



Advances in Thermal Spray Coatings for Gas Turbines and Energy Generation: A Review

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Functional coatings are widely used in energy generation equipment in industries such as renewables, oil and gas, propulsion engines, and gas turbines. Intelligent thermal spray processing is vital in many of these areas for efficient manufacturing. Advanced thermal spray coating applications include thermal management, wear, oxidation, corrosion resistance, sealing systems, vibration and sound absorbance, and component repair. This paper reviews the current status of materials, equipment, processing, and properties' aspects for key coatings in the energy industry, especially the developments in large-scale gas turbines. In addition to the most recent industrial advances in thermal spray technologies, future technical needs are also highlighted.

Keywords abratable, bond coat, CMC, TBC, thermal spray, turbine coating, YSZ

1. Introduction

It has been forecasted that by 2035, electricity generation will account for about 40% of global energy consumption (Ref 1, 2). This global energy demand will be met by a mix of energy solutions including fossil fuels (coal, petroleum, natural gas), biofuels, wind, and solar energy. Thermal spray coatings will continue to enable many applications in all these power generation areas.

Thermal spraying is a group of coating processes in which materials are deposited onto a variety of components in a molten or semi-molten condition to form a coating (Ref 3). The coating materials used include a wide range of metals, ceramics, polymers, and specialized blends of each. Aerospace and industrial gas turbine (IGT) applications make up about 60% of the overall global thermal spray market which includes materials, equipment, consumables, and coating services (Ref 4). The remaining 40% is distributed over a large number of applications in the oil and gas, biomedical, pulp and paper, and electronics industries. This paper will mainly focus on the recent advances, emerging methods, and future needs in the IGT area.

A schematic cross section of an IGT is shown in Fig. 1, where traditional thermal spray coating applications are highlighted with respect to gas turbine locations. Field experience has shown that the lives of both uncoated and coated turbine components such as turbine airfoils depend to a large degree on the type of fuel used, the duration of turbine

operating cycles, and the surface temperature of the component (Ref 5). The trend toward higher firing temperatures increases the need for coatings, as it has been increasingly difficult for the load-bearing superalloy components to have both the required high strength and a satisfactory level of corrosion and oxidation resistance to the harsh environments in which they operate without the use of coatings.

Thermal spray coatings have been mainly employed in the combustor and hot gas path sections where the temperatures of the components exceed the inherent oxidation, wear, and/or corrosion resistance capability of the material. In the past 40 years, considerable development has occurred in increasing the capability of these coatings to resist degradation over long periods of time, under a wide diversity of global operating conditions. Highly sophisticated coating processes equipped with diagnostic tools combined with better understanding and modeling of coating behavior have led to a high standard of coating performance and, therefore, increased fuel efficiency and engine availability (Ref 6, 7).

Thermal spray coatings are widely employed in aero and gas turbines for thermal insulation of critical components; surface sealing and clearance control; atmospheric corrosion protection; high temperature oxidation and corrosion control; abrasion, fretting, and erosion wear resistance; and combinations of these (Ref 5, 8). The high temperature coating supply chain includes developing application-specific raw materials (powder or wire processing), surface preparation techniques, spray equipment, energy efficient heat treatment furnaces, coating characterization, testing, and inspection methods. Recent advances in processing methods and some of the key applications are reviewed in greater detail below.

2. Developments in Coating Equipment and Processes

In the aero and gas turbine industry, coating systems produced by thermal spray include the combustion, plasma

