9.3 Durability of Thermal Barrier Coating Systems (TBCS) to In-Service Particle Encounters

9.3.1 TBCS Architectures

Two possible thermal barrier coating system (TBCS) architectures are shown in Figs. 9.19 and 9.20. Hardware application examples are given in Fig. 9.21. TBCS architectures may comprise an inner ‘bond coat’ and an outer ceramic thermal barrier layer of zirconia (ZrO$_2$). The latter is single phased. It contains ~8wt-% Y$_2$O$_3$ dissolved in solid solution, and its purpose is to stabilise the tetragonal (t) form of zirconia (t-ZrO$_2$) over the in-service operational temperatures encountered by a given turbine blade. The inner bond coat comprises a hot corrosion-resistant ‘diffusion coating’ (Fig. 9.19) or an ‘overlay coating’ (Fig. 9.20), previously described in Section 9.2. One of the most common diffusion coatings for TBCS is Pt-aluminide, whilst several proprietary M-Cr-Al-Y overlays may be chosen (Table 9.3). Diffusion coatings are practically limited by diffusion zone growth kinetics to a thickness of ~50µm (and must be kept below 75µm to avoid crack formation – Meetham, 1986); in contrast, M-Cr-Al-Y overlays (having a metal matrix) are more ductile and can be considerably thicker (~100 to 500µm; Hancock, 1986; Boyce 2012; Darolia, 2013). Sandwiched between the two layers is an additional oxide coating (~1 to 3µm thick) which is developed by heating the prior bond/diffusion-coated nickel alloy parts in air at temperatures ~1000°C. This important constituent is termed a ‘thermally grown oxide’ (TGO) and is typically α-Al$_2$O$_3$; it aids adhesion of the outer zirconia layer. Such layers can appreciably thicken (by several micrometres) during operational use, via the diffusion of Al from the ‘bond coat’ into the TGO. Concerning further aspects of dimensions, the outer t-ZrO$_2$ coating (Figs. 9.19 & 9.20) can be ~100 to 200µm thick, when required for rotating blades, but may be much greater (250 to 500µm) when used for stationary vanes, nozzle guide vanes (NGVs) and combustors (Boyce, 2012; Darolia, 2013). Two methods of application are currently popular: air plasma spraying (APS) or reactive electron beam evaporation PVD.
Figure 9.19 Schematic of a thermal barrier coating system (TBCS) comprising: a diffusion aluminide ‘bond’ coating (either conventional or Pt modified), its thermally grown oxide (TGO) – Al₂O₃ – and a portion of the adjacent APS t-ZrO₂ top coat (next to the TGO) revealing its micro-porosity and splat morphology. The substrate is a polycrystalline Ni-Cr alloy like Inconel 738. It should be noted that a PVD t-ZrO₂ top coat may be used as an alternative to the APS variant shown.

Figure 9.20 An example of a thermal barrier coating system comprising a VPS M-Cr-Al-Y overlay ‘bond’ coating (thermally homogenised and recrystallised), its thermal growth oxide (TGO) and a portion of the adjacent EB-PVD stabilised t-ZrO₂ top coat (next to the TGO) showing its near equi-axed nature. The substrate is a single-crystal nickel alloy (PWA 1484). Micrograph to right: courtesy of Wolfgang Brau & Springer Science. Used with permission. After Brau, 2009.
The former technology is considered to be cheaper and quicker to apply than the latter, although the surface finish is not as good. This has an impact on heat transfer from air/gases that flow over t-ZrO$_2$ surfaces in service. Smooth surfaces encourage laminar flow; rough surfaces stimulate turbulent flow. Arguably, the former are more effective in removing heat from the operating environment. Heat transfer through a TBCS is of prime importance. An important property of t-ZrO$_2$ is that its thermal conductivity ($K$) is invariant with temperature (Darolia, 2013). Further, it is an order of magnitude lower than that of the adjacent nickel aluminide or M-Cr-Al-Y coating component. The primary role of the of t-ZrO$_2$ layer is to restrict heat flow. In addition, once heat arrives at the adjacent nickel aluminide or M-Cr-Al-Y coating surfaces, it is quickly dissipated by their greater thermal conductivity – an effect that is augmented further.
by the use of internal cooling channels placed within the nickel alloy components (Fig. 9.4). This set-up allows any nickel alloy component to be kept at anywhere between 20 to 200°C lower than that of the outer t-ZrO$_2$ coating surface (Darolia, 2013). Greater details of cooling strategies, including convective air flow, are given by Han and Wright (2007) and Boyce (2012).

