

Isothermal Oxidation of Physical Vapor Deposited Partially Stabilized Zirconia Thermal Barrier Coatings

Y.H. Sohn, R.R. Biederman, and R.D. Sisson, Jr.

Thermal barrier coatings (TBCs), consisting of physical vapor deposited (PVD) partially stabilized zirconia (PSZ, 8 wt. % Y_2O_3) and a diffusion aluminide bond coat, were characterized as a function of time after oxidative isothermal heat treatment at 1373 K in air. The experimental characterizations were conducted by X-ray diffraction analysis and scanning electron microscopy (SEM) with energy-dispersive spectroscopy. During cooling to room temperature, spallation of the PSZ ceramic coatings occurred after 200 and 350 h of isothermal heat treatment. This failure was always sudden and violent, with the TBC popping from the substrate. The monoclinic phase of zirconia was first observed on the bottom surface of the PVD PSZ after 200 h of isothermal heat treatment. The failure of TBCs occurred either in the bond coat oxidation products of $\alpha-Al_2O_3$ and rutile TiO_2 or at the interface between the oxidation products and the diffusion aluminide bond coat or the PSZ coating.

Keywords:

oxidation, partially stabilized zirconia, thermal barrier coating

1. Introduction

PARTIALLY stabilized zirconia (PSZ) thermal barrier coatings (TBCs) are being developed to increase the performance and efficiency of a variety of heat engines.^[1] Previous investigations have shown that TBCs can fail due to the prolonged cyclic exposure to a high-temperature oxidizing environment.^[1] The sources of stress causing the TBC failure include the thermal expansion mismatch between the ceramic coating and the metallic bond coat, bond coat oxidation, phase transformation within ZrO_2 , as well as bond coat deformation.^[1-3]

Characterization of thermal fatigue-tested TBCs has revealed that the failure of TBCs frequently is associated with the oxidation products of the MCrAlY bond coat formed at the PSZ ceramic/bond coat interface.^[4,5] The oxidation products of a MCrAlY bond coat consisted of selectively formed $\alpha-Al_2O_3$ as well as $(Al,Cr)_2O_3$, $Ni(Cr,Al)_2O_4$, and/or $NiCr_2O_4$ spinels, and Cr/Ni-rich oxides that were found to form with longer exposure to the high-temperature oxidizing environment.^[6] Fracture paths often were observed within spinels and other Ni/Cr-rich oxides that formed at the interface between these oxidation products and PSZ TBC or the MCrAlY bond coat.^[4,5] It was also observed that the metastable tetragonal (t') phase of plasma-sprayed PSZ ceramic coating^[7] slowly transformed to the monoclinic and cubic phases as a result of thermal cycling.^[4] Although carefully controlled formation, i.e., phase transformation, of the monoclinic phase is responsible for the transformation toughening of PSZ ceramics, the transformation may also degrade the structural integrity of the coating.^[8]

A life prediction model for TBCs was developed based on the experimental observations that the fracture paths frequently were associated with the formation of $Ni(Cr,Al)_2O_4$ and/or

$NiCr_2O_4$ spinels and other Ni/Cr-rich oxides.^[9,10] The formation of these more complex oxides was determined to be the life-limiting event for TBCs. This model describes the aluminum depletion from the bond coat by interdiffusion between the bond coat and the substrate as well as the formation of $\alpha-Al_2O_3$ oxides at the PSZ ceramic/bond coat interface. The formation of spinels and other Ni/Cr-rich oxides (i.e., TBC failure) is estimated to occur when the aluminum concentration in the bond coat drops below 10 at.% according to the oxide formation map.^[11] This aluminum concentration approximately corresponds to the aluminum content when the Al-rich, $\beta-NiAl$ phase disappears from the bond coat. Therefore, the model predicts the TBC failure when the $\beta-NiAl$ phase disappears from the MCrAlY bond coat.^[9,10] Detailed explanation of modeling principles and the results from the verification/experiment of the model are presented elsewhere.^[9,10,12]

On the basis of these previous experimental results, the objective of this work was to study the phase transformations of the PSZ (ZrO_2 -8 wt. % Y_2O_3) ceramic coating and the formation of oxidation products at the interface between the PSZ ceramic coating and the diffusion aluminide bond coat during isothermal oxidation at 1373 K (1100 °C) in air. The phase transformations of the PSZ coatings and the bond coat oxidation will be related to the failure of the PSZ TBCs.

