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DOI:

[10.1016/j.actamat.2017.06.037](https://doi.org/10.1016/j.actamat.2017.06.037)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Wu, L. T., Wu, R. T., Xiao, P., Osada, T., Lee, K. I., & Bai, M. (2017). A prominent driving force for the spallation of thermal barrier coatings: Chemistry dependent phase transformation of the bond coat. *Acta Materialia*, 137, 22-35. <https://doi.org/10.1016/j.actamat.2017.06.037>

Published in:

Acta Materialia

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A prominent driving force for the spallation of thermal barrier coatings: chemistry dependent phase transformation of the bond coat

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Abstract

The influence of substrate and bond coat chemistry on the degradation mechanism leading to the early spallation of thermal barrier coatings (TBCs) has not been well understood despite years of research effort. This is largely due to the sheer number of factors (i.e. interfacial rumpling and oxide growth kinetics) that all seem to contribute to the degradation of TBCs. To clarify the chemical effect, extensive characterizations and in-depth analysis near the oxide-bond coat interface, were carried out on the isothermally exposed TBC specimens. It is evident that the formation of γ' along the grain boundaries can significantly enhance rumpling, while martensitic transformation during cooling creates out-of-plane stresses and causes crack nucleation at the oxide-bond coat interface. These partial phase transformations in the β bond coat system were determined to be a prominent driving force for the TBC spallation. To prevent the early spallation of TBCs, it is necessary to minimize the formation rate of γ' and martensitic phases, which can be achieved by tailoring the inherent substrate/bond coat composition as elucidated in this

paper.

Keywords: phase transformation; platinum aluminide; interfacial adhesion; rumpling

1. Introduction

Diffusion coating has been widely adopted as an intermediate bonding material in state-of-the art thermal barrier coatings. This type of bond coat has tailored compositions to ensure a stable formation of an adhesive alumina scale upon oxidation [1,2,3,4]. Despite being oxidation resistant, these TBCs are prone to spallation failure near the TGO/bond coat interface, driven primarily by the interfacial rumpling of the bond coat during the course of high temperature oxidation and thermal cycling [5,6,7,8]. Rumpling is generally believed to be caused by the mismatch in the coefficient of thermal expansion between the multilayered structures of TBCs and the lateral growth strain of oxide [7,8,9].

Although previous modeling work based on the micro-mechanics of the coating systems provided valuable insight into the TBC degradation behavior, the predicted results (i.e. stress state and rumpling amplitude) often deviate from those obtained from real experimental specimens. This is largely due to the lack of consideration of the influence of bond coat and substrate chemistry on the interfacial evolution (i.e. material properties) of TBC system [7,8,10]. These modeling works, calculated based on simplified geometric and material properties, are only capable of evaluating the relative influence of a particular parameter (i.e. bond coat creep strength) on the overall failure process. In order to make accurate prediction of TBC life, it is necessary to account for the exact material

properties, and their evolution with thermal cycling [11].

Many recent literatures [12,13,14] suggested that the TGO stress evolution and failure mechanism near the TGO/bond coat interface are significantly influenced by both bond coat and superalloy compositions. The lifetime of TBCs were shown to vary more than 3 folds with slight differences in the inherent Pt, Al, Re, Ru, and Ti contents of the bond coat and superalloy. In a recent work by Zhao et al [15], the inward Pt diffusion and the subsequent release of Ti into the TGO layer accompanied by γ' to γ transformation, were found to degrade the lattice boundary coherency at the TGO/bond coat interface, which may lead to the degradation of interfacial adhesion.

The effect of phase transformation on the TBC degradation and failure has also been studied previously. In the modeling works by both Chen [16] and Balint [17], the volume change associated with the β to martensitic transformation was shown to have a significant influence on the stress distribution and interfacial rumpling in platinum modified nickel aluminide bond coat. On the contrary, Tolpygo [18] maintained that the volumetric shrinkage associated with both β to martensitic and γ' has rather small contribution to the interfacial rumpling of TBCs.

In a previous work by the authors [19], the oxide-bond coat interfacial adhesion of several commercial TBCs was measured semi-quantitatively using a cross-sectional indentation technique. The crack rates (i.e. linear slopes of crack lengths vs isothermal exposure time plot) were then plotted against various common TBC degradation parameters (i.e. linear slopes of TGO growth kinetics vs isothermal exposure time plot), in order to identify the key parameters influencing the interfacial adhesion. β to γ' phase

transformation was determined to be one of the most important factors affecting the oxide-bond coat interfacial adhesion. The SRR99 LT Pt-Al and the TMS-82+ HT Pt-Al TBC systems, both of which had relatively faster γ' transformation rate, were found to have the worst interfacial adhesion and spallation lifetime (See Figure 1). Nonetheless, it remained unclear as to how the phase transformation degrades the interfacial adhesion.

Fig. 1. Previous results suggesting that a linear relationship exists between the interfacial adhesion and the rate of gamma prime formation [19]

Preliminary analysis by electron probe microscope analysis (EPMA) indicated that while traces of detrimental TiO_2 were present in the TGO layer of the SRR99 LT Pt-Al specimen, the same oxide formation was not present on the TMS-82+ HT Pt-Al specimen with similar Ti enriched γ' formation near the TGO/bond coat interface (see Figure 2). This implies that the formation of less adhesive oxide cannot be the sole reason leading to the interfacial degradation of TBCs.

Fig. 2. EPMA mapping showing the formation of Ti concentrated γ' in the bond coat region near the oxide-bond interface of the SRR99 LT Pt-Al (containing traces of TiO_2 in the TGO) and TMS-82+ HT Pt-Al after 30 and 100hrs of isothermal exposure, respectively.

