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Performance and Degradation Mechanisms of Thermal Barrier Coatings for Turbine Blades: a Review of Onera Activities

Thermal barrier coatings are used to protect blades and vanes in the hot sections of gas turbines. They consist of a thick porous ceramic layer deposited on a alumina forming metallic bond coat in contact with the nickel-based superalloy substrate. They are designed to prolong the components lifetimes or to increase gas temperature, and therefore efficiency. In service, the structure and composition of the various layers evolve, due to sintering of the ceramic layer, oxidation of the bond coat, and interdiffusion phenomena with the substrate. As a result, the properties of each layer are affected, as is the interfacial toughness. These evolutions, combined with applied external stresses, may lead to bond coat rumpling, crack formation at the bond coat/ceramic interface and the ceramic layer may eventually spall off. In addition to these intrinsic degradation modes, interactions with the environment can accelerate the system degradation. This paper reviews the aging phenomena occurring in thermal barrier coatings at high temperatures and describes their degradation mechanisms, with illustrations from service experience and laboratory tests

Introduction

Thermal Barrier Coatings (TBCs) were developed in the 70's to meet engine manufacturers' requests for improving engine performance and fuel efficiency (increased operating temperatures of turbine section) while reducing emissions and costs (simplified cooling air system, increased component lifetime, reduced maintenance cost, etc.). Today, TBCs are widely used to protect critical metallic parts of aircraft as well as land-based gas turbines (blades, vanes, seals and combustor chambers) from the surrounding hot gases. However TBCs in service are prone to intrinsic and extrinsic degradation phenomena [1] which may considerably restrict their potential. Both academic and industrial research is therefore underway to improve TBCs' reliability and performance [2]. This paper gives an overview of some activities carried out at Onera in this field over the past ten years in connection with the state-of-the-art. It focuses on TBC systems which are deposited on the most stressed high pressure turbine blades.

TBCs: a multilayer, multifunction system

TBCs are a multilayer system (figure 1) with each layer having a specific function and requirement. The top layer provides thermal insulation and consists of a porous ceramic coating with low thermal conductivity. It must also have a high melting point, good oxidation and corrosion resistance, a thermal expansion coefficient closer to that of the underlying metal in order to reduce thermal mismatch stresses, high toughness and strain tolerance. Yttria partially stabilized zirconia (8 wt. % YPSZ) is commonly used as it is one of the few available materials which satisfies all the requirements. It is deposited on rotating components as a layer of about 150 μm by the EB-PVD process (Electron Beam Physical Vapor Deposition). The resulting columnar microstructure shows high strain compliance and good resistance to erosion, but leads to moderately low thermal conductivity ($\sim 1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). A temperature drop of up to 150°C can be achieved through the top layer, thus reducing accordingly the underlying metal temperature.

The ceramic insulating layer is deposited on an oxidation resistant metallic layer (the bond coat) which, during service, forms a protective oxide, mostly alumina. This thermally grown oxide scale (TGO) has to be perfectly adherent to both the top layer and the bond coat in order to insure the chemical and mechanical compatibility of the whole system. The bond coat is for example a diffusion platinum modified nickel aluminide which is obtained by deposition of a thin electroplated platinum layer followed by a vapor phase aluminizing process. The underlying substrate is the first generation nickel-based single crystal superalloy AM1¹ [3].

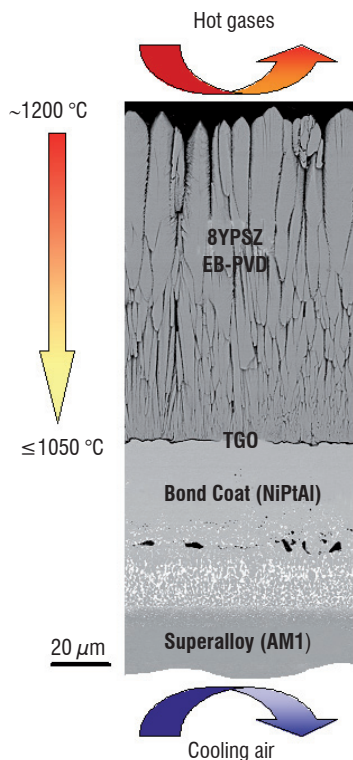


Figure 1 - Typical Thermal Barrier Coating for rotating turbine components

TBCs evolution during service

In service, TBCs are exposed to oxidizing combustion gases and the external surface temperatures can reach about 1200°C. In these conditions, temperature driven phenomena occur such as sintering of the porous ceramic layer, oxidation of the bond coat and interdiffusion with the substrate. Consequently, the structure and composition of the various layers evolve and their properties are affected, as is the interfacial toughness. It will be shown that these evolutions combined with the applied thermal and mechanical stresses may cause the ceramic layer to spall off in the end.

Aging of the ceramic top layer: sintering and phase transformation

Sintering of the top layer occurs rapidly from the first aging times at 1100°C, initially over short length scales and then more slowly over longer length scales. At first, the feather-like edges of the columns are rounded off by surface diffusion and progressively transform into lines of disconnected closed pores. Random bridge formation

between the columns follows (figure 2). These sintering effects are accelerated at higher temperatures. A consequence of these widely documented phenomena [4] is a drop in the top coat strain compliance and thermal insulation capability as illustrated in figure 2 (from [5]). A higher thermal conductivity of the ceramics increases the surface temperature of the metal with deleterious effects on the component life duration. Furthermore an increased Young's modulus of the top coat leads to higher energy stored in the system and can induce anticipated spallation of the TBC (see § Energetic approach of TBC failure, box 3).

