EFFECT OF BOND COAT AND SUBSTRATE CHEMISTRY ON THE INTERFACIAL DEGRADATION OF THERMAL BARRIER COATINGS

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Keywords: Thermal barrier coatings, Phase transformation, Interface

Abstract

Despite the benefit of increased operating temperature of turbine blades, the application of thermal barrier coatings (TBC) has brought the concern of coating spallation during jet engine operations. A significant portion of past research, was therefore, devoted to detailed analysis of the interfacial degradation behavior of TBC by numerical and analytical models. Nonetheless, these models tend to overlook the influence of the degradation on the complicated nature of substrate chemical diffusion/phase transformation. As a result, the predicted TBC lifetime expressed in terms of failure criterion (i.e. thermally grown oxide thickness) often deviate largely from that obtained by real experiment. The purpose of this research work is to clarify the role of substrate chemistry on the interfacial degradation of TBC. Extensive analysis was carried out on a set of systematically prepared commercial TBC subjected to different thermal exposure times. The results clearly indicated that the interfacial adhesion is a dynamic property, which depends on the substrate chemical diffusion/phase transformation. It became evident that the early spallation observed in several β bond coat system was caused by two unique phase transformations. Furthermore, the phase transformation was shown to be closely associated with the inherent chemistry of the substrate.

1. Introduction

To cope with the ever-demanding operating conditions in modern jet engines, state-of-the-art thermal barrier coatings based on yttria-stabilized zirconia (YSZ) has been widely applied on top of the bulk Ni-based superalloy, to thermally protect the underlying alloy from approaching its melting temperature. Due to the porous columnar structure and high ionic diffusivity of YSZ in the ceramic top coat at high temperature, the ingress of oxygen can readily oxidize the underlying substrate, leading to catastrophic failure of the turbine structure. To address this issue, a platinum aluminide (Ni,Pt)Al bond coat, usually made by electrodeposition of a thin layer of platinum, following by a pack aluminization process, is applied between the ceramic top coat and the bulk superalloy. The bond coat is tailored with higher amount of Al content than the bulk alloy, which serves as a reservoir of Al to promote the preferential formation of a protective alumina as the thermally grown oxide (TGO) layer [1-3].

Despite the aforementioned protective measures, the TBC are still prone to spallation failure primarily driven by the interfacial rumpling of the bond coat during the course of high temperature oxidation and thermal cycling [4-7]. The general consensus for the cause of interfacial rumpling is thought to be the mismatch in the coefficient of thermal expansion between the multilayered structures of TBC [6,7]. Several studies have identified that the TGO growth kinetic plays an important role in the TBC lifetime, and that spallation is mainly attributed to the strain energy lying within the TGO [8,9]. However, many experimental investigations

have shown that despite having faster TGO growth rate and more rumpling, certain bond coat and substrate pairs still outperformed others in terms of lifetime [10,11]. Despite considerable progress that has been made on modeling the interfacial evolution of TBC in terms of the stress state and the degree of rumpling, there has been a lack of understanding on how these values could be influenced by the chemical diffusion and phase transformation of bond coat and substrate during thermal cycling [6,7,12,13].

In recent years, additional studies have been dedicated to the study of the effect of bond coat and substrate compositions on the degradation of TBC [14-18]. A previous study by the authors [18] identified the rate of β to γ' transformation driven by Al depletion as a dominant factor in degrading the interfacial adhesion of the TBC samples studied (Fig. 1). It was speculated that the γ' formation containing highly concentrated Ti near the bond coat/TGO interface may weaken the interface by forming TiO_2 . However, preliminary analysis by electron probe microscope Analysis (EPMA) indicated that while traces of TiO_2 was present in the TGO layer of the SRR99 LT Pt-Al specimen, the same phenomenon could not be observed on the TMS-82+ HT Pt-Al specimen (details on the designation of these TBC systems are given in the Experimental section), which also had similar Ti enrichment and poor interfacial adhesion after γ' formation near the bond coat/TGO interface (see Figure 2). This implies that the formation of the less adhesive oxide cannot be the only mechanism causing the interfacial degradation of TBC.