The current manuscript, therefore, seeks to clarify previously unanswered questions concerning the phase transformation induced interfacial degradation mechanism of the bond coat by focusing on the comparison between the evolution of interfacial adhesion [19] and phase distribution with time, and correlating the role of bond coat and substrate chemistry with those degradation phenomena. A systematic analysis on the basis of Electron backscatter diffraction (EBSD) and EPMA chemical mapping was carried out by examining the same set of systematically prepared TBC samples as in the previous study [19]. The results clearly indicated that the γ' formation at the grain boundary of the bond coat and martensitic transformation near the interface act as the prominent driving force for TBC spallation. The extent of these phase transformation phenomena was found to

depend on the inherent Al, Ni, and Ti contents of the as-fabricated bond coat and substrate. A thermodynamic analysis indicated that Cr and Ta contents, if given high enough amount in the bond coat, could alleviate these detrimental phase transformation by stabilizing the β and γ' phases.

2. Experimental details

The same set of TBCs, consisting of three industrial standard single-crystal nickel based superalloys: CMSX-4, SRR99, and TMS-82+, used in the previous study [19], was utilized in this current work. Table 1 shows the nominal chemical composition for these alloys. These fully heat treated alloys (solution and primary aged) were processed using conventional investment casting methods into cylindrical rods (10 mm diameter), having the long axis aligned closely to the $\{001\}$ direction. These rods were further sliced into disk shape (10 mm diameter and 4 mm thickness) and spot welded onto Nimonic sticks. On the other hand, three different bond coats, namely HT Pt-Al (where HT implies a high temperature and low activity aluminization process), LT Pt-Al (where LT implies a low temperature and high activity aluminization process), and Pt-diffusion (without aluminization), were subsequently deposited onto the flat surfaces of the button-shaped discs. The TMS-82+ alloy was paired with all three bond coats for the purpose of studying the effect of bond coat, while CMSX-4 and SRR99 were only paired with LT Pt-Al bond coat to study the influence from superalloy substrate, when the type of bond coat is fixed. Table 2 below provides a summary of the five different TBC systems used in this work.

Table 1

Nominal compositions of the three superalloys used in this work (wt%)

Substrate	Co	Cr	Mo	W	Al	Ti	Ta	Hf	Re	Ru	C	Ni
SRR99	5.0	8.0	-	9.5	5.5	2.2	2.8	-	-	-	-	Bal.
TMS-82	7.8	4.9	1.9	8.7	5.3	0.5	6.0	0.1	2.4	-	-	Bal.
CMSX-4	9.6	6.5	0.6	6.4	5.6	1.0	6.5	0.1	3.0	-	-	Bal.

Table 2

Visual representation of the five TBC systems used in this work

	SUPERALLOY SUBSTRATE		
BOND COAT	CMSX-4	TMS-82+	SRR99
HT Pt-Al		✓	
LT-Pt-Al	✓	✓	✓
Pt diffusion		✓	

The HT Pt-Al and the LT Pt-Al bond coat specimens were prepared by first electrodepositing a thin layer of platinum of 5 and 7 μ m, respectively followed by a vacuum heat treatment at 1100°C for 1 h. Next, 5hrs vapor phase, and 20hrs pack, aluminization processes were applied at 1080°C and 870°C, respectively. The Pt diffusion bond coat specimen was first electroplated with a 10 μ m layer of platinum and then vacuum heat treated at 1150°C for 1hr without the aluminization process. A further heat treatment in argon atmosphere was applied on all specimens for 1hr at 1100C, prior to the deposition of a ZrO₂/7wt% Y₂O₃ (YSZ) top coat of approximately 175 μ m in thickness

by electron beam physical vapor deposition (EB-PVD). Lastly, a vacuum heat treatment (1100 °C, 1hr) and ageing process (870°C, 16hrs) were applied to all specimens for quality assurance purposes.

A total of 25 specimens (5 for each TBC system) were subjected to isothermal exposure at a furnace temperature of 1135°C for 0, 30, 50, 100 hrs. These specimens were then mounted in a StruerCitovac™ vacuum impregnation chamber using a low-shrinkage epoxy resin in order to preserve the specimen edges, and polished to mirror finish for microstructural characterization. A high resolution KEYENCE VHX-1000 optical microscope was used to observe the microstructural features on the entire cross-section of all the specimens. Micrographs across the entire TGO/bond coat interfacial area were taken at 5000x magnification for every specimen. High resolution quantitative elemental analysis was carried out at the TGO/bond coat interfacial area of all the thermally exposed specimens using EPMA (Electron Probe Microscope Analysis). The scans were carried out using a beam size of about 1µm with a current of 20nA and an accelerating voltage of 15kV. A scan area of 30.00 µm x 25.00 µm was selected with step size of 0.1µm in both X and Y

In order to conduct Orientation Imaging Microscopy (OIM) analysis, an additional polishing step was applied to the specimens using the 0.06 µm Buehler Mastermet colloidal silica suspension to ensure the removal of surface deformation, which is essential for EBSD analysis. OIM data collection software was utilized for the orientation analysis near the bond coat/TGO interfacial region of the 0, 30, and 100hrs specimens. A

scan area of 28.000 μm x 25.000 μm was selected with step size between 0.4 and 0.6 μm in both X and Y directions. For specimens with inherently large grains, an additional scan was done using the same step size and area settings as before. Nano-indentation (MTS nano-indentation XP) was carried out along the cross-sectional surface of bond coat for every specimen. A total of 10 indentations were conducted at locations approximately 15 μm below the TGO/bond coat interface on every specimen, and were separated by a distance of at least 20 μm from each other. The indenter load was controlled using a depth limit of 1000nm and a peak holding times of 10s. The hardness results were used to elucidate the mechanical response of the bond coat after the cooling stage.