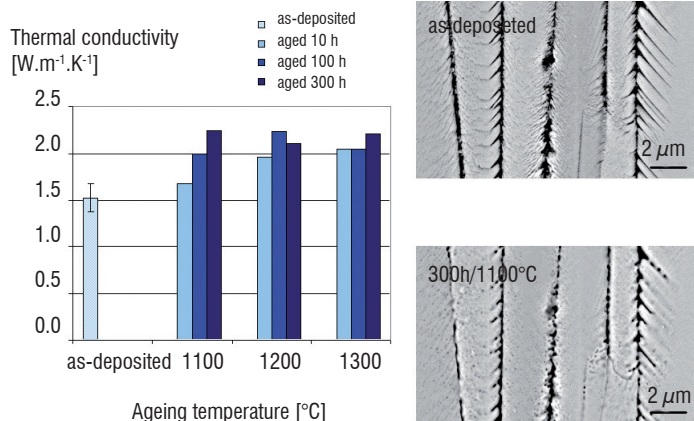


Figure 2 - Effect of sintering on 8YPSZ EB-PVD ceramic top coat microstructure and thermal conductivity (measured at room temperature in air atmosphere with a CO₂ - laser flash technique)

When inter-columnar sintering is sufficiently large, in-plane tensile stresses appear which cause cracks to initiate and grow, giving a mud-like pattern upon cooling [5,6]. These cracks going through the top coat thickness facilitate CMAS infiltration (see § TBC interactions with environment).

Moreover, in the case of YPSZ coatings, crystallographic phase transformations are well known to occur during aging from 1200°C [7]. The initial metastable tetragonal t' phase transforms at high temperature into a mixture of yttria-rich cubic phase and yttria-poor tetragonal phase t which in turn may transform into a monoclinic phase on cooling. As a consequence, cracks due to transformation volume mismatch can appear and the thermal conductivity of the coating may be modified. Nevertheless, Onera work showed [5] from phase fraction estimation by X-ray diffraction and thermal conductivity data as a function of yttria concentration [8] that the phase transformation contributes less than 10% to the evolution of the thermal conductivity of the top coat. This effect is thus of second order compared to the sintering effect.

Bond coat oxidation

In service, the initially β-NiPtAl single phased bond coat loses part of its aluminum content by formation of a highly protective alumina scale which slowly grows according to typical α-alumina growth kinetics, eventually following a transient oxidation period. Nevertheless, some factors can affect the properties of this oxide scale and possibly weaken the resistance of the bond coat / top coat interface, thus contributing to the degradation of the thermal barrier system.

¹ AM1 composition [wt. %] : Ni base, 6.5 Co, 7.8 Cr, 2 Mo, 5.7 W, 5.2 Al, 1.1 Ti, 7.9 Ta

It has been reported that sulfur, present as an impurity in the alloy, dramatically decreases the adherence of the oxide scale [9,10]. If the oxide bonding to the metal is low, growth and/or thermal stresses can induce the spallation of the protective oxide layer or the formation of interfacial voids that is very deleterious for thermal barrier coating systems as shown below. This phenomenon, existing for many alumina-forming alloys, is known as «the sulfur effect».

On β -NiAl, it is widely admitted that the alumina scale grows principally by outward diffusion of aluminum at intermediate temperatures (i.e. θ - Al_2O_3 at $\sim 900^\circ\text{C}$) or by a combination of inward diffusion of oxygen and outward diffusion of aluminum at higher temperatures (i.e. α - Al_2O_3 at $\sim 1100^\circ\text{C}$). Formation of interfacial cavities at the metal/oxide interface was thus observed after the oxidation of NiAl at 900°C . These cavities result from the condensation of metallic vacancies injected in the alloy by the growth mechanism of the oxide or from the nonreciprocal diffusion of the non-oxidized element of the alloy (Kirkendall effect). Studies conducted at Onera [11,12] on NiAl single crystals showed that during the formation of the transient alumina, sulfur segregation at the metal/oxide interface occurs when vacancies are injected during the Al_2O_3 growth. Sulfur segregation is favored at the nickel-rich metallic surface of the interfacial cavities and occurs as long as their surface remains free of oxide, in agreement with Haynes [13] who considered the stabilization of voids by sulfur in a model of cavity growth for a high sulfur content NiAl coating. Once segregated, sulfur remains at the interface at an even higher temperature when the transient cavities are filled by inward anionic growth of the mature α -alumina. Segregated sulfur, trapped at the interface after the θ to α transformation of the scale, weakens the oxide adherence and favors the formation of interfacial voids and the decohesion of the oxide layer under growth and/or thermal stresses (figure 3).

Efforts to limit the detrimental effect of sulfur have focused on different approaches such as desulfurizing the superalloy [10], using low sulfur content superalloys, doping with reactive elements (Y, ...) [13,14] or adding platinum [13]. Indeed platinum was found to reduce sulfur segregation to the free surface [15] and even to eliminate sulfur at the interface [16].

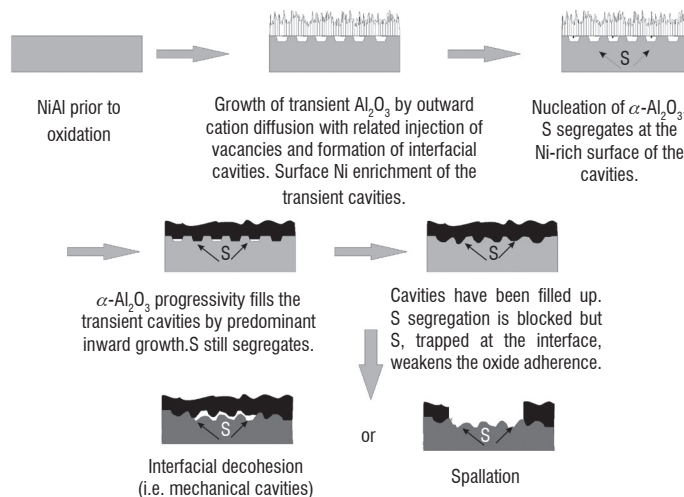


Figure 3 - Model of the sulfur effect at the interface between an aluminide substrate and thermally-grown oxide films (from [12])

The effect of platinum addition on the initial stages of oxidation of cast nickel aluminide intermetallic alloys of low and high sulfur content has been studied at Onera [15]. At 900°C , where a scale of transient alumina θ - Al_2O_3 grows by outward cationic transport, the beneficial effect of platinum is both the size reduction of the interfacial transient cavities and an increase of the transient alumina oxide scale occurrence. This was attributed to an enhancement of the main interdiffusion coefficient of aluminum in the intermetallic by platinum [17]. Therefore adding platinum lowers the oxide-free surface and maintains an Al-rich phase near the surface. According to the Rivoaland model, these two consequences allow for a reduction of the sulfur segregation and consequently an increase in the oxide adhesion.