Fig. 1. Previous results indicating a linear dependency of the interfacial adhesion on the rate of γ' formation [18].

Fig. 2. EPMA mapping showing the formation of Ti enriched 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 100 h of isothermal exposure, respectively.

The current study seeks to clarify the difference in the degradation mechanisms between the SRR99 LT Pt-Al and TMS-82+ HT Pt-Al specimens, utilizing a systematic approach similar to the previous work [18]. The results have clearly indicated that the TBC interfaces may degrade not only by the formation of less adhesive oxides (i.e. TiO_2 or Spinel), but also due to the misfit stress induced in the TGO layer resulting from the martensitic transformation induced

strain and thermomechanical mismatch between the different phases during cooling. Moreover, the results here have clearly demonstrated the previously proposed concept that the TBC spallation life is dependent on the dynamic variation of both the driving force for spallation and interfacial fracture toughness [18].

2. Experimental details

Three industrial standard single-crystal nickel based superalloys were used in this work: CMSX-4, SRR99, and TMS-82+. The nominal compositions for these alloys are listed in Table I. Three diffusional bond coats: HT Pt-Al, LT Pt-Al and Pt-diffusion (where HT implies high temperature low aluminum activity, LT implies low temperature high aluminum activity, and Pt-diffusion refers to platinum diffused without aluminisation), were deposited onto the aforementioned superalloys. Lastly, yttria stabilized zirconia top coats of approximately 175 μm thickness were deposited onto the bond coats using electron beam physical vapor deposition. The detailed material processing can be found in a separate work [18]. In total, five unique TBC systems were prepared for this study (Table II).

Table I. Nominal Composition of the three superalloys used in this work (wt%)

Substrate	Co	Cr	Mo	W	Al	Ti
SRR99	5.0	8.0	-	9.5	5.5	2.2
TMS-82+	7.8	4.9	1.9	8.7	5.3	0.5
CMSX-4	9.6	6.5	0.6	6.4	5.6	1.0

	Ta	Hf	Re	Ru	C	Ni
SRR99	2.8	-	-	-	-	Bal.
TMS-82+	6.0	0.1	2.4	-	-	Bal.
CMSX-4	6.5	0.1	3.0	-	-	Bal.

Table II. Visual representation of the five TBC systems used in this work

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

The as-prepared TBC systems were subjected to isothermal exposures at a furnace temperature of 1135°C for 0, 30, 50, 100 h. Subsequently, microstructural characterizations (both OM and SEM) were conducted to record the interfacial evolution of the TBC with isothermal exposure times. Micrographs across the entire TGO/bond coat interfacial area were taken for every specimen. EPMA (Electron Probe Microscope Analysis) scan was carried out at the TGO/bond coat interfacial area of all the thermally exposed specimens. A beam current of 20 nA was applied with a beam size of about 1 μm , at an accelerating voltage of 15 kV. The scans were done at a step size of 0.1 μm in both X and Y directions for an area of 30.00 x 25.00 μm^2 .

A JEOL FE-SEM equipped with EBSD detector and OIM data collection software was used to carry out the phase and grain orientation analysis near the bond coat/TGO interfacial region of the 0, 30, and 100 h specimens. The scans were done at a step size between 0.4 to 0.6 μm in both X and Y directions, for an area of 28.000 x 25.000 μm^2 . For specimens that had inherently large

grains, an additional scan was conducted using the same step size and area settings as before.

To conduct a thermodynamic simulation on the TBC using the Thermo-Calc software, energy-dispersive X-ray spectroscopy (EDX) was utilized to determine the major alloying compositions near the oxide-bond coat interface of the 100 h isothermally exposed CMSX-4 LT Pt-Al and the 50 h isothermally exposed TMS-82+ LT Pt-Al specimens. A total of 23 point scans were conducted at locations approximately 1-3 μ m below the TGO/bond coat interface on both specimens in order 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 and used in the Thermo-Calc simulation.