For the purpose of carrying out a thermodynamic analysis of the phase distribution in the bond coat near the TGO/bond coat interface, the major compositions of the bond coat close to the interface of the 50hrs and 100hrs isothermally exposed TMS-82+LT Pt-Al and CMSX-4 LT Pt-AL, respectively, were determined using energy-dispersive X-ray spectroscopy (EDX). 23 point scans were taken at locations approximately 1-3 μm below the TGO/bond coat interface on both specimens, so as to avoid collecting secondary electron signals from the TGO layer (i.e. oxygen and aluminum). Average values of the alloying elements in wt% were obtained for the Thermo-Calc simulation in section 3.5.

3 Results

3.1 Microscopic observation near the TGO/bond coat interface

Figure 3a-d shows a comparison of the bond coat regions between two isothermally

exposed superalloys (SRR99 and CMSX-4) paired with the LT Pt-Al bond coats. The two specimens were found to have significantly different phase morphology. The SRR99 LT Pt-Al specimen showed short circuit diffusion along the grain boundaries of β grains, and formed a secondary phase of γ' precipitates after 30hrs in addition to the large γ' observed near the oxide/bond coat interface. Unlike the SRR99 specimen, the 30hrs isothermally exposed CMSX-4 LT Pt-Al specimen maintained a uniform layer of β phase without noticeable existence of γ' precipitates. After 50hrs of isothermal exposure, spallation of the TGO had already occurred on the SRR99 LT Pt-Al specimen, while the TGO layer of the CMSX-4 LT Pt-Al specimen remained intact. Moreover, a lath-like martensitic phase can be found on the CMSX-4 LT Pt-Al along with β phase.

Fig. 3. Optical micrographs showing a comparison of bond coat regions between 30 and 50hrs isothermally exposed (a-d) SRR99 LT Pt-Al and CMSX-4 LT Pt-Al, (e-h) TMS-82+ HT Pt-Al and TMS-82+ LT Pt-Al specimens, showing a unique γ' formation at

the grain boundaries of the SRR99 specimen and a complete martensitic transformation in the HT Pt-Al bond coat, respectively.

Similarly, Figure 3e-h shows a comparison of the bond coat regions between 30 and 50hrs isothermally exposed HT Pt-Al and LT Pt-Al bond coats paired with the same TMS-82+ superalloy. There was a significant difference in the phase distribution of these two bond coats. The TMS-82+ HT Pt-Al specimen had a uniform distribution of martensitic phase (coarse lath structures); while the TMS-82+ LT Pt-Al specimen kept mostly β phase with slight presence of martensites and γ' precipitates after 30hrs of isothermal exposure. With respect to the 50hrs isothermal exposed specimens, large pieces of γ' precipitates began to form on the TMS-82+ HT Pt-Al specimen beside the martensitic phase. The TMS-82+ LT-Pt-Al, on the other hand, started to show a larger presence of martensites and some γ' precipitates along with the β phase.

3.2 EBSD mapping analyses near the TGO/bond coat interface

EBSD pattern maps are utilized in this section to further highlight the unique features in bond coat morphology and phase distribution of the TMS-82+ HT Pt-Al and SRR99 LT Pt-Al specimens, as the EBSD map is able to indicate the grain boundaries by distinguishing the orientation of individual crystals. Note that the Kikuchi pattern of the TGO layer could not be accurately indexed, which is likely due the presence of residual stress, and hence, was deliberately removed from all maps for the ease of viewing. Further, all top coat regions were shown in grayscale (excluded from investigation), since the inverse pole figure for the tetragonal zirconia phase was not included here. Figure 4a,

b shows a side by side comparison of the grain morphology between the HT Pt-Al and LT Pt-Al specimens paired with the same TMS-82+ superalloy, in the as coated condition. Before isothermal exposure, the TMS-82+ HT Pt-Al specimen was found to contain much larger grains than the TMS-82+ LT Pt-Al bond coat.

Fig. 4. EBSD mapping showing a comparison of grain morphology of the bond coat region near the oxide-bond interface of a) TMS-82+ HT Pt-Al and b) TMS-82+ LT Pt-Al prior to isothermal exposure, c) TMS-82+ HT Pt-Al and d) TMS-82+ LT Pt-Al after 30hrs isothermal exposure, showing the characteristically large grain of the HT Pt-Al specimen and the significantly different phase transformation behavior of the two at 30hrs, respectively.

A similar comparison (Figure 4c, d) of 30hrs isothermally exposed specimens shows that the TMS-82+ HT Pt-Al bond coat completely transformed to acicular martensitic phase, while the TMS-82+ LT Pt-Al specimen possessed mostly β phase having enlarged grain size. A significant degradation can be seen in the pattern quality of the 30hrs isothermally exposed TMS-82+ HT Pt-Al, most likely due to lattice distortion associated with the significant martensitic phase transformation. Figure 5 provides a side by side comparison of the phase distribution between the 30hrs isothermally exposed SRR99 LT Pt-Al and CMSX-4 LT Pt-Al specimens. The SRR99 LT Pt-Al specimen had γ' phase at the grain boundary and within the grains of β phase as secondary precipitate. The CMSX-4 LT Pt-Al specimen, on the other hand, had very uniform grains of pure β phase.

Fig. 5. EBSD mapping showing the unique γ' precipitation at the grain boundaries of the SRR99 LT Pt-Al, in contrast to the clean and uniform β phase of the CMSX-4 LT Pt-Al specimen after 30hrs of isothermal exposure.