The transition from θ -controlled to α -controlled kinetics is longer in the presence of platinum in the alloy. This is related to the fact that the growth rate of the transient oxide is still increased (by a factor of 5) by the presence of platinum after initiation of the transition, which leads to the thickening of the oxide scale before formation of a continuous slow-growing α - Al_2O_3 layer. The prolonged transition from

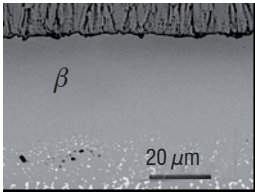
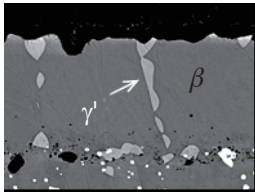
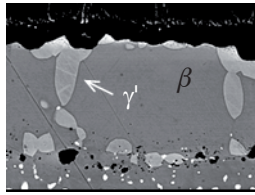
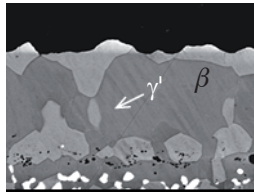
as fabricated	50 cycles at 1100°C		100 cycles at 1100°C		250 cycles at 1100°C	
						
β -NiAl (B2) s: 1.00	β -NiAl (L1 ₀) s: 0.95	γ' -Ni ₃ Al (L1 ₂) s: 0.05	β -NiAl (L1 ₀) s: 0.90	γ' -Ni ₃ Al (L1 ₂) s: 0.10	β -NiAl (L1 ₀) s: 0.75	γ' -Ni ₃ Al (L1 ₂) s: 0.25
B2 : Ni 44, Al 40, Pt 10, Cr 3, Co 3, Ti < 1, Ta < 1 L1 ₀ : Ni 50, Al 30, Pt 8, Cr 6, Co 4, Ti < 1, Ta 1 L1 ₂ : Ni 63, Al 16, Pt 6, Cr 2, Co 5, Ti 1, Ta 6						

Figure 4 - Microstructural evolution of the bond coat as a function of the number of 1h-cycles at 1100°C : different phases surface fraction (s) and chemical composition (at.%)

θ -controlled to α -controlled kinetics observed in the presence of platinum is proposed to favor the stress relaxation in the alumina scale.

Bond coat / superalloy interdiffusion

Besides the oxidation of the bond coat, thermal cycling of the TBC system promotes interdiffusion of various elements between the platinum modified aluminate layer and the underlying superalloy substrate (AM1 in the present case). As a result, the aluminum content of the bond coat becomes lower and lower, so that the initially β -NiPtAl single phase transforms into a γ' -Ni₃Al phase (figure 4). In addition to this inward diffusion of aluminum and platinum, outward diffusion of some elements of the substrate such as cobalt, chromium or titanium also contributes to phase transformation within the bond coat. It should be noted that the chemical composition of these two inequilibrium phases remains constant whereas their volume fraction evolves during thermal cycling: as the initial Al-rich phase is reduced, the aged Al-poor phase extends. Moreover, next to the γ' -Ni₃Al phase (L1₂) a lamellar structure may be observed at room temperature, related to the reverse transformation of the β -NiAl (B2) phase into the martensitic NiAl phase (L1₀) which takes place during the cooling and heating stage of thermal cycling. The occurrence of martensite mainly depends on the Al and Pt content of the bond coat as well as on the nature and content of the diffused elements from the substrate. The phase transformations within the bond coat will have consequences on its mechanical behavior [18].

Intrinsic degradation mechanisms

Stress field and rumpling

As mentioned above, an interfacial stress field develops in thermal barrier systems during thermal cycling, resulting from oxidation growth stresses and thermal stresses due to thermal expansion mismatch between the top coat, the TGO and the bond coat. Piezospectroscopy measurements performed at Onera clearly demonstrate that high compressive in-plane stresses (about 3 GPa) remain at room temperature within the TGO (figure 5, from [19,20]). At the same time, out-of-plane stresses exist because the interface is not flat. They cause the bond coat/TGO interface to deform so that a slight in-plane stress relaxation is observed, due to progressive interfacial roughening, also called rumpling [21]. But resulting out-of-plane stresses also initiate local damage. As a result, geometrical incompatibilities in concave areas combined with voids formation related to oxidation

induce crack interfacial propagation, thus leading to sudden top coat spallation (figure 6). We note that the crack pathway is mixed (going along the TGO/top coat interface or through the TGO) as attested by fracture surface observations.

Large stresses produced in the bond coat by phase transformation, such as the martensitic transformation, may also effectively promote undulation growth. Rumpling is obviously governed by the creep resistance of the bond coat and the mechanical behavior of the highly compressed TGO. The mechanical behavior of the bond coat plays a key role in the relaxation of stresses induced by oxidation and martensitic transformation. In particular, in order to describe the interface progressive roughening, it is essential to know the elastic viscoplastic law of the bond coat in the as-elaborated state and its evolution during thermal cycling linked to the arising phase transformations. An original technique - high temperature instrumented microindentation, up to 1000°C - has been developed at Onera (see box 1) to extract information on the mechanical behavior of the bond coat [22]. The mechanical properties of the different phases (hardness related to yield stress, elastic modulus, creep law) are investigated by means of indentation tests, which enable local measurement within individual phases. For instance, the indentation creep behavior is determined by applying a load of about 0.5 N, and by holding it during several thousand seconds (up to about 1 hour) at different temperatures. An inverse problem analysis is used (analytical approaches and finite element method simulation) to identify the variables of the constitutive law of the materials tested.