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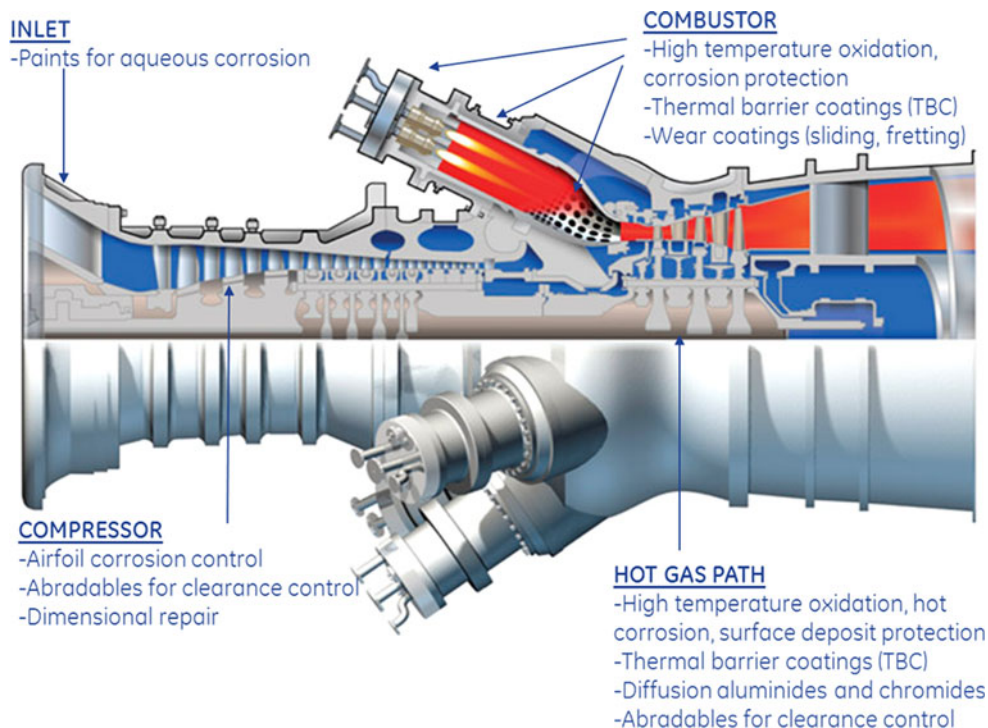


Fig. 1 Traditional gas turbine applications for spray coatings with respect to turbine locations

arc, and electric arc processes. The choice of the process used depends on the application, where careful consideration is given to the coating and component material chemistry combination, part geometry, and coating design requirements, while meeting property and economic targets. Wear-, corrosion-, and oxidation-resistant coatings are produced by high velocity combustion methods such as detonation gun (D-Gun[®] which is a trademark of Praxair, Inc.), high velocity oxy-fuel (HVOF), high velocity air fuel (HVOF), or lower velocity flame spray. Higher temperature plasma processes such as air plasma spray (APS) are commonly used to deposit thermal barrier coatings (TBCs) such as yttria-stabilized zirconia (YSZ) which is also processed by electron beam physical vapor deposition (EB-PVD). In a recent review paper, Feuerstein et al. (Ref 9) compared the technical and economical aspects of various coating processes for aero and IGT applications.

Figure 2 shows an example of the APS deposition of a TBC on an IGT airfoil. Conventional APS guns with radial powder injection, such as the Sulzer Metco 9 MB gun, are widely used for TBC applications. These guns operating at a 40-70 kW power level have been designed using high currents (600-1000 amps) and low voltages (70 V DC) to attain the required power level. This type of design presents the following drawbacks. First, high gun current accelerates anode and cathode erosion resulting in relatively short hardware life. Second, the continuous anode arc root motion to reduce anode wear results in high frequency plasma jet oscillations (1-10 kHz) as shown by the time-resolved images in Fig. 3. The magnitude of these oscillations is in the same order as the spray particle transit time and this results in uneven and insufficient



Fig. 2 An example of air plasma spraying (APS) in action, showing the gun end of the spraying robot, plasma plume, part being sprayed, and controls

particle heating, lower deposition rates, and lower efficiency (Ref 10). For example, the typical deposition efficiency of this type of plasma gun for YSZ powder deposition is about 60% (Ref 11).