Figure 6 compares the differences in the phase distribution between the 100hrs isothermally exposed CMSX-4 LT Pt-Al, TMS-82+ LT Pt-Al and TMS-82+ HT Pt-Al. The CMSX-4 LT Pt-Al specimen experienced a transformation from β phase to a mostly coarse martensitic structure along with minor amount of γ' phase. On the other hand, the TMS-82+ LT Pt-Al specimen had more γ' phase together with a coarse martensitic structure. The pattern quality of the martensitic region is significantly lower relative to the neighboring grains of γ' phase. Lastly, the TMS-82+ HT Pt-Al specimen was found to have significantly large γ' grains along with unrecognizable patterns of martensitic regions.

CMSX-4 LT Pt-Al (100hrs)

TMS-82+ LT Pt-Al (100hrs)

TMS-82+ HT Pt-Al (100hrs)

Fig. 6. EBSD mapping showing the degradation in pattern quality of martensitic region relative to the amount of γ' formation in the bond coat of 100hrs isothermally exposed CMSX-4 LT Pt-Al, TMS-82+ LT Pt-Al 100hrs, and TMS-82+ HT Pt-Al.

The EBSD map of the 100hrs isothermally exposed TMS-82+ Pt-diffusion specimen is compared to that of the 30hrs isothermally exposed SRR99 LT Pt-Al specimen to highlight the apparent difference between the γ and γ' structure of the Pt-diffusion bond coat and the β structure of the LT Pt-Al bond coat (see Figure 7). The TMS-82+ Pt-diffusion specimen had smaller grains of relatively uniform sizes, while, the SRR99 LT Pt-Al specimen consisted larger β grains and γ' precipitates of various sizes. Figure 8 shows a comparison of the misorientation profile of the bond coat grains near the TGO/bond coat interface between the TMS-82+ Pt-diffusion and SRR99 LT Pt-Al specimens. The arrow lines in Figure 7 indicate the location where the line plot was taken from, starting from the left arrow toward the right one. The flat regions of the plot indicate the location and width of each individual grain, as the crystal orientation should be consistent throughout a grain. The TMS-82+ Pt-diffusion specimen consists of grains having consistent size and orientations, while sudden fluctuation in the orientation can be seen within β grain filled with many precipitates in the SRR99 LT Pt-Al specimen.

Fig. 7. EBSD mapping highlighting the inherent difference between the $\gamma + \gamma'$ microstructure of the Pt-diffusion bond coat and the β microstructure of the LT Pt-Al bond coat.

Fig. 8. A comparison of the misorientation profile near the oxide-bond coat region between the TMS-82+ Pt diffusion (top) and SRR99 LT Pt-Al (bottom) after 100hrs and 30hrs of isothermal exposure, with much sharper peaks in the SRR99 specimen indicating regions of γ' precipitation.

3.3 EPMA mapping analysis near TGO/bond coat regions

EPMA analysis was carried out to study the 30hrs and 100hrs isothermally exposed TMS-82+ Pt-diffusion, in order to investigate the chemical diffusion and segregation behavior of its bond coat (see Figure 9). A uniformly depleted Al layer was observed with corresponding enrichment in the Cr content in the 30hrs isothermally exposed TMS-82+ Pt-diffusion specimen. After 100hrs of isothermal exposure, the Ti and Cr chemistry remained very similar to that of the 30hrs isothermally exposed while further Al depletion took place.

Fig. 9. EPMA mapping showing the chemistry near the oxide-bond coat regions of the TMS-82+ Pt-diffusion specimens after 30 and 100hrs of isothermal exposure, with uniformly depleted layer of Al and Ti while enriched with Cr.

Figure 10 gives a side by side comparison of the Ti and Cr contents between the 100hrs isothermally exposed TMS-82+ LT Pt-Al and the CMSX-4 LT Pt-Al. Unlike in the case of the Pt-diffusion coating, Ti-Cr segregation occurred in local patches near the TGO/bond coat interface of the TMS-82+ specimen. The CMSX-4 LT Pt-Al specimen, on the other hand, had fairly consistent Cr distribution with virtually no Ti content close to the interface. Both specimens had trace amount of chromium oxide in the TGO layers.

Fig. 10. EPMA mapping showing a comparison of Cr content near oxide-bond coat interface between TMS-82+ LT Pt-Al and CMSX-4 LT Pt-Al after 100hrs of isothermal exposure, with CMSX-4 showing no obvious Ti presence.

3.4 Hardness by nano-indentation near the TGO/bond coat interface

To study the mechanical property of the bond coat region near the TGO/bond coat interface, hardness results measured by nano-indentation is plotted in Figure 11 here for the 30, 50 and 100hrs isothermally exposed specimens. Note the error bar here represents

the standard deviation of 10 measurements for each specimen. After 30hrs of isothermal exposure, the SRR99 LT Pt-Al specimen had the highest hardness and standard deviation. In general, all specimens except the TMS-82+ Pt-diffusion, underwent an increasing trend in both average hardness and standard deviation between 50 and 100hrs. The TMS-82+ HT Pt-Al had the highest hardness and standard deviation among all specimens listed here after 100hrs of isothermal exposure. The TMS-82+ Pt-diffusion specimen was found to maintain similar hardness values and standard deviation going from 30 to 100hrs.

Fig. 11. A plot showing the hardness values by nano-indentation of various bond coats near the oxide-bond coat interface, with increasing trend in both hardness values and standard deviations.