3. Results

3.1 Microscopic observation near the TGO/bond coat interface

A comparison of the bond coat regions between the SRR99 and CMSX-4 LT Pt-Al systems after 30 and 50 h isothermal exposures is shown in Figure 3. It can be seen that the phase morphology differs significantly between the two alloys. The SRR99 LT Pt-Al specimen exhibited short circuit diffusion along the grain boundaries of β grains, where γ' phase was precipitated after isothermally exposed for 30 h. In addition, large γ' precipitates were also observed near the TGO/bond coat interfacial region. The 30 h isothermally exposed CMSX-4 LT Pt-Al specimen, on the other hand, maintained a uniform layer of β phase without the presence of γ' precipitates. After 50 h of isothermal exposure, TGO spallation had already occurred on the SRR99 LT Pt-Al specimen, whereas the TGO layer of the CMSX-4 LT Pt-Al specimen remained well intact. In addition, CMSX-4 LT Pt-Al was found to contain the martensitic phase (lath structures) along with β phase.

Fig. 3. SEM micrographs showing a comparison of bond coat regions between 30 and 50 h isothermally exposed SRR99 LT Pt-Al and CMSX-4 LT Pt-Al specimens, with a unique γ' formation at the grain boundaries of the SRR99 specimen.

Similarly, Figure 4 shows a comparison of the bond coat regions between the TMS-82+ HT Pt-Al and LT Pt-Al systems after 30 and 50 h isothermal exposures. Again, the phase distribution differs significantly between these two bond coats. The TMS-82+ HT Pt-Al specimen was found to contain a uniform distribution of martensitic phase (coarse lath structures); whereas the TMS-82+ LT Pt-Al specimen maintained mostly β phase with minimal formation of martensites and γ' precipitates after 30 h of isothermal exposure. For the 50 h isothermal exposed specimens, large particles of γ' precipitates appeared on the TMS-82+ HT Pt-Al specimen alongside martensitic phase. The TMS-82+ LT Pt-Al, on the other hand, began to show a larger distribution of martensites and some γ' precipitates beside the β phase.

Fig. 4. SEM micrographs showing a comparison of bond coat regions between 30 and 50 h isothermally exposed TMS-82+ HT Pt-Al and TMS-82+ LT Pt-Al specimens, with a complete martensitic transformation in the HT-Pt-Al bond coat.

3.2 EBSD mapping analyses near the TGO/bond coat interface

The unique features in the bond coat morphology and phase distribution of the TMS-82+ HT Pt-Al and SRR99 LT Pt-Al specimens are further highlighted in this section by EBSD mapping. It should be noted here that the EBSD pattern of the TGO layer could not be accurately indexed (most likely due to its large residual stress induced crystal distortion), and hence, was purposefully removed from all maps for the ease of viewing. In addition, the inverse pole figures of all the EBSD maps in this study refer only to the bond coat (note the top coat had been excluded as shown in grayscale). Figure 5 shows a comparison of the grain morphology between the TMS-82+ HT Pt-Al and LT Pt-Al specimens in the as coated condition. Prior to 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.

After 30 h of isothermal exposure, the TMS-82+ HT Pt-Al bond coat transformed completely from the as coated β phase to an acicular martensitic phase, while the TMS-82+ LT Pt-Al specimen kept mostly its β phase with enlarged grain size (Figure 6). Significant degradation can be seen in the pattern quality of the 30 h isothermally exposed TMS-82+ HT Pt-Al, which is most likely

due to lattice distortion associated with the significant martensitic phase transformation.

Figure 7 provides a comparison of the phase distribution between the SRR99 LT Pt-Al and CMSX-4 LT Pt-Al specimens after 30 h isothermal exposure. The SRR99 LT Pt-Al specimen was found to exhibit the formation of γ' phase at the grain boundary and within the matrix of β phase as secondary phase. The CMSX-4 LT Pt-Al map, on the other hand, showed very uniform grains of clean β phase.