Yet a further feature of t-ZrO$_2$ coatings shown in Figs. 9.19 and 9.20 is that they show high in-plane strain tolerance. In the case of EB-PVD ZrO$_2$ variants, this is made possible by the existence of relatively large gaps (>0.5µm) between the vertically oriented grain boundaries (Fig. 9.22a); these enable lateral expansion and contraction of the ZrO$_2$ layer without fracture, during regular thermal cycling (this is especially important for aircraft GTEs where endurance to frequent engine stop/starts is required). In contrast, APS-ZrO$_2$ variants, containing horizontally oriented micro-porosity (located between individual solidified coating ‘splat’), provide a similar means of attaining the necessary strain tolerance, although this is arguably less effective than vertical cracked EB-PVD ZrO$_2$. This disparity has led to efforts to produce a new and improved method of spray deposition: a hybrid technology termed ‘plasma spray PVD’ or simply ‘PS-PVD’ (Jordon et al, 2004). Here, very fine (<5µm) ZrO$_2$-8wt-%Y$_2$O$_3$ ceramic source powder is passed through a plasma torch (in partial vacuum) and completely vaporised before being condensed (solidified) on a nickel alloy substrate (coated with a suitable overlay). The substrate is negatively biased during deposition, yielding a process that has a very much improved ‘throwing power’ compared to APS or VPS techniques. Fortuitously, vertically oriented cracks and quasi-columnar grains develop during solidification, providing PS-PVD ZrO$_2$ coatings with a strain tolerance similar to that of EB-PVD variants. Moreover, the rates of deposition are higher for PS-PVD ZrO$_2$ coatings, compared to EB-PVD, which enables a higher manufacturing throughput and (arguably) a lower treatment cost per component. The technology can also be used to apply coatings to non-blade GTE components, like combustor liners, where conventional EB-PVD cannot be used. Given that this is a new technology, the competitiveness of PS-PVD versus APS and VPS has yet to be fully evaluated.

9.3.2 Durability to Particle Chemical (CMAS) and Mechanical (Erosion) Attack

Whether a GTE is land based, as is the case for industrial power generating variants, or is being deployed to provide propulsion for aircraft or ships, its internal working surfaces frequently encounter airborne mineral (ceramic-like) particles. This can result in mechanical (erosion) or chemical (CMAS) attack of nickel alloy surfaces protected with a TBCS. Encounters with mineral particles are amongst the highest in the Middle East, where desert sand is ubiquitous. Here, various mineral particles can be encountered (de Wet et al, 1993), including sand (quartz, α-SiO$_2$), gypsum (CaSO$_4$.2H$_2$O), albite (NaAlSi$_3$O$_8$), calcite (CaCO$_3$), microcline (KAlSi$_3$O$_8$) and dolomite (CaMg(CO$_3$)$_2$). Concrete dust from building structures is a further source of...
particulates. However, incidents of aircraft straying through volcanic dust clouds (Grindle & Burcham, 2003) in many different parts of the globe have added to concerns regarding GTE operational safety. Particle sizes ~100µm can be easily carried into the turbine section and can cause marked damage. Volcanic ash particles have been grouped under the acronym ‘CMAS’ to indicate the common ceramic phases they contain – CaO, MgO, Al₂O₃ and SiO₂. Depending on the proportions of these phases, the ash may have a basic (alkaline) or acid character. This factor becomes important when GTE hardware surfaces are sufficiently hot (~1250°C) to cause the particles to melt and stick. As is well known, oxide ceramic materials are particularly prone to alkaline attack. This causes t-ZrO₂ to become dissolved, a situation that can be made more pronounced in very high-temperature (~1300–1500°C) laboratory experiments. These show (de Wet et al, 1993; Ndamka, 2014) that t-ZrO₂ can be dissolved and re-precipitated with a spherical morphology (Fig. 9.22b). Such effects do not take place at similar temperatures when the mix of CMAS oxides has a more acid character. Nonetheless, some deterioration of the t-ZrO₂ takes place (Ndamka, 2014).