3.5 Simulation of phase transformation by Thermo-Calc

To clarify the effect of Cr content on the phase distribution of bond coat, a thermodynamic software, named Thermo-calc was used to identify the phase distribution of the LT Pt-Al bond coat system when prepared on the CMSX-4 alloy. Essential input, including isothermal temperature used (1409K) and the bond coat compositions near the TGO/bond coat interface of the 100hrs isothermally exposed CMSX-4 LT Pt-Al specimen were specified in the software. It is assumed that the system is in a stable equilibrium state after certain amount of time. Note that the bond coat compositions were obtained from the EDX analysis result as mentioned in the experimental section (see Table 3).

Table 3

The nominal composition in wt% of the CMSX-4 LT Pt-Al and TMS-82+ LT Pt-Al bond coats as specified in the Thermo-Calc calculation

Bond coat composition	Co	Cr	Mo	W	Al	Ti	Ta	Re	Pt	Ni
CMSX-4 LT Pt-Al	6.691	3.158	0.502	1.998	11.117	0.0104	5.345	0	20.429	50.211
TMS-82+ LT Pt-Al	4.898	2.887	0.476	1.863	11.787	0.316	3.704	0	22.531	50.902

Figure 12a demonstrates the mole-fraction of different phases near the TGO/bond coat interfaces of the 100hrs isothermally exposed CMSX-4 LT Pt-Al alloy based on the calculation in Thermo-Calc as a function of Cr content. It can be seen that the mole

fraction of β phase increases with higher Cr content, while the γ' phase decreases accordingly. The dotted line shows the actual phase constitutions in the 100hrs isothermally exposed CMSX-4 LT Pt-Al specimen. Similarly, the effect of Ta content on the bond coat phase distribution was conducted on the 50hrs isothermally exposed TMS-82+ LT Pt-Al. The purpose here is to see if a low Ta content, such as in the case of SRR99 LT Pt-Al specimen, could have an influence on the γ' transformation behavior. The bond coat compositions used for Thermo-Calc input were once again obtained from EDX line scans near the oxide-bond coat interface (see Table 3). Thermo-calc results in Figure 12b also shown an increase in the mole fraction of β phase with increasing Ta content, while the γ' phase decreases accordingly. However, the extent of the phase variation seems to be much less than the case of Cr.

Fig. 11. The mole fraction of different phases existing near the TGO/bond coat interface of the bond coats in a) CMSX-4 LT Pt-Al 100hrs, and b) TMS-82+ LT Pt-Al 50hrs specimens as a function of varying Cr and Ta contents, respectively. These elements generally help stabilizing β phase.

4 Discussion

4.1 Interfacial evolution during thermal exposure

Table 4 is a summary of the phase evolution of the five TBC systems with corresponding hardness of bond coats between 30 and 100hrs isothermal exposures, and their TGO stress obtained from the previous study [19]. The stress measurement was carried out at room temperature using a Renishaw 1000 Raman microscope system. All the measurements were conducted following strictly stipulated standards of the photo-luminescence piezo-spectroscopy method, including calibration with strain-free single crystal sapphire sample and probing from at least 5 different locations (refer to the experimental section of [19] for more details). The TGO stress level seems to be closely associated with the phase constituents of the bond coat. The TMS-82+ Pt-diffusion specimen, which underwent phase transformation from as coated $\gamma' + \gamma$ to pure γ phase after isothermal exposures, was measured to have the highest TGO stress throughout thermal exposure. This is due to the highly creep resistant nature of the γ' and γ phases, which prevented the bond coat from any significant plastic deformation under TGO growth strain and CTE mismatch during cooling. In addition, the high hardness values of the Pt-diffusion bond coat may further increase TGO residual stress at lower temperature.

The TMS-82+ HT Pt-Al, with its unique martensitic transformation at early isothermal hours, was determined to have the highest TGO stress among the three β bond coat systems. The 30hrs isothermally exposed TMS-82+ LT Pt-Al, on the other hand, began with relatively lower TGO stress consisting of multiple phases, and continued to show an

upward trend in TGO stress until 100hrs of isothermal exposure. Unlike the TMS-82+ LT Pt-Al, the CMSX-4 specimen actually experienced slight reduction in TGO stress between 30 and 100hrs isothermal exposures, despite having transformed to martensitic and γ' phases. This is likely due to the large and continuously increasing rumpling trend of the CMSX-4 specimen between 30 and 100 hrs isothermal exposures measured in the previous study [19], which allowed certain amount of stress relaxation in the TGO. In contrast, the TMS-82+ LT Pt-Al had virtually no increase in rumpling between 30hrs and 50hrs, during the time when martensitic transformation began to form..

Table 4

A summary of the phase evolution, hardness, and TGO stress of all the TBCs studied between 30 and 100hrs of isothermal exposure

	Phase evolution, hardness, and TGO stress during thermal exposure		
	30hrs	50hrs	100hrs
SRR99 LT Pt-Al	γ' precipitates (g.b. and near interface) + β Stress : 0.237GPa Hardness: 7.197GPa	-N/A (Spalled)	-N/A
TMS-82+ HT Pt-Al	All lath martensitic structure	Martensitic + γ' (significant)	Martensitic + γ' (large amount)