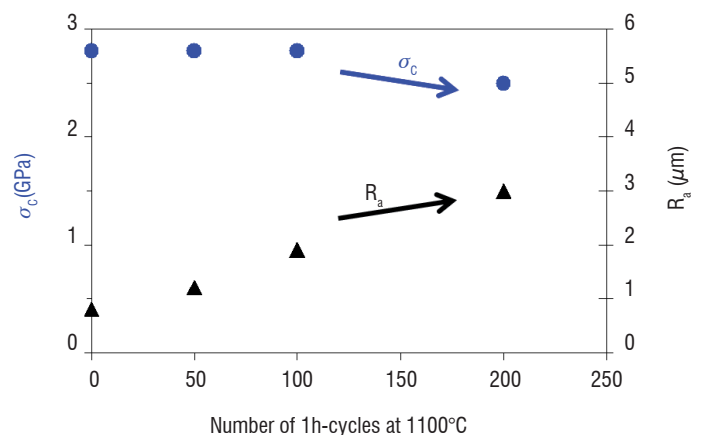


Figure 5 - Evolution of residual compressive in-plane stresses (σ_c) in the TGO and arithmetical mean roughness (R_a) of the bond coat/TGO interface as a function of the number of 1h-cycles at 1100°C

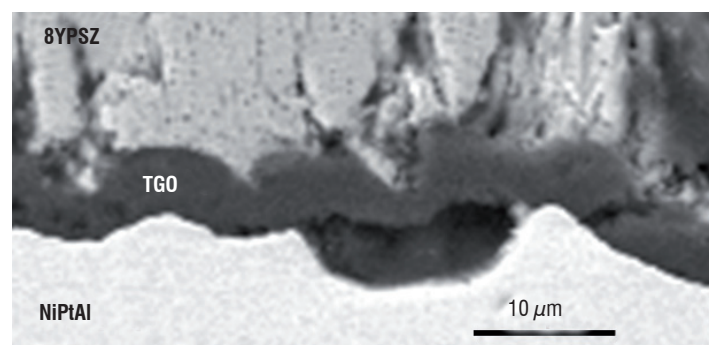
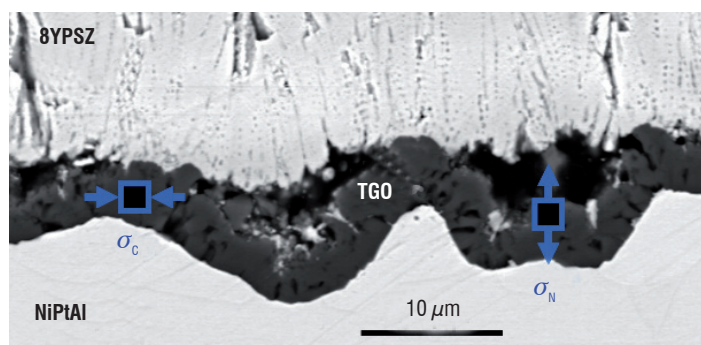


Figure 6 - Interfacial geometrical incompatibilities generated by out-of plane stresses (σ_N) and voids due to oxidation

Box 1 - High temperature instrumented microindentation system

(B. Passilly, Onera – Department of Composite Materials and Structures)

General description - Principle

The vacuum chamber contains two translation stages (horizontal X and Y axis), on which the load sensor, the sample holder, the sample, and a furnace are fixed. This X-Y stage enables the horizontal sample to move from under a microscope to under the indenter. The indenter and the sample are located inside small furnaces which are separately resistively heated up to the test temperature (up to 1000°C). The displacements are measured using a differential capacitive technology.

Time, load and indenter displacement are recorded simultaneously during the loading, holding and unloading phases.

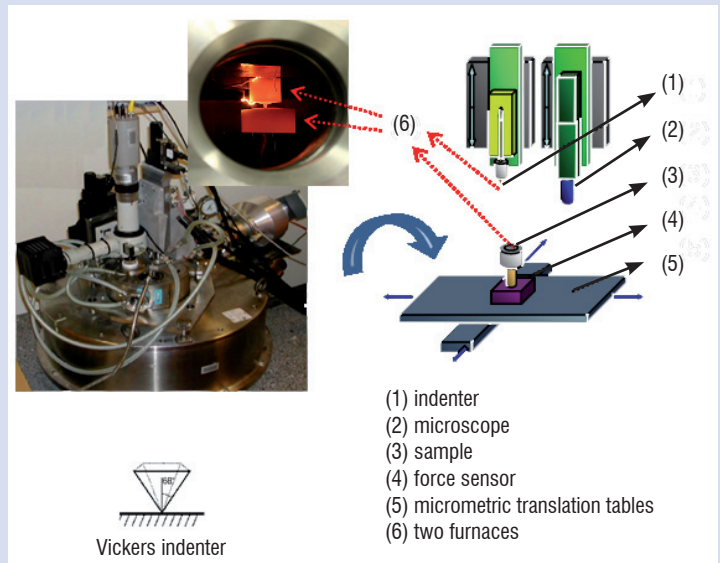


Figure B1-01 - Microindentation equipment

Data analysis

Adapted from the approach by Sargent and Ashby - *Indentation creep*. Mat. Sci. Technol., 8 (1992) 594-601

Norton law
$$\dot{\epsilon} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n \cdot \exp\left(-\frac{Q}{RT} \right)$$

Penetration depth
$$h_{calc}(t) = \left[h_0^{2n} + B(T) \cdot n \cdot \exp\left(-\frac{Q}{RT} \right) \right]^{\frac{1}{2n}}$$

- fitting experimental curves $h_{exp}(t)$ for different $T \rightarrow n, B(T)$
- variation in $B(T) \rightarrow Q$

