The Potential for the Improvement of High Performance Thermal Barrier Coatings

Masakazu OKAZAKI
Department of Metallurgy, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, Japan 113-8656.

Abstract: The growing market for industrial gas turbines has led to an increased demand for large, cost-effective units of high efficiency. A critical issue in the development of such units is the durability of hot section components, especially first stage blades and vanes to which thermal barrier coatings (TBCs) are applied. This paper introduces the current state of the art in the production of TBCs, and discusses their various degradation mechanisms. Special emphasis is placed on the potential for the development of a new generation of TBC systems through the control of microstructure and porosity, as well as through new processing techniques.

Key words: Advanced Gas Turbines, Thermal Barrier Coatings (TBCs), Top coat, Bond Coat, Thermally Grown Oxide (TGO), Electron Beam Physical Vapor Deposition (EB-PVD), Thermal Conductivity, Micropore, Control of Microstructure.

1. INTRODUCTION

Industrial gas turbines have been used as electrical generators by both utilities and private industrial companies [1–7]. In the 1960s and 1970s, utilities used them primarily to provide peaking power, that is, electricity at the highest demand periods of the day. In the 1970s and especially in the 1980s, combined cycle applications became widespread. In the combined cycle, exhaust gases were used to make steam in a boiler, and this was used to generate additional electricity with a steam turbine. Today, many simple and combined cycle gas turbine plants have been built on a world-wide basis to provide additional power as well as to replace aging power plants. In recent times combined cycle gas turbines with peak temperature of 1500°C have been developed. These units operate at thermal efficiencies greater than 55% [3, 7]. Industrial gas turbines have the advantage that they can be purchased in modular units to reduce the financial risk associated with building large, conventional coal-fired steam or nuclear plants [7]. Smaller industrial gas turbines are also used to provide electricity in remote locations as well as to provide the mechanical drive for numerous applications.

The durability of a gas turbine is principally limited by the components operating at high temperatures in the turbine sections, in particular the first stage nozzle and blades. Although many efforts have been made to develop new heat resisting materials during the last few decades (e.g., ceramics and their composites), Ni-base superalloys are still the most common structural materials used in advanced gas turbines [3]. In some applications the turbine gas inlet temperatures are in the range of 1500–1600°C. Such temperatures are much higher than the approximately 950°C that the superalloys themselves are able to withstand. The added temperature resistance is due in large part to the presence of thermal barrier coatings (TBCs) on microstructurally controlled Ni-based superalloys. These TBCs, as well as serpentine cooling passages and film cooling [3,5], are essential for the control of the metal temperature. It is no exaggeration to state that next generation gas turbines can not be developed without advanced TBC systems.

This paper reviews the degradation mechanisms of TBCs as well as the prospects for the production of even more durable TBCs.

2. GENERAL TBC SYSTEMS

2.1. TBC Systems

A TBC system consists of an insulating ceramic outer layer (top coat) and a metallic inner layer (bond coat) between the ceramic and substrate [8]. A schematic of a typical system is shown in Fig. 1. The top coat employed in current state-of-the-art TBCs is zirconium oxide or zirconia with 6 to 8% (in wt%) stabilized yttria (YSZ). The yttria partially stabilizes the tetragonal phase to improve its strength, fracture toughness and resistance to thermal cycling. The YSZ is characterized by a low thermal conductivity, relatively high (compared with other ceramics) thermal expansion coefficient and good erosion resistance. The thermal conductivity of YSZ is about 2.2–2.6 W/mK in the dense form [11]. The addition of Yttria leads to the creation of O²⁻ vacancies to maintain the electrical neutrality of the ionic lattice [10]. Both the yttrium and the O²⁻ vacancies are effective in reducing thermal transport and thus the thermal conductivity of YSZ decreases with increased yttria content. An yttria concentration in the range of 6–8 wt% is generally used since this composition maximizes spallation life due to the formation of the metastable t phase [9]. This phase has a complex microstructure consisting of twins and antiphase boundaries which retards crack propagation and prevents the transformation of the zirconia into the monoclinic phase (4% volume change) on cooling.
structure consisting of twins and antiphase boundaries which retards crack propagation and prevents the transformation of the zirconia into the monoclinic phase (4% volume change) on cooling.