One specific source of chemical attack is from molten particles of gypsum (CaSO₄) – a major constituent in Middle East sand. In one example, this mineral was observed (Brau, 2011; Brau & Mechnich, 2011) adhered to the surfaces of an EBPVD-ZrO₂-coated blade extracted from the turbine section of one GTE, operated in an aircraft by Lufthansa, after 17,000 hours’ service (Figs. 9.23 to 9.25). Gypsum has a melting point of 1460°C and when molten, can infiltrate along the vertically oriented columnar grain boundaries of an EB-PVD t-ZrO₂ top coat. This serves to ‘bond’ or ‘weld’ together the individual columnar grains (Fig. 9.25), making the t-ZrO₂ coating less strain tolerant and more prone to catastrophic fracture during subsequent (i) operational thermal cycling, and/or (ii) erosion by particle bombardment (Ndamka, 2013).

All t-ZrO₂ top coats of any given TBCS have a finite lifetime, making it important to understand their modes of failure. Here, it is worthwhile briefly presenting some important observations regarding their response to bombardment by high-velocity particles which cause eventual deterioration by erosion. Diffusion or overlay-coated surfaces without any t-ZrO₂ top coats can also suffer in the same way (Tabakoff, 1999; Nicholls et al, 1999).

Figure 9.23 Ventilated blade (from a GTE turbine section) retrieved after 17,000 hours’ operational use (equivalent to 3000 operational cycles). Note build-up of CMAS deposits towards trailing edge of the pressure face (arrow). Courtesy of Wolfgang Brau, Peter Mechnich and Wiley Publications (J. American Ceramic Society). Used with permission. After Brau & Mechnich (2011).
The erosion rate (E) of a material is a dimensionless quantity that can be defined as (Hutchings, 1992):

$$E = \frac{\text{mass of material removed from surface}}{\text{mass of particles striking surface}}$$  \hspace{1cm} \text{(Equation 9.2)}

Sometimes this is expressed, rather pedantically, in units of g/kg (Nicholls et al, 1999) or mg/g (Tabakoff, 1999). The rate of attack of material by erosion varies with the angle of incidence between the particle trajectory and the material surface. When the highest rate of degradation occurs at an angle of incidence of 90°, the material response is defined as ‘brittle’, whereas if maximum erosion happens at an angle of incidence of 30°, it is defined as ‘ductile’. (Also refer to Section 6.2, Chapter 6.) This can be slightly misleading. Some ceramic materials can show ductile erosion behaviour; here, the ceramic absorbs or sustains deformation by a mechanism of micro-crushing – where fractures have a short length and either do not cause immediate failure or only permit the removal of ‘small’ fragments of material. In contrast, ceramic materials that show brittle erosion behaviour will allow longer fractures to form, leading to the removal of ‘large’ fragments of material. Both scenarios are depicted in Fig. 9.26.