2. Experimental Procedure

The thermal barrier coating system used in this study consisted of 125- μm thick electron beam physical vapor deposited (EB-PVD) ZrO_2 -8 wt. % Y_2O_3 ceramic coating on 40- μm diffusion aluminide bond coat. The superalloy substrate was René 80H. To investigate the microstructural and microchemical change in the PSZ coating and the bond coat oxidation products during high-temperature exposure, isothermal heat treatment was conducted at 1373 K for 50, 100, 200, and 350 h in air. All TBC specimens were cooled in air after the isothermal heat treatment.

The phase analysis was conducted on the as-deposited and the heat treated TBC using X-ray diffraction with copper $K\alpha$ radiation. The X-ray diffraction (XRD) pattern was obtained

Y.H.Sohn, R.R. Biederman, and R.D. Sisson, Jr., Materials Engineering Laboratories, Mechanical Engineering Department, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609-2280.

Table 1 X-ray diffraction analysis for isothermal heat treatment of PVD ZrO₂-8 wt.% Y₂O₃ coatings

Heat treatment time, h	PSZ surface	Nonequilibrium tetragonal		
		a, Å	c, Å	c/a
As-deposited	Top	5.1104	5.1620	1.0101
50	Top	5.1064	5.1591	1.0103
100	Top	5.0972	5.1516	1.0107
200	Top	5.1039	5.1617	1.0113
200	Bottom	5.0896	5.1528	1.0124
350	Top	5.1336	5.1061	1.0121
350	Bottom	5.1026	5.1605	1.0113

radiation. The X-ray diffraction (XRD) pattern was obtained from the top surface of the PSZ coating as well as the bottom surface of the spalled PSZ coating. The X-ray diffraction patterns from the (111) and (400) regions of the metastable tetragonal (*t'*) phase were obtained to detect the presence of the monoclinic (*M*) and cubic (*F*) phases. Quantitative phase analysis could not be performed due to the crystallographic texture of the PVD coating. The microstructure of the TBC systems was characterized by scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS). Emphasis was given to the ceramic (PSZ)/bond coat interface and the bond coat oxidation products. The microconstituents on the fracture surfaces, i.e., bottom surface of the PSZ coating and the top surface of the metallic bond coat, were also characterized using XRD and SEM with EDS.

3. Results and Discussion

After 50 and 100 h of isothermal heat treatment at 1373 K, no failure was observed upon cooling for the TBCs. However, approximately 40 to 50 area percent of the PSZ ceramic coating spalled after 200 h, and 100 area percent spalled after 350 h. The PSZ ceramic coating was observed to fail violently after approximately 5 min of air cooling. This experimental lifetime value of the TBCs with the diffusion aluminide bond coat (between 100 and 200 h) is longer than the predicted value of 72 h for similar TBCs with MCrAlY bond coats, as predicted by the authors' model.^[9,10,12]

3.1 Phase Changes in PVD ZrO₂-8 wt.% Y₂O₃ Coating

The X-ray diffraction (XRD) patterns in the (111) and (400) regions for the as-deposited and the isothermally heat treated ZrO₂-8 wt.% Y₂O₃ samples are presented in Fig. 1(a) and (b). The 50- and 100-h heat treatments showed no significant difference from the as-deposited PSZ sample.^[13] Table 1 presents the two lattice parameters for the tetragonal phase in PSZ coatings before and after the isothermal heat treatment. As seen in Fig. 1(a), no monoclinic (*M*) phase was observed on the top surface of the as-deposited sample. From the (400) region in Fig. 1(b), the two peaks, i.e., (004) and (400), from tetragonal phase were found for the as-deposited PVD PSZ coating. The lattice parameters of the as-deposited tetragonal phase were measured to be $a = 5.1104 \text{ \AA}$ and $c = 5.1620 \text{ \AA}$ with the c/a ratio of 1.0101 as shown in Table 1. This c/a ratio corresponds to approximately 9.3 wt.% Y₂O₃, determined from Miller's Eq 1,^[7]