The top coat is applied either by air, low pressure plasma sprayings (APS, LPPS, respectively), or by electron beam physical vapor deposition (EB-PVD) [9, 12-14]. An APS coating contains porosity and microcracks (Fig. 2), both of which are useful to redistribute thermal stress. However, both of these features are deleterious since they promote corrosion and oxidation within the top coat [9]. LPPS coatings are of high purity and a low degree of porosity. An EB-PVD is characterized by a columnar grain structure and a thermally grown oxide layer (TGO) between the top coat and the bond coat (Fig. 3). The individual grains of the columnar structure are bonded at their base, but have a weak bond between grains [9]. The TGO is formed during the deposition a little, and continues to grow in service, and is critical to life of the EB-PVD coating, as will be discussed. The major advantage of the columnar microstructure is that it reduces thermal stress built-up in the coating. Thermal strains within the coating are accommodated by free expansion of the column into the gaps, resulting in lower internal stress. However, a disadvantage of the columnar structure is that the thermal conductivity twice as high as that of an APS coating [15].

The metallic bond coat (usually either by aluminide coating or MCrAlY alloy coating) aids in the adhesion of the ceramic top coat, and also protects the substrate from hot corrosion and oxidation. This bond coat also plays important role in reducing the thermal stress created by the thermal expansion mismatch between substrate and top coat. Both the APS and LPPS processes are used to deposit the MCrAlY alloys. High velocity oxygen fuel spraying (HVOF) is also applied.

2.2. Microstructure of YSZ Top Coat by EB-PVD

One of current efforts to improve the performance of TBCs is directed at the control of microstructure of YSZ top coat. A discussion of the current microstructure of the YSZ top coat as deposited by EB-PVD is given in this section.

As previously discussed, the TBC produced by EB-PVD has a columnar microstructure that is predominantly aligned perpendicular to the plane of the coating (see Fig. 3) [16]. A finer distribution intracolumn pores also exist. The elongated intercolumnar pores increase the compliance of the coating in the plane of the substrate, and lead to the improved spallation lifetime of the TBC. For the deposition temperatures typically employed to obtain good coating adhesion, the substrate is heated up to T/Tm (where T and Tm are the substrate temperature and the melting point of the deposited material, respectively). During this process, substrate rotation is required to obtain sufficient inter- and intra-columnar porosity. This rotation causes flux shadowing and a varying deposition rate. The resulting competitive growth process leads to tapered, poorly bonded columns aligned perpendicular to the substrate surface and the formation of the finer intra-columnar pores, Fig.3. The large, through thickness intercolumnar pores are supposed to be ineffective at reducing heat transfer through the thickness of coating. However, the fine intra-columnar pores contribute a moderate reduction in the thermal conductivity as they are generally inclined to the direction of heat flow. Nevertheless, EB-PVD coating still has a considerably higher thermal conductivity than their APS counterparts [17].

3. FAILURE OF TBCs

The nature of the TBC failures of particular concerns...
The Potential for High Performance TBCs

are:
(i) cracking in the ceramics layer which results in a partial spalling of the TBC;
(ii) cracking along the interface between the thermally grown oxide (TGO) and the bond coat which results in the entire spalling of TBC [20-28]; and
(iii) sintering of the ceramic layer where the temperature is the highest [18, 19].

The failure mechanism of TBCs is strongly dependent on coating process [29, 30] from another point of view. Prolonged exposure to a high temperature oxidizing environment may lead to coating failure. The stresses that lead to failure come from thermal expansion mismatch between the ceramics and metallic layers, and bond coat oxidation also plays an important role. Other factors include the possibility of ceramic sintering and bond coat inelasticity. A major challenge in the development of more durable TBCs is to improve the resistance to spalling.