Fig. 5. EBSD mapping showing a comparison of grain morphology of the bond coat region near the oxide-bond interface of the TMS-82+ HT Pt-Al and TMS-82+ LT Pt-Al prior to isothermal exposure, with the HT Pt-Al bond coat having much larger grains.

Fig. 6. EBSD mapping showing the lath martensitic structure of the TMS-82+ HT Pt-Al specimen, in contrast to the β phase of the TMS-82+ LT Pt-Al after 30 h of isothermal exposure.

Fig. 7. EBSD mapping showing the unique γ' precipitation at the grain boundaries of the SRR LT Pt-Al, in contrast to the clean and uniform β phase of the CMSX-4 LT Pt-Al specimen after 30 h of isothermal exposure.

Figure 8 shows a comparison between the phase distribution of CMSX-4 LT Pt-Al, TMS-82+ LT Pt-Al and TMS-82+ HT Pt-Al after 100 h of isothermal exposure. The CMSX-4 LT Pt-Al specimen underwent a transformation from β phase to mostly coarse martensitic structure together with minor amount of γ' phase. The TMS-82+ LT Pt-Al specimen, on the other hand, showed the presence of more γ' phase along with a coarse martensitic structure. The Kikuchi pattern of the martensitic region in the TMS-82+ LT Pt-Al specimen is relatively unclear in comparison with the CMSX-4 specimen. Lastly, the formation of much larger γ' grains could be found in the TMS-82+ HT Pt-Al specimen with patterns of martensitic regions below recognition.

Fig. 8. EBSD mapping showing a comparison of the extent of Kikuchi patent degradation of three TBC after 100 h isothermal exposure.

Figure 9 compares the phase and microstructure morphology between the 100 h isothermally exposed TMS-82+ Pt-diffusion and the 30 h isothermally exposed SRR99 LT Pt-Al, which highlights the inherent difference between the γ and γ' structure of the Pt-

diffusion bond coat and the β structure of the LT Pt-Al bond coat. It can be seen that the TMS-82+ Pt-diffusion specimen consisted of small grains of more or less uniform sizes, whereas, the SRR99 LT Pt-Al specimen contained much larger β grains with γ' precipitates of various sizes.

Fig. 9. 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.

3.3 EPMA mapping analysis near TGO/bond coat regions

EPMA analysis was carried out to study the chemical diffusion and segregation behavior of the 30 h and 100 h isothermally exposed TMS-82+ Pt-diffusion bond coat (see Figure 10). After 30 h of isothermal exposure, the Al content near the TGO/bond coat interface of the TMS-82+ Pt-diffusion specimen was uniformly depleted with corresponding enrichment in the Cr content. The Ti content was found to segregate below the Cr enriched layer at the exact location where Cr depletion occurred. It can be seen that the overall chemistry of the Ti and Cr segregation after 100 h of isothermal exposure remained very similar to that of the 30 h, while further Al depletion took place. Traces of chromium oxide can be found in the TGO layer for both exposure times.

Fig. 10. EPMA mapping showing the chemistry near the oxide-bond coat regions of the TMS-82+ Pt-diffusion specimens after 30 and 100 h of isothermal exposure, with uniformly depleted layer of Al and Ti while enriched with Cr.

Figure 11 provides a direct comparison of the Ti and Cr distribution between the TMS-82+ LT Pt-Al and the CMSX-4 LT Pt-Al specimens after 100 h of isothermal exposure. Similarly, Ti-Cr segregation was found in the TMS-82+ LT Pt-Al specimen, except that the segregation occurred in small patches along bond coat region near the TGO/bond coat interface rather than layers as in the previous case. On the other hand, the CMSX-4 LT Pt-Al specimen showed a rather consistent Cr distribution with much less Ti content near the interface. Chromium oxide was detected in the TGO layers of both specimens.

Fig. 11. EPMA mapping showing a comparison of Cr and Ti contents near oxide-bond coat interface between TMS-82+ LT Pt-Al and CMSX-4 LT Pt-Al after 100 h of isothermal exposure, with CMSX-4 showing no obvious Ti presence.