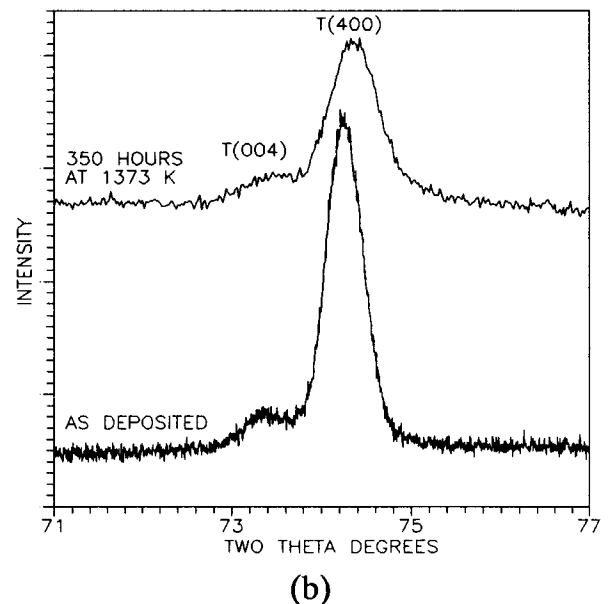
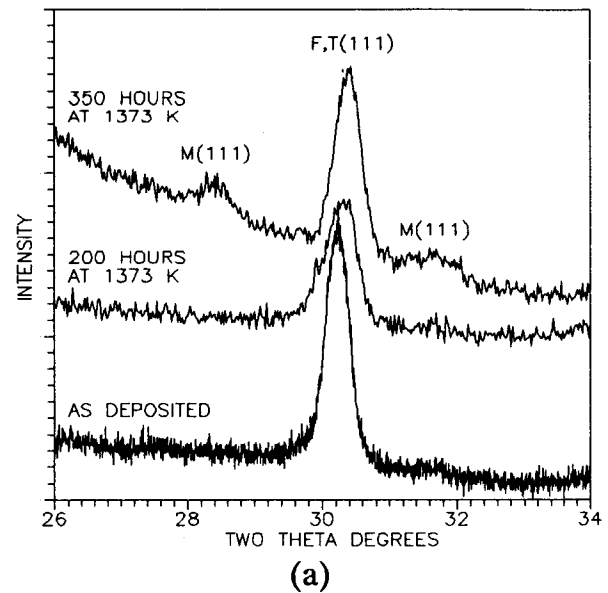


Fig. 1 XRD patterns in the (111) and the (400) region for the top surface of the as-deposited and isothermally heat treated ZrO₂-8 wt.% Y₂O₃ samples.

which relates the c/a ratio and the Y₂O₃ content within the PSZ tetragonal phase:

$$\text{at. \% YO}_{1.5} = \frac{(1.0223 - c/a)}{0.001309} \quad [1]$$

The high concentration of Y₂O₃ suggested that the physical vapor deposited ZrO₂-8 wt.% Y₂O₃ coating consisted of the

