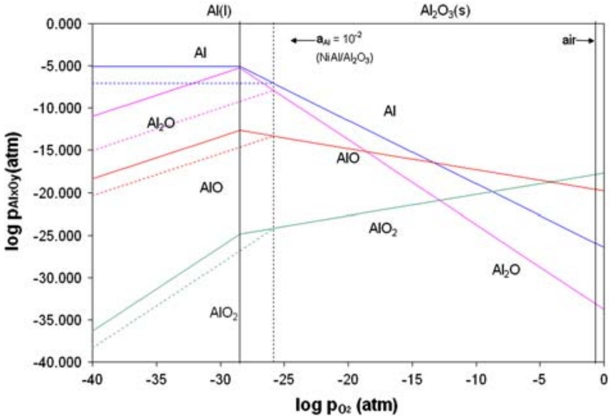

Fig. 9—Vapor species diagram for the Al-O system at 1200 °C.

dissolved in it. Upon thermal exposure, the metastable TGO grows outward, forming the intermixed zone, and eventually transforms to the equilibrium α-Al_2O_3, resulting in further precipitation of zirconia. Once the α-Al_2O_3 appears, subsequent TGO growth produces the columnar zone of the TGO.

Some of the results presented appear to be somewhat at variance with the preceding mechanism.

(1) The original work by Stiger *et al.*[1,2] indicated that the TGO in an as-deposited TBC on a Pt-modified aluminide bondcoat was α-alumina, but subsequent exposure still produced an intermixed zone. A likely explanation is that the small area examined by TEM for the as-processed specimen contained α-alumina, but a substantial fraction of the interfacial area was still covered by metastable (θ, γ) aluminas.
(2) Other specimens with a polished NiCoCrAlY bond coat also indicate the zone forms early then stops growing. One normally expects NiCoCrAlY to rapidly form α. This result suggests that this is perhaps not the case for alumina nucleated in the presence of a YSZ flux. Further TEM studies will be required to test this hypothesis.

V. SUMMARY AND CONCLUSIONS

1. The intermixed zone can form during TBC deposition but only in situations where there are pre-existing alumina needles or where there is excessive oxidation during TBC deposition.
2. In most cases, the zone forms or grows during subsequent high-temperature exposure.
3. The zone formation in all cases, except upon deposition into preformed alumina needles, requires an outward-growing oxide (θ- or γ-alumina or spinel) and ceases when the transformation to α-alumina occurs.

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