3.4 Simulation of phase transformation by Thermo-Calc

The Thermo-Calc software was used to clarify the effect of Cr content on the phase distribution of the LT Pt-Al bond coat system paired with the CMSX-4 alloy. A set of parameters including the isothermal temperature used (1408 K), and the bond coat compositions near the TGO/bond coat interface of the 100 h isothermally exposed CMSX-4 LT Pt-Al specimen were specified in the calculation. We assumed that the system is in a stable equilibrium state after certain amount of time. Note that the bond coat compositions were taken from the EDX analysis result as detailed in the experimental section (see Table III).

Table III. 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	Co	Cr	Mo	W	Al
CMSX-4 LT Pt-Al	6.69	3.16	0.50	2.00	11.12
TMS-82+ LT Pt-Al	4.90	2.89	0.48	1.86	11.79
	Ti	Ta	Re	Pt	Ni
CMSX-4 LT Pt-Al	0.010	5.35	0	20.43	50.21
TMS-82+ LT Pt-Al	0.32	3.70	0	22.53	50.90

Figure 12a is a plot of the mole-fraction of different phases near the TGO/bond coat interfaces of the 100 h isothermally exposed CMSX-4 LT Pt-Al alloy based on the calculation in Thermo-Calc as a function of Cr content. The results show an increase in the mole fraction of β phase corresponding to a decrease in the γ' phase with increasing Cr content. The dotted line shows the relative distribution of the bond coat phases in the actual 100 h isothermally exposed CMSX-4 LT Pt-Al specimen. A similar analysis was

carried out to study the effect of Ta content on the phase distribution of the 50 h isothermally exposed TMS-82+ LT Pt-Al. The purpose here is to see if an inherently low Ta content, such as in the case of the SRR99 LT Pt-Al specimen, could have an influence on the γ' transformation behavior. Again, the bond coat compositions used for Thermo-Calc analysis were taken from EDX line scans near the oxide-bond coat interface (see Table III). Thermo-Calc results given in Fig. 12b also indicated an increase in the mole fraction of β phase corresponding to a decrease in the γ' with increasing Ta content. However, the extent of the phase variation seemed much less in this case.

Fig. 12. The mole fraction of different phases existing near the TGO/bond coat interface of the bond coats in a) CMSX-4 LT Pt-Al 100 h, and b) TMS-82+ LT Pt-Al 50 h 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

The results reported in previous sections gave detailed information regarding phase evolution with thermal history, which provide insights into the degradation mechanism of TBC and offer clues on the cause of early spallation. Table IV is a summary of the phase evolution of the TBC, and their corresponding TGO stress obtained from the previous work [18] using the photo-luminescence piezo-spectroscopy and the R2 peak shift estimation. The phase constituents of the bond coat seem to have a huge influence on the

TGO stress level. The TMS-82+ Pt-diffusion specimen with its $\gamma + \gamma'$ composition was measured to have the highest TGO stress. The CMSX-4 LT Pt-Al specimen having pure β phase after 30 h of isothermal exposure had a slightly lower TGO stress than that of the TMS-82+ HT Pt-Al with all martensitic structure at 30 h (~2.29 GPa vs. 2.45 GPa). It should be noted here that the martensitic transformation is known to undergo molar volume shrinkage during cooling, and mostly likely, creates additional stress on the TGO layer (more on this will be discussed in Section 4.3).