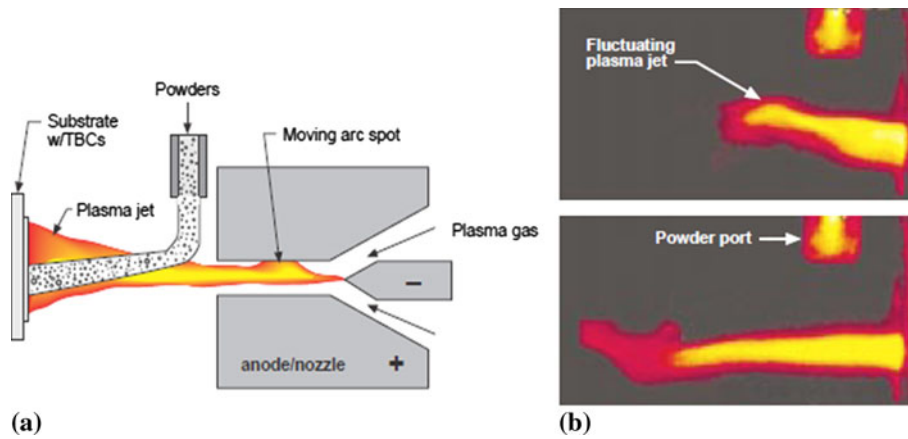


Fig. 3 (a) Traditional high current, low voltage plasma gun with radial powder injection and (b) consecutive time-resolved images showing plasma jet fluctuations leading to inefficient and variable powder deposition

In light of the current global availability and price challenges on rare earth oxides such as yttria, it is imperative for the TBC community to use higher efficiency deposition processes. In the last decade, higher power (100-200 kW) and more efficient commercial plasma spray guns such as Sulzer Metco TriplexPro™-200 (Ref 12, 13), Progressive 100HE (Ref 14, 15), cascade guns (Ref 16), and Praxair TFAFA Plazjet gun have been developed using a low current (~500 A) and high voltage (~200-380 V) design. This type of plasma gun has a longer anode life due to the low current, high voltage design. The deposition efficiency of this type of plasma gun for YSZ powder is as high as 80%. Because of the high power level and larger spray footprint, coating production cycle time can be substantially reduced without compromising coating quality. Another advantage of the low current, high voltage design is the feasibility of low helium and helium-free spray parameters for high power levels, which is desirable given the current global scarcity of helium supply.

The development of advanced coatings and processing methods is also an active field. One such example is the suspension or solution precursor plasma spray (SPS or SPPS) process which has been used to create TBCs with novel microstructures exhibiting columnar structures similar to that of EB-PVD-deposited TBCs (Ref 17-19). The SPS process can be an economical alternative to EB-PVD for TBC deposition where relatively thin TBCs (~250 μm thick) are needed. It has also been demonstrated that the SPS process can produce TBCs with the lowest reported thermal conductivities, while not sacrificing thermal cyclic durability (Ref 18).

The cold spray process is another emerging thermal spray technology being investigated for a number of engineering applications. The number of research papers, patents, and patent applications on cold spray technology has grown exponentially in the last decade (Ref 20-23). In the cold spray process, powder particles are propelled at supersonic velocities onto the surface of a part to form a coating. Because of the high deposition rates, the process has the potential to repair cracks and restore dimensions in recessed regions caused by corrosion and erosion. In the

cold spray process, the powders are not melted and deposition occurs at low temperatures. Therefore, the process can deposit dense coatings and filler materials that are well bonded to the substrate, relatively free of oxidation, with porosity similar to vacuum plasma-sprayed metallic coatings, and with no heat-affected zone in the base material (Ref 24). Furthermore, cold spray can be used to deposit abrasion coatings with filler materials (Ref 25).

In addition to the equipment and process developments mentioned above, supporting technologies are equally important. For example, prior to thermal spray coating, the surfaces to be coated are prepared, often by abrasive blasting, to provide a rough surface for thermal spraying. After TBC coating, the surfaces are polished for aerodynamic efficiency. In some cases, coating processes might require post-coating densification and smoothing. In addition, IGT airfoils can be quite large and have complex surfaces which need complete uniform blasting, polishing, or densification. In recent years, new designs for automated equipment have been made commercially available such as rotary indexing sand blasting systems, TBC polishing and cooling hole clearing systems, and surface peening systems. These machines will continue to evolve to further improve manufacturing productivity and quality.