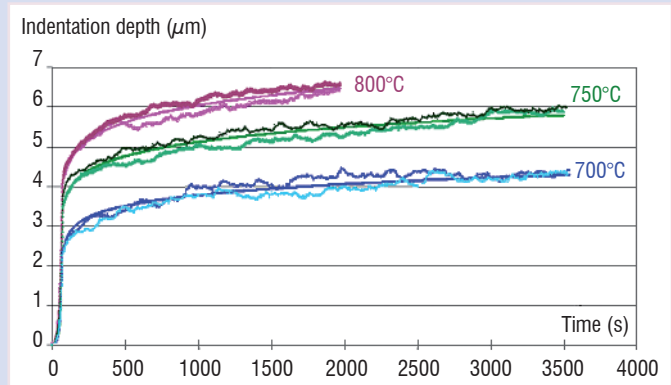
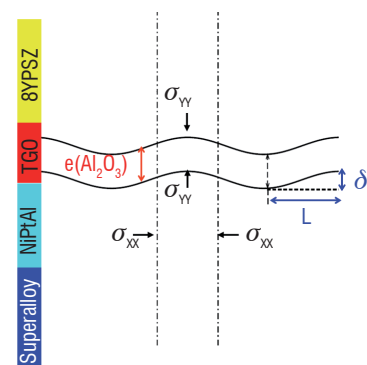


Figure B1-02 - Example: indentation creep (0.5 N load) of NiPtAl bond coat

Interface evolution modeling

In order to better understand the TBC degradation mechanisms, a semi-analytical model describing the interface evolution during thermal cycling is used at Onera. This model, which is based on Hutchinson studies [23], considers the TBC system as a macroscopic multilayered structure, in which complex behavior laws are used for each layer. It has to be specified that the creep law of the bond coat injected into the model is the one determined by high temperature instrumented microindentation and that the interfacial roughness is drawn as a sinusoidal undulation (figure 7). This computation is designed to quantify the interface roughening, related to the in-plane and out-of-plane stress development with the aim of specifying a damage criterion. The model is being validated by comparing its predictions with experimental observation of rumpling. Onera's current work focuses on getting essential data in order to build a physically-based model, able to assess thermal barrier spalling on turbine blades.



Input data of the computation:
Oxidation kinetic, martensitic transformation, hardening, creep laws, thermal expansion coefficients, initial undulation geometry

Output data of the computation:
In-plane and out-of-plane stresses (σ_{xx} and σ_{yy})
Undulation amplification (δ)

Figure 7 - Semi-analytical modeling of the TBC multilayered structure

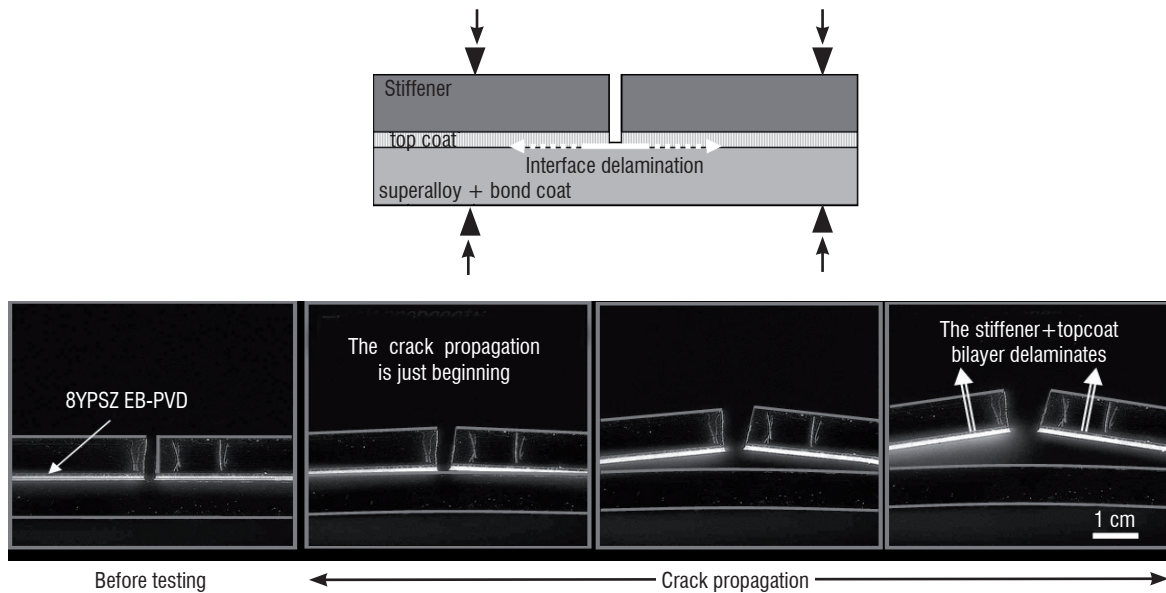


Figure 8 - Four-point bending test

Energetic approach of TBC failure: Lifetime prediction

The sudden failure of TBC systems is due to rapid propagation of interfacial cracks, initiated by complex phenomena linked to the oxidation mechanisms and to the evolution of the interfacial area stress field and intrinsic interface adhesion properties. An energetic model [24,25] was studied at Onera [20] with the aim of proposing a possible guide for predicting TBC system lifetime, which is a goal of prime importance. An energy balance is used for the lifetime assessment, by comparing evolution of the interfacial fracture toughness with the evolution of the stored strain energy in the ceramic layers (top coat and TGO).

To get a quantitative assessment of TBC system adhesion and to better understand how the interfacial strength is damaged by microstructural degradations during thermal cycling, an original approach

was developed based on the design and implementation of a specific test (a modified 4-point bending test – figure 8 [19]).