	Stress: 2.446GPa Hardness: 4.555GPa	Stress: 2.327GPa Hardness: 4.825GPa	Stress: 2.485GPa Hardness: 8.290GPa
TMS-82+ LT Pt-Al	Mostly β + martensites + γ' (trace) Stress: 1.183GPa Hardness: 4.520GPa	β + martensites (significant) + γ' (more trace) Stress: 1.775GPa Hardness: 4.679GPa	Martensitic + γ' (significant) Stress: 1.854GPa Hardness: 5.322GPa
CMSX-4 LT Pt-Al	All β Stress: 2.288GPa Hardness: 5.167GPa	β + martensites (significant) Stress: 2.170GPa Hardness: 4.564GPa	Martensitic + γ' (significant) Stress: 2.091GPa Hardness: 5.733GPa
TMS-82+ Pt-diffusion	Uniform γ layer near the interface Stress: 2.682GPa Hardness: 6.553GPa	Uniform γ layer near the interface Stress: 2.840GPa Hardness: 6.315GPa	Uniform γ layer near the interface Stress: 2.880GPa Hardness: 6.41GPa

4.2. Phase transformation induced strain and rumpling

Qualitative and semi-quantitative assessments of local plastic strain by utilizing both the changes in the EBSD pattern quality and grain misorientations have long been conducted

in many previous studies [20-22]. It is believed that the progressive degradation in the pattern quality of the martensitic regions shown in Figure 6 earlier corresponds to an increasing severity of plastic strain. According to the HT XRD results by Chen et al [16], the molar volume of the $L1_0$ martensite is approximately 2% smaller than that of the β , which induces a transformation strain of about -0.7% during cooling. They, along with several other researchers [17], believe that this volume shrinkage due to martensitic transformation can generate additional stress during thermal cycling in the bond coat, and thus, can significantly enhance rumpling growth.

The role of martensitic transformation in causing rumpling should be questioned in the case here with isothermal single cool-down tests. As pointed out in a previous literature [18], rumpling amplitude tends to accumulate slowly, as the amount of undulation developed per cycle is rather small. It should be noted; however, that the martensitic transformation may contribute to lowering interfacial fracture energy by creating out-of-plane stresses at the bond coat/TGO interface (i.e. crack opening). Although, the volume shrinkage associated with β to γ' phase transformation is significantly larger than that of β to martensitic phase (i.e. 8 to 38% change depending on whether Al depletion occurred predominantly by oxidation or inter-diffusion) [18], it should be noted; however, that the process takes place at a much higher temperature range, in which the creep rate is high. As a result, much of the TGO growth stress is relaxed in the form of rumpling, which is evident from the low stress level and high rumpling rate of TMS-82+ LT Pt-Al specimen determined in the previous work by the authors [19]. In contrast, the β to martensitic transformation occurred in a significantly shorter time span (i.e. cooling) at a

much lower temperature range (i.e. less creep relaxation), in which the strain generated by the martensitic transformation, together with the CTE mismatch between the coating layers, contributes as additional crack inducing elastic strain at the bond coat/TGO interface without much rumpling. This is evident from the high stress and low rumpling rate of TMS-82+ HT Pt-Al specimen found in the previous work by the authors [19].

Tolpygo et al argued in their previous work [18] that reverse martensitic transformation during cyclic thermal exposure has no discernible effect on the rumpling of bond coat. This argument, however, does not conform to our results shown in this work. When martensites were found as the dominant phase (volume %) in the bond coat, such as in the case of the 30hrs isothermally exposed TMS-82+ HT Pt-Al and the 100hrs isothermally exposed CMSX-4 LT Pt-Al 100hrs specimens, there was much less pattern degradation (i.e. severity of plastic strain) in their corresponding EBSD mappings as oppose to the cases where γ' phases co-existed with martensites (i.e. TMS-82+ HT Pt-Al and TMS-82+ LT Pt-Al at 100hrs). Moreover, their assumption that no martensitic transformation occurred in their two-zone cycling temperature range lacks the consideration that the M_s temperature increases with Al depletion and interdiffusion of various alloying additions during oxidation, hence, should be considered as a dynamic parameter [23,20,24]. Clearly, the additional strain generated by the martensitic transformation may cause rumpling with increasing thermal cycles when the M_s temperature is high enough for creep relaxation to take place in the bond coat.

4.3. Interfacial instability due to misfit stress

The results presented so far have led us to believe that co-existence of phases with inherently very different thermomechanical properties could induce a misfit stress in the TGO layer during thermal cycling, leading to crack formation at the TGO/bond coat interface and thus coating spallation. This idea is supported by the increasing standard deviation values of the hardness measurements from various bond coat systems as shown in Figure 11. As more and more γ' phase began to precipitate out alongside the martensitic structure after 100hrs of isothermal exposure, a drastic increase in both hardness and standard deviation values from those of the 50hrs thermally exposed samples can be seen for all Pt-Al systems, especially for the TMS-82+ HT Pt-Al specimen (see Figure 11). In the previous work by the authors [19], the standard deviation values of TGO stress measurements of the TMS-82+ HT Pt-Al specimen were determined to be significantly higher than other TBC systems at 80 and 100hrs of isothermal exposures (see Table 5).

Table 5

A comparison of the TGO stress measurements between the different TBCs at 80 and 100hrs isothermal exposures [19]. Note that the TMS-82+ HT Pt-Al values (highlighted in bold) have relatively higher standard deviation and obvious increase in hardness.

TBC systems	80hrs	100hrs
CMSX-4 LT Pt-Al	2.130GPa $\pm$ 0.088	2.091GPa $\pm$ 0.299
TMS-82+ LT Pt-Al	1.815GPa $\pm$ 0.088	1.854GPa $\pm$ 0.108
TMS-82+ HT Pt-Al	2.012GPa $\pm$ 0.252	2.485GPa $\pm$ 0.384

TMS-82+ Pt-diffusion	$2.880\text{GPa} \pm 0.108$	$2.880\text{GPa} \pm 0.176$
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The proposed concept can be better understood by studying the Pt-diffusion bond coat system. In the previous work [13], the TMS-82+ Pt-diffusion specimen had virtually no rumpling behavior throughout its entire thermal cycling test, as compared to other TBC systems. Furthermore, the TMS-82+ Pt diffusion specimen was ranked highly in terms of interfacial adhesion among the TBCs studied in the previous work [19], despite having the highest TGO stress of all specimens during thermal exposure.