3.1. TBC Sintering

Sintering of the TBC has been observed during high temperature exposure. For example, Zhu and Miller [18] have observed 0.1% shrinkage of plasma-sprayed YSZ exposed for 15 hrs. at 1200°C by dilatometry measurement. The sintering has also been observed in TBCs deposited by the EB-PVD that have been exposed for 10 hrs. at 1200°C [19]. The sintering increases the Young's modulus, residual stress, and thermal conductivity; all of which are undesirable changes for TBCs.

3.2. TGO

Experience with gas turbines has shown that bond coat oxidation and the ability to resist spalling of the top coat from the bond coat are critical factors determining coating life. It is now well known that the ability of a bond coat to form an α-alumina layer with negligible transient oxidation is a critical factor in controlling the durability of TBCs. The bond coats develop a thermally grown oxide (TGO) during fabrication (Fig. 4). The TGO also grows during the exposure in air environment. It is observed that the TBCs which have bond coat with good alumina former are durable, and the eventual occurs within the ceramic layer rather than at the TGO interface [20]. On the other hand, the bond coats which tend to produce significant amount of spinel in the oxide layer are more easily spalled at the zirconia/bond coat oxide interface and generally exhibit shorter lives [21]. It has been reported that the deleterious effects of the spinels formed after prolonged exposure is due to the depletion of Al from the bond coat [22].

In general the bond coat/ceramic interface is not smooth, but is very rough, especially when the top coat was performed by APS process. The stress state at the bond coat/ceramic interface caused by thermal expansion mismatch and oxidation has been determined by FEM analysis for such a hypothetical sinusoidal interface [23]. It has been found that in the early stage of TGO formation the stress in the plane of the coating are compressive, whereas the radial component alternates between a state of tension above the sinusoidal asperities and compression above the valleys (Fig. 4). The regions of biaxial compression and radial tension promotes delamination cracking at the asperities. This situation is changed significantly as the thickness of the TGO increases. The analysis indicates that when the thickness of the TGO has increased sufficiently, the radial stress at the valleys changes from compression to tension, which leads to crack propagation in a region where they were previously unable to advance [23].

Failure in EB-PVD coatings often occurs either at the TGO/TBC or the TGO/bond coat interface [24]. Clarke and Christensen [25, 26] have measured large residual compressive stress as high as 3 GPa in the TGO layer. Evans et al. [27] have analyzed the thermo-mechanical stress and shown that it can lead to the initiation of cracks at the TGO/bond coat interface. Ratchetting effect caused by the cyclic plasticity in the substrate [27] and TGO/bond coat interface embrittlement due to sulfur impurities [26] can promote the failure of EB-PVD TBCs. Thus, control of these factors is clearly a critical issue in the development of more durable systems.

3.3. Effect of Coating Process

The thermal protection and spallation life times of TBC layers produced via APS and EB-PVD are significantly different. TBCs produced by APS have a thermal conductivity in the range of 0.8-1.0 W/m K. This is significant since the natural convection heat transfer coefficients for gas turbine engine surfaces are on the order of 0.001 W/m² K. The stress state at the bond coat/ceramic interface caused by thermal expansion mismatch and oxidation has been determined by FEM analysis for such a hypothetical sinusoidal interface [23]. It has been found that in the early stage of TGO formation the stress in the plane of the coating are compressive, whereas the radial component alternates between a state of tension above the sinusoidal asperities and compression above the valleys (Fig. 4). The regions of biaxial compression and radial tension promotes delamination cracking at the asperities. This situation is changed significantly as the thickness of the TGO increases. The analysis indicates that when the thickness of the TGO has increased sufficiently, the radial stress at the valleys changes from compression to tension, which leads to crack propagation in a region where they were previously unable to advance [23].