The whole set of experimental data, particularly the adhesion energy (from the 4-point bending test) and the residual stress assessments (from piezospectroscopy analysis – box 2), allows for a comparison of the energy needed to fracture the interface and the available energy which can induce the interfacial crack propagation (box 3). From this mechanical modeling, a spallation criterion has been defined that gives an estimate of the TBC system lifetime. The predicted lifetime (as the adhesion energy and the available energy intersect) has proved to be consistent with experiments (observed TBC spontaneous spallation). This energetic approach can be used to build a physically-based model, which can assess thermal barrier spallation on turbine blades. This model, developed at Onera, was very recently discussed in the review paper from Hutchinson [26].

Box 2 - Piezospectroscopy analysis

(F. Lepoutre, Onera – Department of Composite Materials and Structures)

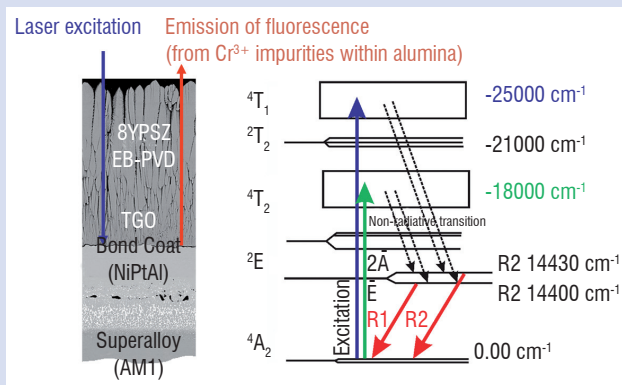


Figure B2-01- Principle

Principle

Piezospectroscopy is a non-contact technique which allows for measurement of the in-plane stresses within the TGO. It uses the spectroscopic displacement of fluorescence lines (R1, R2) emitted after the excitation by a laser of Cr³⁺ impurities in alumina when the stresses relax [27]. The principle of this measurement is similar to the one used in the diamond anvil pressure cell.

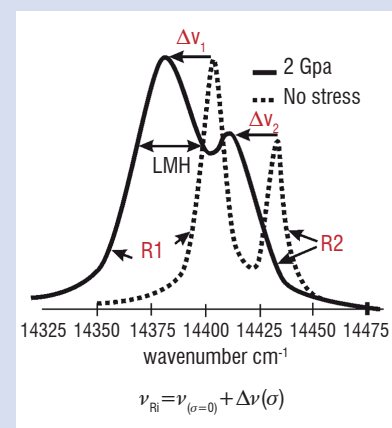


Figure B2-02- Spectroscopic displacement of fluorescence lines

Box 3 - Energetic approach of TBC failure

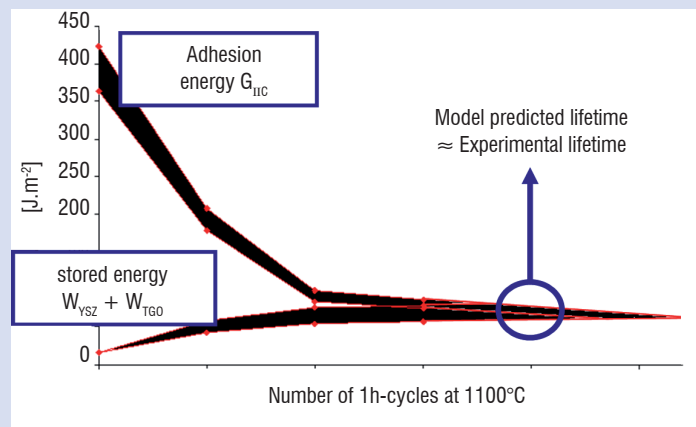


Figure B3-01 - Evolution of adhesion energy (G_{IIc}) and available energy (W) for interfacial crack propagation during thermal cycling at 1100°C

Calculation of the adhesion energy

During the spontaneous buckling and growth of TBC scales, the interfacial loading rapidly tends to pure mode II. The pure mode II values of adhesion energy (G_{IIc} , $\psi = 90^\circ$) can be estimated from our 4-point adhesion values (G_c , $\psi = 40^\circ$) using the empirical relation proposed by [28].

ψ = mode mixity angle = parameter measuring the ratio between mode II ($\psi = 90^\circ$) and mode I ($\psi = 0^\circ$) loadings during the crack propagation.

Influence of experimental data on TBC lifetime prediction

It is to be noted that an experimental uncertainty is attached to the interfacial fracture toughness evolution, and that some parameters used for the elastic stored energy calculation also induce some inaccuracy. In particular, the top coat Young's modulus, which increases during thermal cycling, due to sintering phenomena and environmental interactions (CMAS infiltration) must be precisely quantified in order to refine the lifetime prediction.

Calculation of the driving energy for TBC failure

For each ceramic layer ($i = \text{YPSZ or TGO}$)

$$W_{stored}(i) = (1 - \nu_i^2) \sigma_i^2 e_i / 2 E_i$$

e_i = thickness

E_i = in-plane Young's modulus

ν_i = Poisson's ratio

σ_i = in-plane stresses (assumed to be biaxial and isotropic in the plane of the layer)

TBC interactions with environment

As already mentioned, the surface of TBCs on turbine blades and vanes located in the hottest sections of gas turbine engines can reach temperatures up to 1200°C in operating conditions. At such temperatures, thermal barrier coatings are susceptible to corrosion by molten calcium-magnesium-alumino-silicates (CMAS) resulting from the ingestion of siliceous mineral debris (dust, sand, ash) contained in the hot gases arriving in the turbine. In the literature, few studies [29,30] can be found investigating, on ex-service blades or vanes, the damage resulting from CMAS attack on the TBC, especially when the top coat is elaborated by EB-PVD [31]. The first studies conducted at Onera in this field have thus consisted of microstructural characterizations of the interaction between CMAS and EB-PVD TBC observed on high pressure turbine blades removed from service. The main results of this study are reported below.

The initially white TBC surface is covered after service by a brownish deposit strongly adhering to the blade surface. This deposit is present mainly on the pressure side and leading edge whereas a large part of the suction side surface is free from deposits (figure 9).