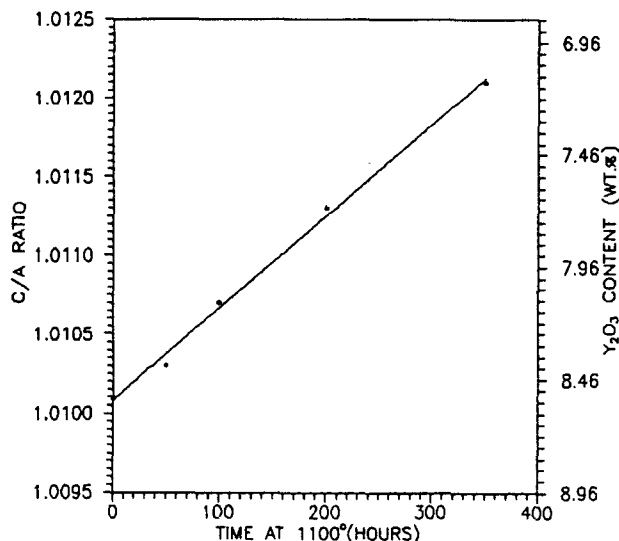


Fig. 2 Changes in the c/a ratio and corresponding Y_2O_3 content for the top surface of the nonequilibrium tetragonal ZrO_2-8 wt. % Y_2O_3 after isothermal heat treatment.

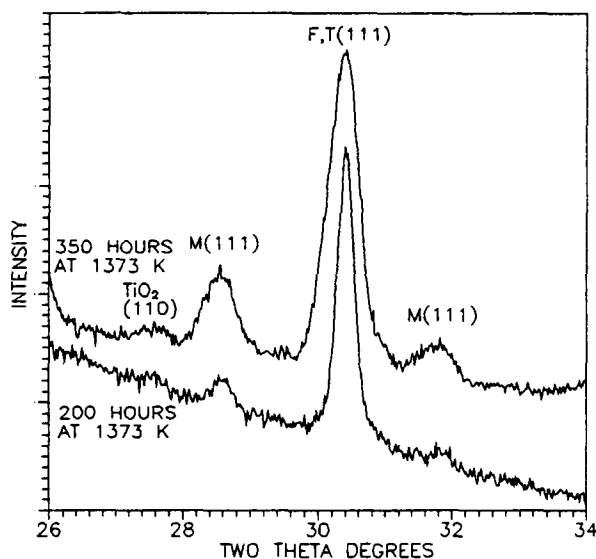


Fig. 3 XRD patterns in the (111) region for the bottom surface of the 200- and 350-h isothermally heat treated ZrO_2-8 wt. % Y_2O_3 samples.

nonequilibrium tetragonal (t') phase. After 50, 100, 200, and 350 h of heat treatment at 1373 K, the c/a ratio was found to increase, as shown in Table 1 and Fig. 2. The increase in c/a ratio corresponds to a decrease in Y_2O_3 content of the tetragonal phase, as seen in Eq 1 and in Fig. 2.

As seen in Fig. 1(a), the monoclinic phase was not observed after 200 h of isothermal heat treatment on the top surface of the PSZ coating. However, on cooling after 350 h at 1373 K, the monoclinic phase was detected, as shown in Fig. 1(a). This observation corresponds to the c/a ratio increase (i.e., Y_2O_3 content decrease). The lower Y_2O_3 content in the tetragonal (t') phase promotes the formation of high-temperature equilibrium

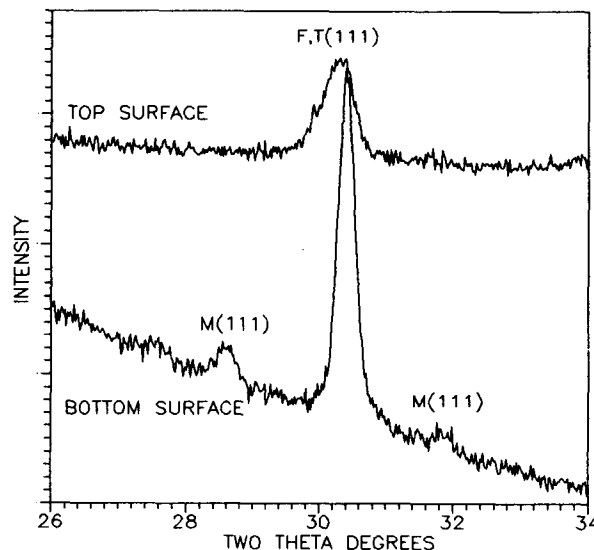


Fig. 4 XRD patterns for the top and the bottom surface of the spalled ZrO_2-8 wt. % Y_2O_3 after 200 h of isothermal heat treatment at 1373 K.

tetragonal (T) phase, which transforms more easily to a monoclinic phase during cooling. Therefore, the monoclinic phase developed progressively as the isothermal heating time increased. The monoclinic phase was also detected on the bottom surface of the spalled TBC after 200 and 350 h of isothermal heat treatment, as shown in Fig. 3. Figure 3 shows the increase in the amount of the monoclinic phase on the bottom surface of the spalled PSZ ceramic coating as the duration of the isothermal heat treatment increased.