Tabakoff (1999) showed the erosion of diffusion bond coatings like Pt-aluminide to be ductile in character. He observed maximum erosion when these materials were bombarded by fly ash particles (pre-heated to 815°C) propelled at an impingement angle of ~30°, with an impact velocity of 366m/s. The reported erosion values were 10 times lower than those of an uncoated nickel alloy substrate, Ni-9Cr-5.5Al-10Co-1.5Ta-1.5Ti-2.4Mo (MAR-M246). Nicholls et al (1999)
compared the erosion behaviour of an M-Cr-Al-Y overlay bond coat with that of sintered monolithic t-ZrO$_2$, APS-t-ZrO$_2$ and EB-PVD t-ZrO$_2$ when using an impact angle of 90°. These workers used 100µm particles of Al$_2$O$_3$ to bombard their test surfaces. In the one experimental set-up, the particles were pre-heated to 910°C and propelled at a velocity of 230m/s; in another, particles were kept at ambient temperature (~20°C), at which they attained a velocity of ~140m/s. Their results (Fig. 9.27) indicate that thermal barrier systems having an EB-PVD t-ZrO$_2$ top coat are more erosion tolerant than those deploying an APS t-ZrO$_2$ top coat. They also reported maximum erosion attack at an impact angle of 90°; under these conditions, the M-Cr-Al-Y overlay bond coating was more erosion resistant than either t-ZrO$_2$ variant (Fig. 9.26). This is unsurprising since such high-impact angles cause the least erosion for ductile materials (Hutchings, 1992). Of high importance,
however, was their observation that EB-PVD t-ZrO$_2$ coatings display erosion-induced fracture within a narrowly confined near-surface region where cracks cannot grow beyond the confinement of their open columnar grain boundaries (Fig. 9.26b). In the case of APS-deposited t-ZrO$_2$, however, crack lengths are much larger (for a given impacting particle force), as these defects are able to propagate...
along inter-splat boundaries (Fig. 9.26a). This causes larger fragments of coating material to be removed compared to EB-PVD t-ZrO₂, where crack lengths are shorter. Accordingly, a significantly higher rate of erosion of APS-deposited t-ZrO₂ takes place (Fig. 9.27).

In a bid to develop alternatives to the present-day reliance on TBCS using EB-PVD t-ZrO₂ top coats like that shown in Fig. 9.20, one major company, GE, has evaluated the erosion and impact resistance of more than two hundred alternative compositional and microstructural variants (Darolia, 2013) – an effort that was, unfortunately, unsuccessful. However, one interesting finding, based on field test results, was that turbine section blades fitted with a novel external EB-PVD t-ZrO₂ coating with a ‘herringbone’ or zigzag columnar patterned grain structure (US Patent 7,318,955) – e.g., see Fig. 9.28 – showed better damage tolerance against particle erosion than conventional vertically aligned, columnar t-ZrO₂ top coats. The wavy grain structure had the effect of limiting fracture growth to planes parallel to, but at significant distance from, the EB-PVD t-ZrO₂/TGO interface, reducing the amount of material that could be removed following a given quantity of particle bombardment. However, some workers disagree with this inference (Schulz et al, 2004) and report a lowering of erosion resistance when using herringbone-structured t-ZrO₂ coatings. In the same review, the same structures are claimed to lower thermal conductivity; in principle, this would further reduce heat flow through the ZrO₂ component of the thermal barrier coating system. However, at the time of writing, the extent of uptake of the herringbone-structured top coat design (Fig. 9.28), relative to conventional straight-columned t-ZrO₂ coatings (Fig. 9.22a), is unknown.

Doping t-ZrO₂ with small concentrations (2–5wt-%) of rare earths (such as the oxides of Dy and Gd) can have the beneficial effect of reducing the thermal conductivity (K) and, coincidently, also make them more resistant to CMAS attack. However, particle impact tests on such materials (Wellman & Nicholls, 2007; Ndamka, 2013) have shown a worsening in erosion resistance. Hence, up to the time of writing, the challenge remains in place to develop new and improved TBCS materials and designs.
References