Figure 9 – After service high pressure turbine blade: pressure side covered by CMAS brownish deposit

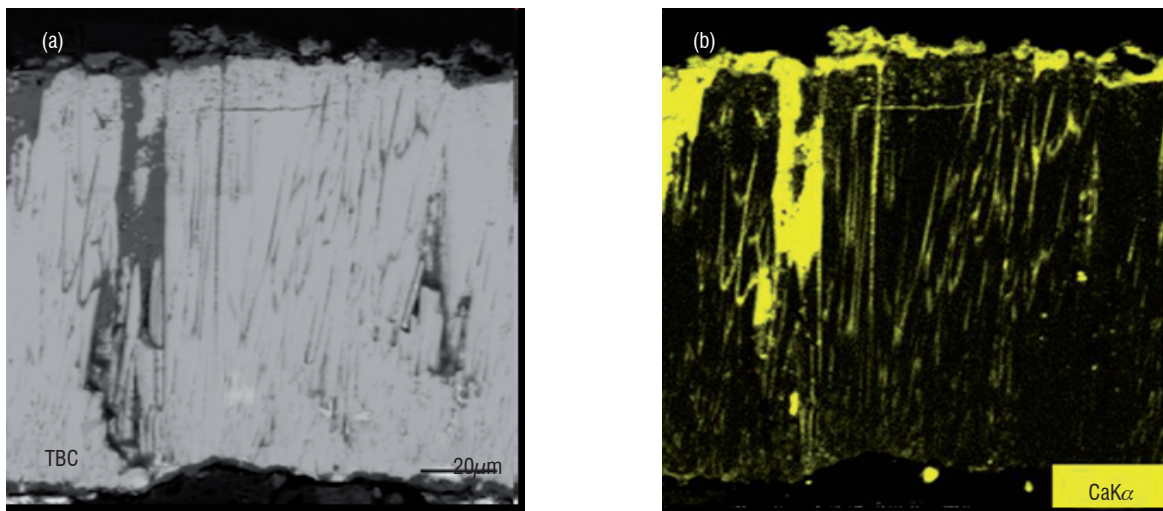


Figure 10 - TBC top coat infiltrated by CMAS (SEM image (a) and corresponding elemental map of Ca ($K\alpha$ line), (b))

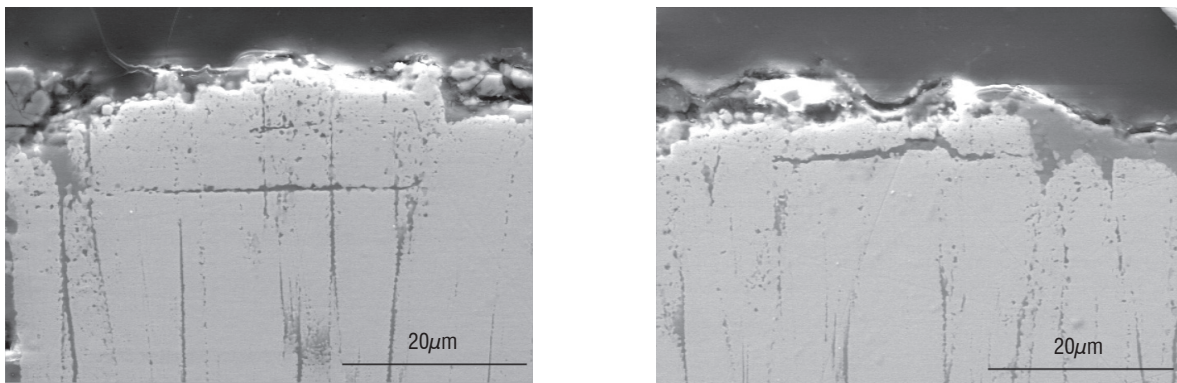


Figure 11 - Delamination cracks in the TBC (pressure side)

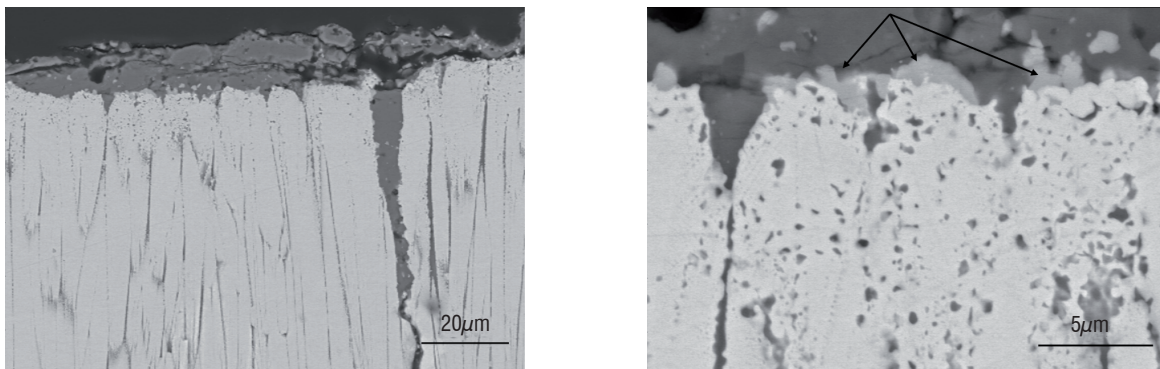


Figure 12 - Degradation of the column tips and formation of a new phase (arrows)

Energy dispersive spectroscopy (EDS) performed on the blade surface reveals the presence of oxides of Ca, Mg, Al, and Si, indicative of CMAS as well as metallic elements Ti, Fe, Ni, certainly originating from debris of metallic turbine components. The deposition of such mineral dust on the blades appears to be detrimental as soon as the TBC surface temperature is high enough to cause such deposits to melt. As a result, significant TBC damage is observed in the hottest zones of the pressure side.