3. Applications

In selecting a coating for a specific turbine application, one should consider many competing challenges. Generally, the design requirements, component geometry, and part performance needs determine the type of coating and the process to be used to create that coating.

As described in previous sections, thermal spray coatings are widely used in energy generation to enable efficient turbine operations. A 1% improvement in turbine efficiency can mean millions of dollars in savings to an electrical power producer delivering electricity to its customers at the lowest cost (Ref 26). Efficiency increase can be achieved by maximizing the temperature at which the

combustion gas enters the hot section. As the turbine inlet temperatures reach over 1400 °C, the hot section components should be able to not only carry the thermo-mechanical loads but also resist possible environmental degradation for tens of thousands of hours. The components are often designed for maximum high temperature strength, and the environmental resistance is achieved by appropriate selection of coating process, chemistry, and microstructure for each specific application.

3.1 Thermal Protection Coatings for Superalloy Components

TBCs are used to lower the surface temperatures of superalloy components employed in gas turbines as well as propulsion engines so that gas inlet temperatures can be increased without melting the superalloys to achieve high energy conversion efficiencies (Ref 27). A thermal gradient is formed across the component wall by applying the TBC system on the external wall with simultaneous cooling of the inner surfaces. A TBC system is a multilayer coating structure which consists of a low thermal conductivity ceramic outer layer (i.e., top coat) and a metallic inner layer (i.e., bond coat) between the ceramic and the substrate as illustrated in Fig. 4. During service, the bond coat forms a thin layer of thermally grown oxide (TGO). This TGO layer helps to adhere the top layer as well as to prevent oxygen diffusion through the bond coat. During this time, the bond coat and superalloy substrate try to reach chemical equilibrium and form an interdiffusion zone (IDZ) at the bond coat/superalloy interface. In many cases, the top coat and bond coat are applied by thermal spraying. Typically, the top coat is 0.1-1 mm thick, while the metallic bond coat thickness ranges between 0.05 and 0.5 mm. It has been reported that the TBCs can reduce surface temperature of the bond coat layer as much as 150 °C (300 °F) (Ref 28).

The traditional TBC system top coat composition has been 6-8 wt.% yttria (Y_2O_3)-stabilized zirconia (ZrO_2) (7YSZ or 8YSZ) for the last 20 years. It is advantageous because it has a high tolerance for thermal shock, low thermal conductivity, and a higher melting point than most oxides (Ref 29). Two examples of 7YSZ plasma spray cross-sectional microstructures are compared in the optical micrographs as shown in Fig. 5 for the porous and dense vertically cracked TBCs (DVC-TBC, Ref 30-32). The porous TBC microstructure shown in Fig. 5a contains about 10-20% porosity, whereas the DVC TBC in Fig. 5b is characterized by the intentional vertical cracks providing much needed strain tolerance for advanced machines and contains less than 5% porosity.

While the YSZ top coat provides an excellent barrier to heat, MCrAlY coatings where M represents Co, Ni, Fe, or combinations thereof and aluminide coatings are commonly used to impart environmental resistance to the superalloy components while also being used as bond coats to provide a rough surface for the top coat to adhere to. These metallic coatings will be covered in more detail in section 3.2 below.