Figure 4 shows the X-ray diffraction patterns from the (111) region of the top and the bottom surface of the spalled PSZ coating after 200 h of isothermal heat treatment. As shown in Fig. 4, although no monoclinic was observed on the top surface, the bottom surface of the spalled coating contained the monoclinic phase. The formation of the monoclinic phase results in a disruptive volume expansion of 3 to 5 vol.%,^[8] which could degrade the structural integrity of the ceramic coating. Similar results were obtained for the 350-h heat treated PSZ coating, as shown in Fig. 5. Although the monoclinic phase was found on the top surface of the PSZ coating after 350 h at 1373 K, significantly more monoclinic phase was observed on the bottom surface of the spalled coating after 350 h as the complete spallation of the ceramic coating occurred. Analysis on the fraction of the cubic phase could not be performed due to the crystallographic texture of the PVD coatings and broadening of the peaks from the (400) region, as shown in Fig. 1(b).

The monoclinic phase was found to develop as the result of isothermal heat treatment at 1373 K. Increase in the amount of monoclinic phase was observed as the isothermal heating time increased both on the top and the bottom surface of the PVD PSZ coating. The development of the monoclinic phase was also accompanied by the increase in the c/a ratio of the tetragonal phase (i.e., a decrease in the Y_2O_3 content of the nonequilibrium tetragonal phase). The monoclinic phase was first observed only on the bottom surface of the spalled PSZ coating

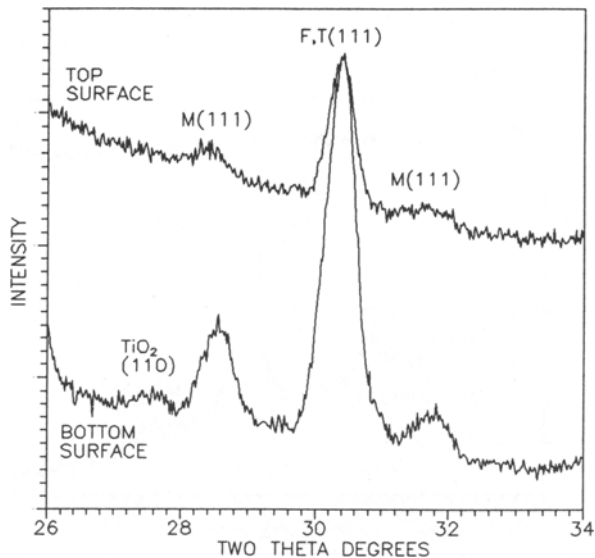


Fig. 5 XRD patterns for the top and the bottom surface of the spalled ZrO_2 -8 wt.% Y_2O_3 after 350 h of isothermal heat treatment at 1373 K.