Table IV. A summary of the phase evolution and TGO stress of all the bond coats studied between 30 and 100 h of thermal exposure [18]

	Phase evolution and TGO stress during thermal exposure		
	30 h	50 h	100 h
SRR99 LT Pt-Al	γ' precipitates (g.b. and near interface) + β Stress: 0.24GPa	-N/A (Spalled)	-N/A (Spalled)
TMS-82+ HT Pt-Al	All lath martensitic structure Stress: 2.45GPa	Martensitic + γ' (significant) Stress: 2.33GPa	Martensitic + γ' (large amount) Stress: 2.49GPa
TMS-82+ LT Pt-Al	Mostly β + martensites + γ' (trace) Stress: 1.18GPa	β + martensites (significant) + γ' (more trace) Stress: 1.78GPa	Martensitic + γ' (significant) Stress: 1.85GPa
CMSX-4 LT Pt-Al	All β Stress: 2.29GPa	β + martensites (significant) Stress: 2.17GPa	Martensitic + γ' (significant) Stress: 2.09GPa
TMS-82+ Pt diffusion	Uniform γ layer near the interface Stress: 2.68GPa	Uniform γ layer near the interface Stress: 2.84GPa	Uniform γ layer near the interface Stress: 2.88GPa

From our previous study [18], the CMSX-4 LT Pt-Al and TMS-82+ HT Pt-Al were the only specimens to have experienced a decline in TGO stress between 30 and 80 h of isothermal exposure, and in the case of CMSX-4 LT Pt-Al, the decline continued all the way to 100 h (Fig. 1). These two TBC were also previously determined to have an unexpected improvement in the interfacial adhesion between 30 and 100 h [18]. These observations suggest that the stress relaxation of the TGO by creep (i.e. rumpling of bond coat) can significantly influence the adhesion of TBC, and once again verified our previous proposed concept that the interfacial adhesion is a dynamic property. The TMS-82 LT Pt-Al, on the other hand, started out with relatively lower TGO stress having multiple phases after 30 h isothermal exposure, and continued to show an increasing trend in TGO stress until 100 h of isothermal exposure.

The SRR99 LT Pt-Al and the TMS-82+ HT Pt-Al specimens were particularly interesting due to their inherently different phase

evolution and relatively poor interfacial adhesion when compared to other TBC. As shown in section 3.1 and 3.2, the SRR99 LT Pt-Al specimens experienced a rapid transformation from the as coated β to γ' phase by means of grain boundary diffusion, resulting in the formation of γ' phase at the grain boundary. This phenomenon is quite exclusive to the SRR99 LT Pt-Al specimens, as no other TBC prior to 200 h of thermal exposure duration, displayed β to γ' phase transformation along the grain boundaries. The TMS-82+ HT Pt-Al specimen, on the other hand, was found to undergo a complete transformation from the as coated β to a coarse martensitic structure after 30 h of isothermal exposure. In fact, this phenomenon was not observed on any other TBC studied in this work, regardless of the thermal exposure time. The TMS-82+ HT Pt-Al specimen is also unique in that the grain size of its as coated β phase appears to be much larger than those of the LT Pt-Al type. The larger grains can be explained by the fact that the aluminization processes of the TMS-82+ HT Pt-Al were carried out at a relatively high temperature of 1080°C in a low activity aluminum environment, and grain growth tends to be much rapid due to a higher diffusivity of atoms at high temperatures.

4.2 Accelerated γ' formation due to outward diffusion of Ti

It is known that the activation energy for chemical diffusion along the grain boundary, where vacancies due to defects and dislocation are present, is much lower than that required by lattice diffusion. Therefore, it makes sense that the grain boundaries are the preferred route for Al diffusion during high temperature oxidation. The TBC coated SRR99 specimen, together with all other TBC systems, should theoretically promote Al diffusion through the grain boundaries of the bond coat upon forming Al_2O_3 during thermal exposure. However, the question still remains as to why the formation of the γ' phase along the grain boundaries was exclusively observed on the SRR99 LT Pt-Al in early isothermal times. As previously confirmed by EDX, EPMA, and Thermo-Calc simulation [18], Ti and Ni contents have the tendency to segregate to Al depleted region, corresponding to the location of γ' phase. The SRR99 LT Pt-Al specimen, having a relatively higher Ti and Ni content (see Table I), was previously measured to have the fastest TGO growth kinetics and the γ' phase formation rate [18]. It is therefore believed that the inherently high Ni and Ti contents of the SRR99 alloy lead to a greater difference in chemical potential / free energy between the substrate and coating, which drives the Al diffusion process by ways of the grain boundary.