As the industrial requirements for TBC surface and/or bond coat temperatures increase, the industry-wide

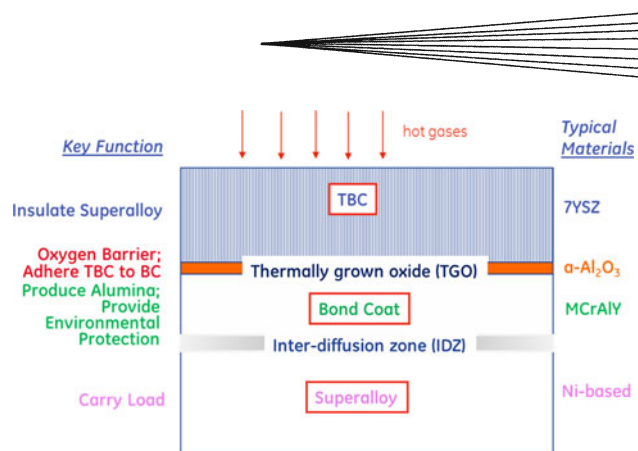


Fig. 4 Typical thermal barrier coating system used in combustor and turbine sections in an IGT

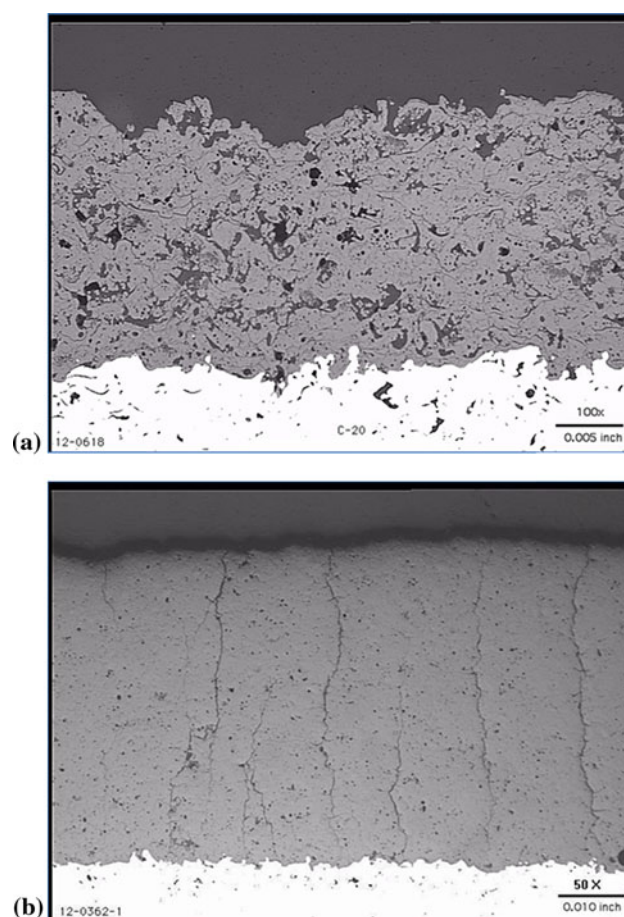


Fig. 5 Examples of (a) porous TBC and (b) DVC TBC microstructures used for thermal protection of superalloy components

concerns are related to YSZ TBC property degradation (APS as well as EB-PVD coatings) which drives the research for new ceramic coatings with lower thermal conductivity, increased phase stability, and sintering resistance (Ref 33-35).

3.1.1 Phase Stability Improvement of TBCs. The zirconia-rich portion of the phase diagram of the ZrO_2 - Y_2O_3

system is shown in Fig. 6 where pure ZrO_2 goes through a tetragonal (t) to monoclinic (m) transformation at 1170 °C upon cooling (Ref 36). Since this transformation is accompanied by about 3% volume increase and therefore microcracking and possible coating failure /delamination, an optimum of 6-8 wt.% (3.4-4.5 mol.%) yttria or other oxides are added to partially stabilize zirconia in its cubic (c) or tetragonal form to below room temperature (Ref 37).