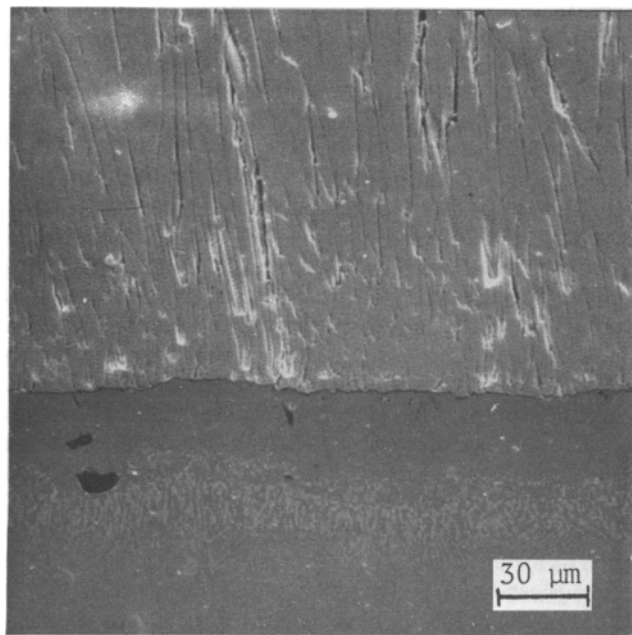


Fig. 6 SEM micrograph of the cross section of the as-deposited ZrO_2 -8 wt.% Y_2O_3 coating.

after 200 h of isothermal heat treatment. Also, significantly more monoclinic phase was observed on the bottom surface than the top after 350 h of isothermal exposure. These results are different from the plasma sprayed PSZ coating, which developed more monoclinic phase on the top surface of the coating as a result of thermal cycling.^[4]

The development of monoclinic phase is controlled by the grain size and chemical composition (i.e., Y_2O_3 content) of the

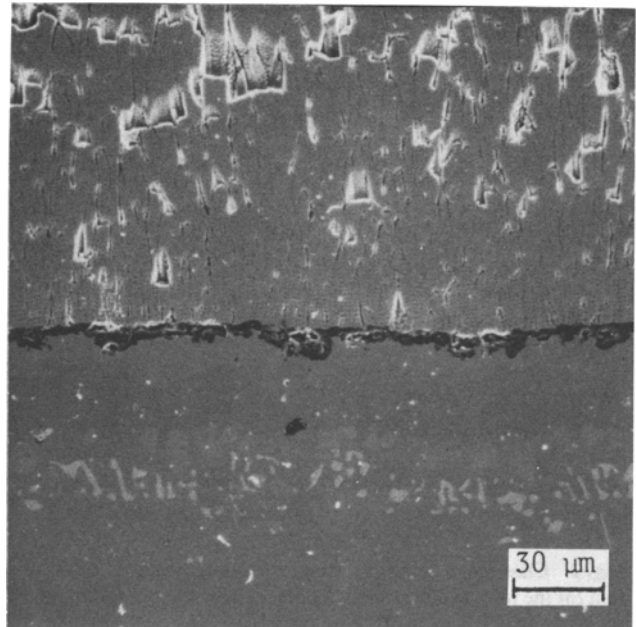


Fig. 7 SEM micrograph of the cross section of the isothermally heat treated (50 h) ZrO_2 -8 wt.% Y_2O_3 coating.

tetragonal phase. At 1373 K, the metastable tetragonal phase (t') phase slowly decomposes to the cubic (F) and the tetragonal (T) phases. On cooling, the tetragonal phases can transform to monoclinic if the grain size is large enough and the Y_2O_3 content is low enough.

3.2 Oxidation Products of Diffusion Aluminide Bond Coat

Cross-sectional SEM micrographs for the as-deposited and isothermally heat treated (50 h) EB-PVD TBCs are presented in Fig. 6 and 7. In Fig. 6, the top region is the columnar-grained EB-PVD PSZ coating, and the bottom region is the superalloy substrate. The diffusion aluminide bond coat is visible between the PSZ coating and the superalloy substrate. Various intermetallic and TCP phases were also found at the interface between the bond coat and the superalloy substrate due to the deposition of the diffusion aluminide bond coat. As shown in Fig. 6, a thin layer (less than 1 μm) and some internal oxidation products were observed for the as-deposited TBCs. According to energy-dispersive spectroscopy (EDS), this bond coat oxidation product was Al_2O_3 , which formed during processing. After 50 h of heat treatment at 1373 K, a significant increase in the average thickness (3 μm) of the oxidation product was observed, as shown in Fig. 7. According to the backscattered electron image (BEI) by SEM at high magnification (see Fig. 8) and EDS, the bond coat oxidation products consisted mostly of $\alpha\text{-Al}_2\text{O}_3$ (region A), rutile TiO_2 (region B), and HfO_2 (region C). The formation of $\alpha\text{-Al}_2\text{O}_3$ and rutile TiO_2 was also confirmed by X-ray diffraction.^[13] These oxidation products continuously formed at an average parabolic oxide growth rate of 0.0054 mg^2/cm^4 per hour and resulted in approximate thickness of 5 μm after 350 h at 1373 K.^[13] No other oxidation prod-