Failure in EB-PVD coatings often occurs either at the TGO/TBC or the TGO/bond coat interface [24]. Clarke and Christensen [25, 26] have measured large residual compressive stress as high as 3 GPa in the TGO layer. Evans et al. [27] have analyzed the thermo-mechanical stress and shown that it can lead to the initiation of cracks at the TGO/bond coat interface. Ratchetting effect caused by the cyclic plasticity in the substrate [27] and TGO/bond coat interface embrittlement due to sulfur impurities [26] can promote the failure of EB-PVD TBCs. Thus, control of these factors is clearly a critical issue in the development of more durable systems.

Fig. 4. Effect of thermally grown oxides (TGs) on crack advance [23].
nificantly lower than the 1.5-1.9 W/mK reported for the EB-PVD coating [29]. The APS coating therefore provides superior thermal protection. However, their use is limited by their poor spallation resistance. EB-PVD TBC layers, however, have up to ten times the spallation life time than their APS counterparts [17].

The difference of the thermal and mechanical properties by these two processing routes results from differences in the morphology of the porosity present within the TBC layer, compare Figs. 2 and 3. In APS layers, inter-spot pores result from the impingement of molten droplets onto a substrate (Fig. 2). These pores are roughly aligned parallel to the substrate surface, and are accompanied by microcracks and fine grain boundaries. In this case, the pores provide a high impedance to heat flow through the thickness of the coating resulting in a TBC with low thermal conductivity. The spallation life of these coatings is believed to be governed by a combination of the disc-like coating defects and by the thermal stress resulting from the significant mismatch of thermal expansion coefficient between the TBC layer and the underlying substrate. These cracks eventually result in the spallation of the coating [30]. On the other hand, the EB-PVD YSZ coating has elongated pores aligned perpendicular to the substrate surface (Fig. 3).

4. POTENTIALS FOR NEXT GENERATION TBC SYSTEMS

4.1. Multi-Layers Top Coat

It is not necessary to point out that new TBC top coat materials need to be developed. One interesting suggestion is given by Zhu and Miller [18]. They have compared the sintering behavior of YSZ with Yttria-stabilized hafnia to show that the sintering rate of the latter was clearly slower than that of the former over the high temperature ranged between 1100 and 1300°C. A low thermal conductivity of zircon (ZrSiO₄) has been reported which makes it attractive [31]. Ceria stabilized zirconia may offer reduced thermal conductivity and enhanced phase stability at high temperature if the fully stabilized version is considered [32].

A mixture of several oxides, or multi-layers top coat, is expected to be a new frontier TBC material. However, oxides have their individual vapor pressures. In the case where the vapor pressure of two or more constituents differ too much, a homogeneous composition of the coating cannot be achieved by one-source evaporation of a mixture or an alloy of the materials.

In an interesting approach to solve the above problem, two source evaporation method is achieved, applying a EB-PVD technique [33]. In this method two-source evaporation is achieved by heating two sources by a single electron beam. Usually the electron beam is scanned over one pool in two directions for a certain amount of time and then shifted to the next pool where a different deflection pattern may be used. Depending on the time a material needs to become solidified after the electron beam has been removed for the molten pool, there is a critical frequency below which a multi-layer forms on the substrate; e.g., alternating coating of ceria-rich and zirconia-rich layers.

4.2. Control of EB-PVD TBC Systems

As shown in Sec. 2.2, the TBC layers produced by EB-PVD have a columnar microstructure with elongated inter- and intra-columnar pores, which must contribute to reduce the thermal conductivity and to increase the compliance of the coating. Thus, one approach to improve TBC system performance must be to control such a microstructure of EB-PVD TBC systems: e.g., to optimize the pore morphologies in order to reduce the thermal conductivity, while still retaining a high in-plane compliance. Lower thermal conductivity lead to the temperature reductions at the TGO/bond coat interface which slows the rate of thermally induced failure mechanisms.