The strong adhesion of the Pt-diffusion bond coat can be attributed to its microstructural uniformity near the bond coat/TGO interface. Contrary to the β to γ' /martensitic transformation in Pt-Al bond coat systems, the γ' to γ transformation of Pt-diffusion bond coats does not involve large volume change, and hence, does not produce either rumpling growth or misfit strain. Moreover, the absence of Ti segregation near the bond coat/TGO interface means that TiO_2 would not form in the TGO layer. Unlike the Pt-diffusion system, the TMS-82+ LT Pt-Al and TMS-82+ HT Pt-Al systems had relatively less interfacial adhesion/spallation lifetime with a continuous growing rumpling amplitude during thermal exposure (as shown in Ref 19).

4.4 A prominent driving force for spallation

The results of this work have clarified the difference in the degradation behavior between the SRR99 LT Pt-Al and TMS-82+ HT Pt-Al specimens after 30 and 100hrs of isothermal

exposure, respectively. Figure 13 provides a schematic explanation of the TGO stress evolution and the interfacial degradation process during isothermal heating and subsequent cooling of the two specimens. During isothermal holding, TGO began to thicken on both specimens; however, the SRR99 LT Pt-Al had a much faster oxidation kinetic with traces of TiO_2 present at the TGO/bond coat interface while the TMS-82+ HT Pt-Al specimen maintained mostly pure alumina. The lateral TGO growth due to the formation of new oxide within the scale interior was constrained by the underlying metal substrate, which led to an in-plane compression of the oxide scale. This existence of lateral growth strain at isothermal temperature is known to cause creep in both the scale and bond coat, and thus induces surface undulation [9]. In addition, the volume shrinkage associated with γ' formation led to a local stress concentrated zone in the TGO above the γ' grain. This uneven strain response between the β and γ' regions would further enhance rumpling growth.

Fig. 13. A qualitative illustration of the TGO stresses evolution and interfacial degradation during isothermal heating and subsequent cooling of the 30hrs isothermally

exposed SRR99LT Pt-Al and the 100hrs isothermally exposed TMS-82+ HT Pt-Al. The SRR99 had more rumpling due to γ' formation at the grain boundary, while the TMS-82+ had a relatively higher residual stress in the TGO due to martensitic transformation.

It is interesting to note that despite having a thicker TGO and more γ' formation, the TMS-82+ HT Pt-Al after 100hrs isothermal oxidation had significantly less rumpling compared to the SRR99 LT Pt-Al after 30hrs isothermal oxidation (See Ref 16). As pointed out in a previous work by Tolpygo [25], the bond coat was observed to swell during high temperature oxidation due to Kirkendall effect, leading to surface undulation of the bond coat. As described in that work [25], there seemed to be an uneven response to bond coat swell, where the inner grains of bond coat swelled more (i.e. undulation peaks) than the grain boundaries (i.e. undulation valleys). Based on this phenomenon, it is believed that unique γ' formation along the grain boundaries of the SRR99 specimen further contributed to additional surface undulation due to the volume shrinkage (i.e. uneven strain) of β to γ' transformation, making the specimen more rumpled locally than other specimens.

During cooling, TGO stress began to increase due to the CTE mismatch between the different phases of the bond coat and the TGO layer. The bond coat contracted more and thus applied a compressive stress on the TGO, while the TGO induced a tensile stress on the bond coat. The TMS-82+ HT Pt-Al was different from the SRR99 LT Pt-Al in that its β phase began to transform into a coarse martensitic phase, accompanied by molar volume shrinkage during cooling. This transformation likely led to a higher stress-build

up in the TGO layer above the martensitic phases relative to the regions above γ' in the HT Pt-Al specimen at room temperature, which may cause crack opening at the TGO/bond coat interface.

The SRR99 LT Pt-Al, on the other hand, had much less stress gradient across the TGO, where regions above the β had more stress relaxation than those above the γ' , as β was more susceptible to creep at high temperature. The main reason for the early spallation of the SRR99 LT Pt-Al can be associated with its faster rumpling growth, while the formation of the less adhesive TiO_2 at the TGO/bond coat interface likely contributed to the spallation. As shown in the previous work [19], while SRR99 LT Pt-Al attained the highest rumpling magnitude and γ' formation rate prior to spallation, other specimens (i.e. TMS-82+ LT Pt-Al and CMSX-4 LT Pt-Al after 100 and 200hrs of isothermal exposure) were found to gain even higher rumpling magnitude and more γ' formation, yet continued to survive well into 200hrs of isothermal exposure.

In the previous work [19], a semi-quantitative plot of the variation of the driving force G for spallation and the interfacial fracture toughness G_c with isothermal exposure was given to show the remaining lifetime of the TBCs used in this work between 30 and 100hrs. The previous concept is again demonstrated by the degradation behavior of the SRR99 LT Pt-Al and TMS-82+ HT Pt-Al specimens shown in this work. For instance, the formation of TiO_2 at the TGO/bond coat interface of the SRR99 LT Pt-Al, resulting in the loss of interfacial adhesion, can be treated as a factor for driving the G_c value lower during isothermal exposure. On the other hand, the martensitic transformation of the

TMS-82+ HT Pt-Al during cooling, leading to a stress build-up in the TGO, may be considered as a factor behind an increasing G value.