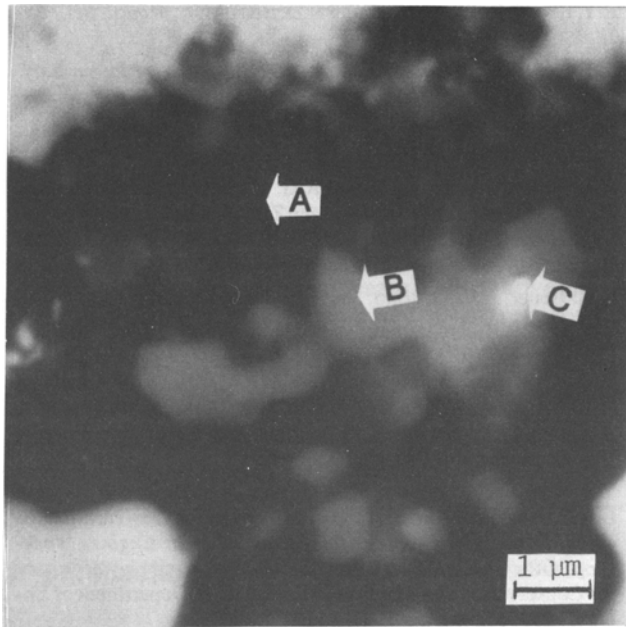


Fig. 8 Backscattered electron image of the oxidation products on the cross section of the isothermally heat treated (50 h) ZrO₂-8 wt.% Y₂O₃ coating.

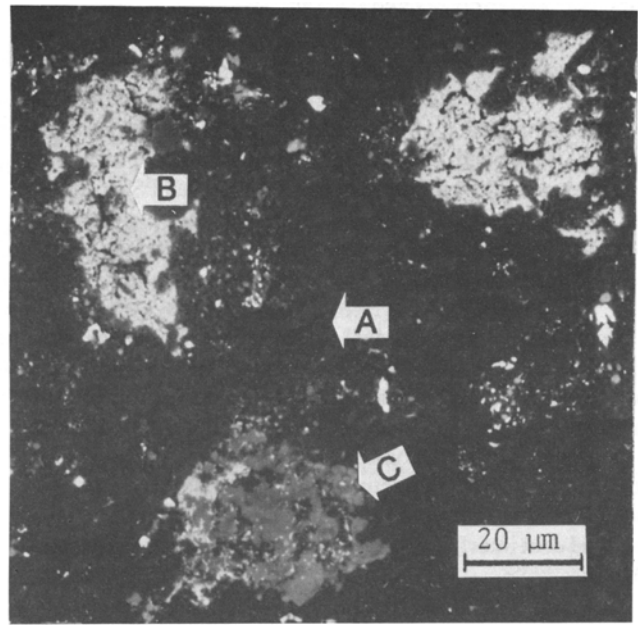


Fig. 9 Backscattered electron image of the bottom surface of the spalled ZrO₂-8 wt.% Y₂O₃ coating.

ucts were found to form with longer isothermal heat treatment. Hence, the oxidation products for the diffusion aluminide bond coat were determined to be different from the oxidation products of the MCrAlY alloy bond coats such as (Al,Cr)₂O₃, Ni(Cr,Al)₂O₄ spinel, and Cr/Ni-rich oxides.^[6]