In an effort to improve (i.e., reduce) the thermal conductivity of TBCs without increasing thermal stress, a technique known as glancing angle deposition (GLAD) has been developed [34]. This technique is appropriate to any physical vapor deposition system in which the incident flux is well collimated. In this case, the adatom angle of incidence was altered by inclining the substrate between two fixed angles, so that the inclination of the angle of the substrate with respect to the source was greater than 70 degree. By alternating the inclination angle and the dwell time at each position, films with a low relative density (porosity up to 85%) were produced. Using the GLAD technique, it has been shown to be possible to deposit zirconia films with mint rolled microstructure, with inclined intercolumnar pores [34]. Zig-zag shaped pores were also demonstrated (Fig. 5 [34]). However, this kind of process may not be economical, because the use of a highly inclined substrates lead to a low intrinsic material utilization efficiency.

One approach to improve the deposition efficiency of electron beam evaporation is the use of an electron beam directed vapor deposition (EB-DVD) process [35]. This approach employs electron beam evaporation and a trans-sonic helium gas jet into which the vapor is entrained and deposited onto a substrate. It has been shown that by coupling this approach with the substrate manipulation, it is possible to create the YSZ coatings with zig-zag morphologies and with a greatly reduced thermal conductivity (≈0.8 W/m K) [15,36].

4.3. Bond Coat

Bond coats in TBC systems play very important roles of protecting the substrate from environmental attack as well as relaxing thermal stresses resulting from thermal expansion mismatch between Ni-base superalloy substrate and ceramic top coat. This layer is also essential to achieve a good adherence of ceramic top coat. The platinum-modified nickel-aluminide, β-(Ni,Pt)Al is very commonly used as a bond coat for EB-PVD TBCs. It is usually deposited by platinum electroplating followed by a chemical vapor deposition (CVD) process. The high activity CVD process is one of standard methods. A
pack cementation method is also often employed. As previously discussed, the adherence of the top coat is strongly affected by the oxidation resistance of the bond coat. The oxidation resistance depends on the level of impurities in $\beta-(\text{Ni},\text{Pt})\text{Al}$, in particular, sulfur and phosphorus. These impurities are introduced during the bond coat process as well as by diffusion from the substrate. Sulfur is not a desirable element in forming a protective oxide, as it leads to poor adherence. The traditional high activity CVD process in which aluminum-bearing alloys are involved in the coating resort at high temperature may suffer from a contamination of impurities during deposition. A candidate method to avoid the above undesirable effect has been developed which uses a low Al activity chemical vapor deposition (CVD) aluminizing process [37]. In this process, the coating gas generator is generated at low temperature outside the coating chamber. This method not only reduced the coating impurities during the process but also removed them from the substrate.

Grit blasting of the platinum-modified nickel-aluminide bond coat surface is believed to be essential in achieving good adherence of the bond coat. However, impurities may be often introduced from the grit blast media. For example, V.K. Tolpygo et al. [38] have observed the contamination of the $\beta-(\text{Ni},\text{Pt})\text{Al}$ bond coat due to alkali and alkaline earth element, resulting in significant acceleration of oxide growth. The high growth rate, combined with roughing of the bond coat surface, resulted in cracking and the spalling of the scale. Thus they concluded the grit blasting had a detrimental effect on TBC durability. On the contrary, a merit has also been reported by Haynes [39]. The grit blasting primarily involved prevention of void growth near the interface, likely due to either removal of excess surface impurities or acceleration of $\alpha$-alumina formation. These investigations indicate that the promotion of good adherence together with a low impurities content are desirable characteristics.