While it has attempted to clarify phase transformation induced interfacial degradation in this section, it should be reminded that the degradation behavior of TBC coated turbine blades in actual operating conditions may deviate from those depicted here. During a typical flight cycle, the turbine entry temperature varies from time to time according to the engine rating required to perform necessary maneuvers (i.e. takeoff, climb, cruising, landing, etc.). This is very much different from the long heating duration at the peak temperature with a single rapid cooling (i.e. isothermal dwelling) used in this work. Since the turbine blades in actual engine operation experiences fluctuating cycles of temperatures varying from intermediate to maximum engine rating, substantial portion of the residual stress induced by martensitic transformation, for instance, may be relaxed by bond coat creep. Hence, the relatively weak interfacial adhesion of the HT Pt-Al bond coat measured at ambient environment may not necessary reflect its actual performance in aerospace engines. Nonetheless, isothermal exposure was selected over cyclic exposures to ensure a smooth planar interface for indentation placement, while enabling the study of the influence of the inherent bond coat and substrate chemistry.

4.5. Mitigation of undesirable phase transformation by compositional design

In TBCs, Al diffuses faster through the grain boundaries of the bond coat upon forming Al_2O_3 during thermal exposure. Nonetheless, it remains unclear as to the reason why such a phenomenon was only observed on the SRR99 LT Pt-Al in early isothermal times.

According to previous EDX, EPMA, and Thermo-Calc simulation results [19], Ti and Ni contents tends to segregate to Al depleted region, where the γ' phase is located. Considering that the SRR99LT Pt-Al specimen has relatively higher Ti and Ni contents (see Table 1) with the fastest TGO growth kinetic and γ' phase formation rate [19], it is reasonable to say that Ni and Ti enhanced the speed of Al depletion process through the grain boundaries of the SRR99 bond coat, which in turn, migrated to those regions to form γ' phase

Many previous literatures have reported on the detrimental effect of TiO_2 formation in degrading the adherence of TGO scale [19,26,27,28]. The relatively weak interfacial adhesion of the TMS-82+ HT Pt-Al specimen; however, was not related to TiO_2 , since no obvious Ti was detected (see Figure 1) in the TGO scale. The TMS-82+ HT Pt-Al had considerably lower amount of Ti in the γ' was considerably lower than the SRR99 LT Pt-Al specimen (1.20 vs. 2.84 wt%), which may be the reason behind the absence of TiO_2 .

Thermo-Calc simulation in section 3.5 indicated that Cr and Ta tend to stabilize the β phase, preventing the early formation of γ' . However, the effect of Cr seemed to be much greater than that of Ta. A comparison of the EPMA compositional mapping between the TMS-82+ LT Pt-Al and CMSX-4 LT Pt-Al specimens (Figure 10) revealed that Cr, if having sufficient concentration, can largely inhibit the diffusion of Ti content outward to the bond coat surface. Despite having higher bulk Ti content than the TMS-82+ LT Pt-Al specimen (see Table 1) the CMSX-4 LT Pt-Al was shown previously

[19] to have slower γ' formation. It should be stressed that the phase stability of bond coat may also be influenced by other alloying elements within the bulk superalloy. Nonetheless, the results indicate that Cr plays an important role in preventing early γ' formation.

In a previous study by Smialek et al [29], the martensitic transformation temperature, M_s in β -NiAl alloy was found to increase as a result of Al depletion during oxidation and alloy/bond coat inter-diffusion. According to Hangen et al [23], the martensitic transformation does not undergo complete (i.e. 100%) transformation right below the M_s , but instead continues to increase in volume fraction with decreasing temperature (i.e. increasing cooling). As shown by the EDX line profile scan of the Pt-Al bond coats in the work of Wu et al [13], the Al content in within a distance of 20 μ m from the TGO/bond coat interface of the HT Pt-Al specimen was found to be approximately 7 at% lower on average than that of the LT Pt-Al. These findings suggest that the complete transformation to coarse martensite in the HT Pt-Al bond coat type is likely due to the inherently low Al contents.

5 Conclusion

The results of this work have led to the following conclusions:

- The interfacial degradation behavior has been associated with the phase transformation of bond coat during thermal cycling. This is reflected by the

variation of interfacial rumpling and TGO stress with bond coat hardness values, which are dependent on the phases present.

- The co-existence of different phases with inherently different thermomechanical properties may generate a misfit stress in the TGO layer, leading to misfit strain and interfacial rumpling.
- The experimental results have clarified the difference in the degradation mechanism between the SRR99 LT Pt-Al and TMS-82+ HT Pt-Al specimens. Early spallation of the SRR99 LT Pt-Al was most likely caused by its fast rumpling rate due to γ' formation at the grain boundary, while formation of weakly adherent TiO_2 scale due to Ti-rich γ' precipitates near the bond coat/TGO interface likely contributed to the interfacial degradation. The early spallation of the TMS-82+ HT Pt-Al was mainly driven by the misfit strain in the TGO as a result of the volume shrinkage (i.e. out-of-plane stress) associated with the martensitic transformation.
- Thermo-Calc and EPMA analysis indicated that Cr and Ta, if given high enough amount, has the effect of preventing diffusion of Ti toward to the TGO/bond coat interface by stabilizing the β and/or γ phases. In addition, the amount of Al concentration and rate of Al depletion of the bond coat near the TGO/bond coat interface are crucially tied to the undersirable martensite transformation.

Acknowledgements

Our appreciation goes to Ms. Hong Gao and Dr. Tadaharu Yokokawa of the National Institute for Materials Science (NIMS, Japan) for facilitating the analysis of EBSD and

EPMA, respectively.

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