EPMA results in Figure 2 and 11 of the SRR99 LT Pt-Al and TMS-82+ LT Pt-Al specimens, respectively, confirmed traces of Ti in the TGO layer, while Ti enriched γ' precipitates were present near the TGO/bond coat interface. The detrimental effect of TiO_2 formation in degrading the adherence of the alumina scale is well documented [19-21]. The same degradation mechanism, however, does not seem to apply to the case of the TMS-82+ HT Pt-Al specimen. Despite having Ti containing γ' precipitates near the TGO/bond coat interface, no obvious Ti could be detected (see Figure 2) in the TGO scale from multiple EPMA maps taken at various locations along the interface. The concentration of Ti in the γ' precipitates of the TMS-82+ HT Pt-Al was considerably lower than that in the SRR99 LT Pt-Al specimen, which may be the reason behind the absence of TiO_2 . The degradation of the TMS-82+ HT Pt-Al specimen will be discussed in section 4.3 and 4.4.

According to the results in section 3.4, Cr and Ta can stabilize the β phase, delaying the formation of γ' . Nonetheless, Cr seemed to be more effective 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 11) revealed that Cr can effectively inhibit the diffusion of Ti content outward to the bond coat surface. In fact, the CMSX-4 LT Pt-Al, having relatively higher Cr content in the bulk alloy (see Table I), was shown to have relatively slower γ' formation despite having more bulk Ti content than the TMS-82+ LT Pt-Al specimen [18]. It should be noted that the stability of a certain phase may as well be influenced by other alloying elements in the bulk superalloy. Nonetheless, the results suggested that Cr plays a critical role in the prevention of early γ' formation.

4.3 Martensitic transformation due to Al depletion

Previous work by Smialek et al [22] indicated that the martensitic transformation temperature, M_s , in β -NiAl alloy increases when Al depletion occurs as a result of oxidation and alloy/bond coat inter-diffusion. They suggested that Al depletion with corresponding increase in the Ni content would decrease the ordering force of the stoichiometric NiAl, making the martensites as the dominant phase upon cooling. The previous EDX line profile study of the Pt-Al bond coats by Wu et al [17] showed that the Al content in the HT Pt-Al bond coat within a distance of 20 μm from the TGO/bond coat interface is slightly lower (~ 7 at. % lower on average) than that in the LT Pt-Al. These findings suggest that the complete transformation to coarse martensite in the HT Pt-Al bond coat type is most likely due to its inherently low Al content, hence, having a higher M_s . It has been well known for decades that 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 [23] (i.e. increasing cooling).

According to the EBSD results shown earlier, significant degradation in the pattern quality was commonly found on specimens that underwent β to martensitic transformation. This degradation tends to worsen with increasing thermal exposure, going from 30 to 100 h. Qualitative and semi-quantitative assessments of local strain/deformation by utilizing both the changes in the EBSD pattern quality and grain misorientations have long been conducted in many previous studies [24-26]. Hence, it is believed that the progressive degradation in the EBSD pattern quality corresponds to the increasing severity of strain/deformation in the martensitic regions due to thermal exposure.

The High Temperature X-ray diffraction results in the work by Chen et al [27] indicated that the molar volume of the L1₀ martensite is approximately 2% smaller than that of the β , causing a transformation strain of about -0.7 % during cooling. This volume shrinkage due to martensitic transformation does generate additional stress during thermal cycling in the bond coat, and thus, can further increase rumpling growth [28]. It should be pointed out that the martensitic transformation in our specimens generated strain for the most part, as the experiment involved only isothermal exposure with a single cool-down process. EBSD results of 100 h isothermally exposed specimens revealed that the degradation of the martensites patterns tend to be the most severe when large γ' precipitates were formed as neighboring grains (see Figure 8). Based on this observation, it is proposed that the adjacent γ' grains, along with the TGO scale, may impede the contraction of