Firstly, when the CMAS becomes molten, its low viscosity enables its infiltration into the TBC intercolumnar gaps, porosity and cracks, down to the TGO layer (figure 10). Such observations have already

been reported in the literature and a failure mechanism has been proposed [30,32]: upon cooling, the melt freezes and the infiltrated TBC becomes rigid, losing its strain tolerance. Delamination cracks can thus develop in the coating leading to progressive TBC spallation during in-service thermal cycling. An illustration of this mechanism is presented in figure 11.

Secondly, a chemical interaction takes place between the molten CMAS and the 8YPSZ top coat ceramic, degrading the column tips and the porous morphology, especially in the upper part of the coating (figure 12). The initially fine-scale intracolumnar porosity and the feather-like porosity are replaced by larger pores filled with CMAS.

Moreover, a new phase is observed at the interface between the CMAS and the TBC (figure 12, right image).

EDS semi-quantitative analysis performed on the CMAS layer on the TBC surface indicates (table 1) that it is mainly constituted of CaO, MgO, Al₂O₃, SiO₂ but also contains a large amount of iron oxide Fe₂O₃. The presence of iron oxide is important to note as it allows, via the formation of low temperature eutectics, for the silicate mixtures present at the TBC surface to have melting points lower than or close to 1200° C, which is the temperature generally supposed for the TBC surface.

	CaO	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	Fe ₂ O ₃	ZrO ₂	Y ₂ O ₃
Composition (wt. %)	25.7	7.5	13.9	34.5	4.5	10.8	2.3	0.7

Table 1 - CMAS chemical composition as observed on ex-service blade

The CMAS also contains minor amounts of zirconium and yttrium suggesting dissolution of 8YPSZ into the molten CMAS. This result, which is of major importance as it identifies the mechanism by which the CMAS acts, has already been observed by Borom [30] and Braue [31] during investigation of ex-service turbine components and by Stott [33] and Krämer [34] during laboratory experiments using synthetic CMAS.

EDS semi-quantitative analysis performed on the interfacial new phase reveals that it is mainly constituted of (Ca, Ti, Fe, Zr) oxide (table 2). The presence of zirconium suggests that this phase results from the interaction between molten CMAS and dissolved zirconia. The formation of a new phase in the interfacial reaction zone has been rarely observed. Only Braue [31] observed and identified a Ca-Zr-Fe silicate on an ex-service first stage high pressure turbine blade. Stott [33] and later Krämer [34] postulate that YPSZ dissolves into the CMAS until the zirconia solubility limit is attained. The excess zirconia is then re-precipitated as a fine grain structure depleted in yttria. It seems that, in our case, the excess zirconia is re-precipitated as a new phase containing Zr and some of CMAS chemical elements.

	Al	Si	Ca	Ti	Fe	Zr	y	Mg	O
Composition (at.%)	0.9	0.6	6.1	12.5	3.2	10.8	2.1	0.3	63.5

Table 2 - New interfacial phase chemical composition

As a conclusion, ex-service blade microstructural characterization has shown that CMAS corrosion occurs more particularly in the

hottest zones of the blade pressure side. Two types of interaction between CMAS and TBC are observed: CMAS infiltration into the TBC microstructure (intercolumnar gaps, pores, cracks) and chemical attack of the TBC according to a dissolution-re-precipitation mechanism. Both interactions lead to the progressive degradation of the TBC top coat, via delamination cracks due to TBC rigidification and loss of column integrity and porous morphology. In order to measure the detrimental effect of CMAS attack, the energetic approach of TBC failure (box 3) can be used: the effect of CMAS infiltration is described as an increase in the top coat Young's modulus. With the hypothesis of a Young's modulus value of 200 GPa for the CMAS infiltrated TBC [32], it can be seen that the predicted life time is clearly reduced (figure 13).

This degradation mode is a growing concern, as in the future, gas temperature in the engine and therefore the temperature at the surface of thermal barrier should increase.

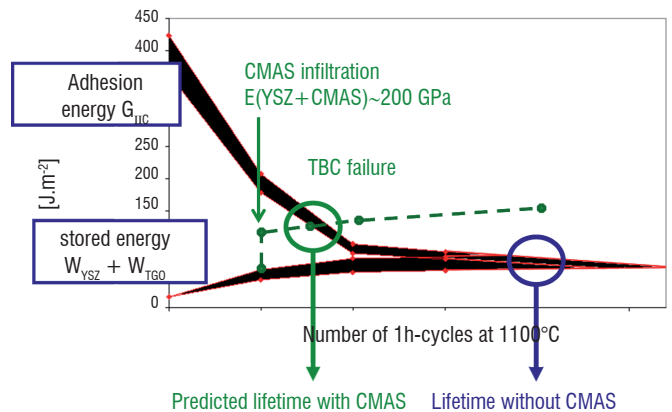


Figure 13 – Predicted effect of CMAS attack on TBC lifetime

Conclusion: towards TBCs with extended working lives

From the above short overview of the aging and degradation mechanisms of a present «standard» TBC system (AM1 single crystal superalloy / NiPtAl bond coat / 8YPSZ EB-PVD top coat), it is clear that advanced thermal barrier systems operating at higher temperatures and/or for very long durations (commercial aircraft applications for example) need further developments. These should involve materials, mechanical and modeling aspects. Examples of possible improvement fields are low thermal conductivity and high stability ceramic top coats, environmental protection, bond coats with optimized TGO formation and controlled interdiffusion, as well as better understanding of failure mechanisms and prediction of lifetime. Some of these points are detailed in a separate paper [35] ■

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Acronyms

TBC (Thermal Barrier Coating)

YPSZ (Yttria Partially Stabilized Zirconia)

EB-PVD (Electron Beam-Physical Vapor Deposition)

TGO (Thermally Grown Oxide)

CMAS (Calcium-Magnesium-Alumino-Silicates)

EDS (Energy Dispersive Spectroscopy)

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