Figures 9 and 10 show the BEIs taken by SEM for the bottom surface of the spalled TBC and the spalled region on the metal, respectively. In Fig. 9, the bottom surface of the spalled TBC consisted mostly of α -Al₂O₃ oxidation product (region A), as well as the bottom surface of the ZrO₂-8 wt.% Y₂O₃ coating (region B). Small amount of rutile TiO₂ (region C) was also observed on the fracture surface in Fig. 9. The spalled region on the metal showed mostly the metallic top surface of the diffusion aluminide bond coat (region A) and α -Al₂O₃ (region B), as shown in Fig. 10. The same figure also reveals the small amount of residual PSZ coating (region C) within the α -Al₂O₃ region. The white particles that are visible in both Fig. 9 and 10 are HfO₂ or residual PSZ particles.

The observations in Fig. 9 and 10 suggested that the fracture took place within the bond coat oxidation products as well as the interface between the oxidation products and the bond coat or the ceramic coating. Also, the fracture path seems to follow more of the interface between the oxidation products and the diffusion aluminide bond coat. Previous studies have shown that, for thermally cycled plasma sprayed TBCs with MCrAlY bond coats, the fracture path largely involved the interface between the PSZ coating and the oxidation products.^[4,5] Thus, the difference in the fracture path suggested that the fracture mechanisms may be different for plasma sprayed PSZ with MCrAlY bond coat and physical vapor deposited PSZ with a diffusion aluminide bond coat.

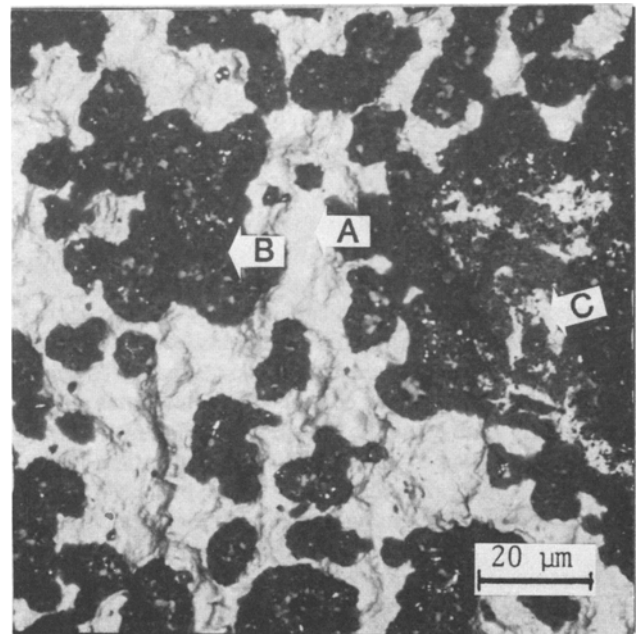


Fig. 10 Backscattered electron image of the TBC spalled region on the metal for the ZrO₂-8 wt.% Y₂O₃ coating.

4. Summary and Conclusions

Phase transformation of physical vapor deposited partially stabilized zirconia thermal barrier coatings and the formation of the oxidation products of the diffusion aluminide bond coat during the isothermal heat treatment were experimentally in-

vestigated. After 200 and 350 h at 1373 K, partial and complete failure of the TBC was observed, with violent spallation of the PSZ coating during cooling. According to the X-ray diffraction analysis, the as-deposited nonequilibrium tetragonal coating slowly decomposed at 1373 K, and the monoclinic phase subsequently developed on cooling. The monoclinic phase was first detected on the bottom surface of the spalled PSZ coating after 200 h of heat treatment. Also, more monoclinic phase was developed on the bottom surface than the top surface of the spalled PSZ coating after the isothermal heat treatment of 350 h.

Microstructure analysis of the TBCs revealed that the oxidation products of the diffusion aluminide bond coat consisted mostly of $\alpha\text{Al}_2\text{O}_3$ and some rutile TiO_2 . The fracture of the PSZ coating occurred within these oxidation products as well as at the interface between the oxidation products and the bond coat or the PSZ coating. The fracture path for the isothermally heat treated TBCs was observed to follow more of oxidation products/bond coat interface than the oxidation products/PSZ interface.

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