martensites during cooling by imposing a tensile strain. This force exerted on the martensites is likely to be proportional to the size of γ' precipitates formed in the surroundings. Hence, TMS-82+ HT Pt-Al, having the most γ' formation 100 h into isothermal exposure, was shown to have the most severely degraded EBSD map. On the other hand, the CMSX-4 LT Pt-Al specimen with significantly less γ' formation than the TMS-82+ LT Pt-Al after 100 h of isothermal exposure, had noticeably less degradation in its EBSD map. Note that the amount of γ' precipitates formation near the TGO/bond coat interface was thoroughly quantified on these TBC systems in the previous work [18], and used as reference for comparison here.

4.4 Thermomechanical misfit induced by phase transformation

It is proposed here that the co-existence of β , martensite, and γ' phases with inherently very different thermomechanical properties may induce a misfit stress in the TGO layer during thermal cycling, leading to an increase in rumpling amplitude of the TGO/bond coat interface. This concept can be best understood by studying the interfacial evolution of the TMS-82+ Pt-diffusion specimen. This specimen was shown to undergo a uniform Al depleted layer near the TGO/bond coat interface, with corresponding enrichment in Cr. The segregation of Ti was also observed right beneath this Al-depleted and Cr-enriched layer. This compositional distribution profile seems to be maintained between 30 h and 100 h of isothermal exposure, while the as-coated $\gamma' + \gamma$ phase gradually transformed to a single γ phase microstructure.

In a previous work [17], the TMS-82+ Pt-diffusion specimen was found to exhibit no rumpling behavior throughout its entire thermal cycling test, in comparison with other TBC systems. In addition, the TMS-82+ Pt diffusion specimen had some of the best interfacial adhesion among the TBC studied by the authors [18], despite having the largest TGO stress of the entire specimen set during thermal exposure. The reason behind these phenomena can be related to the uniform layer of γ phase microstructure near the bond coat/TGO interface. Unlike the β and martensitic transformation of Pt-Al bond coat systems, there is no significant volume change associated with γ' to γ transformation, and hence, does not produce rumpling growth [29]. Moreover, the Pt-diffusion systems do not have Ti segregation near the bond coat/TGO interface, and thus would not form TiO₂ in the TGO layer. Contrary to the Pt-diffusion system, the TMS-82+ LT Pt-Al and TMS-82+ HT Pt-Al systems had relatively poor interfacial adhesion/spallation lifetime and continuous growth rumpling amplitude during thermal exposure [18].

Conclusion

The results of this work lead to the following conclusions:

- The early spallation of the β bond coat systems is associated with two unique phase transformation phenomenon during thermal cycling: 1) γ' formation at the grain boundary and 2) complete martensitic transformation in early isothermal exposure.
- The progressive degradation in the EBSD pattern quality of the martensitic regions due to increasing γ' phases nearby has suggested that a misfit stress may be generated in the TGO layer due to the inherently different thermomechanical properties between different phases.

- The experimental results have clarified the difference in the degradation mechanism between the SRR99 LT Pt-Al and TMS-82+ HT Pt-Al specimens. The early spallation occurred in the SRR99 LT Pt-Al most likely due to the precipitation of Ti concentrated γ' phase near the TGO/bond coat interface, and subsequently, led to the formation of the less adhesive TiO_2 in the TGO layer. The early spallation of the TMS-82+ HT Pt-Al was mainly driven by the strain accumulation in the TGO as a result of the molar volume shrinkage associated with β to γ' transformation during cooling
- 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.
- The results of this work has once again demonstrated that the TBC spallation lifetime bears close relationship with the variation of interfacial fracture toughness G_c (critical strain energy release rate) and the driving force G (strain energy release rate) [18].

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. In addition, we would like to extend our gratitude to Dr. Hiroshi Harada and Dr. Kyoko Kawagishi of NIMS, Japan, and Mr. Rodney Wing of Chromalloy – UK for the provision of research facilities and specimens.

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