Grit blasting is often carried out to prepare the substrate surface to remove mold debris from cast Ni-base superalloys before bond coating, as well as before top coating. This process may introduce a formation of cellular microstructure in advanced Ni-base superalloy substrates (e.g., single crystal and directionally-solidified alloys). This kind of microstructure has been confirmed to be formed when the substrate alloys were exposed to actual service conditions of gas turbines. This microstructural change is also promoted by the machining which is aimed the refurbishment of the components [40]. Once the cellular microstructure is formed, the high temperature strength is remarkably reduced [40]. The composition of single crystal superalloys in which grain boundary strengthening elements are generally free is believed to be closely related to the undesirable effect [40]. More recently an interesting method has been developed to prevent the above problem [41]. The method is based on the new idea that grain boundary strengthening elements should be supplemented by applying over-

Fig. 5. Schematic illustration of zig-zag shape film with controlled pores [34].

lay coating. It was shown that a trial coating employing a selected metallic alloy was very effective to recover the degraded fatigue strength [41]. The observations of the fatigue crack initiation site, the fracture mode, the crack propagation morphologies near the prior interface, strongly supported the validity of the methods. The employment of this kind of metallic coating as a bond coat may open a new road for new generation TBC systems.

4.4. Life Extension and Repair

It is not necessary to point out importance of rejuvenation and repair technologies to extend the useful life of a components. Rejuvenation can be defined as a regeneration of a microstructure leading to the restoration of mechanical properties equivalent to those of the original prior to initial service. The techniques relating to welding, bonding and new material design are essential, although all of them are on the way of development [3].

Weld repair is generally limited to the low stress tip regions of the components. Typical welding has been performed using manual Gas Tungsten Arc Welding (GTAW). The weld filler material is basically a low strength, solid solution strengthened Ni-base alloy because of their high ductility and thereby reducing crackings. Repairs that use higher strength and more oxidation resisting weld filler materials is tried [42]. A highly concentrated heat source, lower heat input, automation and judicious application of preheat and controlled cooling are critical, which involves laser beam welding, electron beam welding and Plasma Transferred Arc Welding (PTAW).

The joining and repair of directionally-solidified and single crystal alloys is a most difficult matter. In the past many of these alloys were thought to be unweldable, and only very limited repairs were possible. Recently a new weldable Ni-base superalloy, MGA 2400, has been developed in Japan. Research indicates that this material possesses creep properties, thermo-mechanical fatigue properties, as well as the microstructural stability for long term exposure, that are comparable to or more excellent than traditional alloys [43]. It is noted that after a period of service the application of a newly developed metallic
bond coat may serve minimize the effect of the fatigue damage induced by the prior service [41].

Liquid phase diffusion sintering uses a combination of a high melting point powder (which is typically a composition similar to superalloy) and a low melting point powder (that is typically a braze with boron as the melting point depressant). The powders are put on the area to be repaired, followed by the sintering in vacuum below the melting point of the base material. This method is shown to be successfully applied to the second stage stator [3,44].

5. CONCLUDING REMARKS

For these decades considerable progresses have been made in obtaining a basic understandings on the failure mechanisms of TBCs, and this understanding is essential for further improvement in these coatings. One important question today is, can the results obtained by one group of researchers be quantitatively compared with those obtained by others, and to what extent are the results influenced by lack of the reproductivity of new processing techniques. This is due to the fact that there are too many process parameters which can affect the performance of TBCs which strongly depend on "experiences". Now is a time to develop cooperative efforts in order to benefit from the knowledge established in each filed and in each research institution. As a step in this direction, a Subcommittee on "Superalloys and Coatings" (chaired by Prof. M. Okazaki, The Univ. Tokyo, Japan), has been established in The Society of Material Science, Japan (JSMS) in 1998. This subcommittee is engaged in collaborative research on the high temperature strengths of superalloys, metallic coatings and TBCs. One of the current projects is to construct a new methodology to evaluate adhesion strength of coating in TBCs, as function of process and damage parameters. Author urges other researchers in this field to join in this effort.

Acknowledgment-The author wish to express his gratitude to the members of the Committee of High Temperature Strength of Materials, JSMS, for their encouraging and cooperating the subcommittee, "Superalloys and Coatings". A great thanks is also expressed to Prof. A.J. McEvily, The University of Connecticut, USA, for his fruitful discussions.

REFERENCES

5. Rolls-Royce ply., The Jet Engines, Chap. 9, Japan Aeronautical Engineers Association, Tokyo, (1986).