When 8YSZ is plasma sprayed, the molten particles are quenched to form a metastable tetragonal phase, t' (Ref 38), which does not transform to the monoclinic state upon cooling. However, at typical use temperatures, the t' phase can transform to the equilibrium mixture of the cubic and transformable tetragonal phases, compromising TBC durability (Ref 39, 40). In an engine operation, the kinetics of this transformation is dependent on the temperature that the component surface experiences as well as the duration at that temperature. Therefore, the phase stability may become a limit for the current YSZs as the operating temperatures are moved upward for efficiency gains. As discussed in the following sections, the recent thermal spray literature has focused on better understanding of the mechanisms for the current YSZ phase transformations with aging, limiting the amount of oxide impurities in the starting powders to slow down the phase transformation kinetics, and looking for new and better TBC compositions.

In one of the earlier studies, Ballard et al. (Ref 41) reported no difference between the phase stability of plasma-sprayed 8YSZ porous and cracked microstructures for exposure times of up to 10,000 h. Exposures at 982 °C showed minimal change in the monoclinic content, whereas exposures at 1204 and 1315 °C resulted in

increasing amounts of monoclinic phase with time, reaching a maximum of 40% at longer time exposures at the highest temperature as predicted by the phase diagram. In a more recent study (Ref 42), it was shown that t' -8YSZ phase decomposition into a mixture of Y-rich (t' , c) and faster transformable Y-lean (t, m) phases follows a Hollomon-Jaffe-type parameter, $T [27 + \ln(t)]$, over a wide range of aging times (t , in hours) and temperatures (T , in Kelvin).

It has been suggested in Ref 43 and 44 that the plasma-sprayed YSZ stability may be improved by limiting the oxide impurity content in the starting powder. Taylor et al. (Ref 44) reported limiting total impurity oxide content in YSZ (for example, SiO_2 , Al_2O_3 , CaO , MgO , TiO_2) to less than 0.15 wt.% in delaying the tetragonal to monoclinic phase transformation. Other approaches to improve on the high temperature stability of YSZ are to coat with fully stabilized zirconia (Ref 45), to use alternative stabilizers such as Gd_2O_3 -stabilized ZrO_2 (Ref 46), and to identify alternative TBC materials to YSZ. As alternate TBC materials, investigations have included rare earth zirconates, $M_2Zr_2O_7$, where M is a rare earth element such as Gd, La, Y (Ref 47-50), yttria-stabilized HfO_2 (Ref 51), and yttrium-based garnets (Ref 52).

3.1.2 Ultralow Thermal Conductivity TBCs. Porous air plasma-sprayed 7YSZ TBC coatings (with porosity of 10-20% by volume) can have thermal conductivities significantly lower (0.9-1.1 W/m·K) than that of fully dense, monolithic 7YSZ (>2 W/m·K) as the splat boundaries and pores in APS structures lie parallel to the surface and perpendicular to the temperature gradient (Ref 8). By contrast, although the thermal conductivity of EB-PVD 7YSZ TBC (1.7-1.8 W/m·K) is not as low as that of porous APS 7YSZ coatings, EB-PVD TBCs are nevertheless preferred for thin aero blade TBCs because of the strain tolerance imparted by the microstructure (Ref 8). As a comparison, air plasma-sprayed DVC 7YSZ TBC (with lower porosity of ~5% and vertical cracks) has compatible thermal conductivity to that of EB-PVD 7YSZ TBC.

In recent years, designing turbine machinery for higher temperatures has triggered many studies to develop advanced TBCs with significantly lower thermal conductivities than current 7YSZ coatings. Termed as “low k TBCs,” these coatings would allow the use of thinner coating systems, achieve greater temperature reductions through the coating systems at higher engine operating temperatures, and help maintain substrate temperatures at a lower level, while the back-side cooling can be significantly reduced, improving the overall turbine efficiency.

Since heat is conducted by lattice waves (phonons) as well as by electromagnetic radiation (photons) in TBCs, approaches to reducing thermal conductivity have included creating lattice imperfections such as grain boundaries, solute cations, and oxygen vacancies which scatter lattice waves (Ref 53) as well as larger imperfections (size in order of microns) as photon scatters such as porosity and inclusions (Ref 54). Therefore, low k research has focused on doping YSZ with ions heavier than yttrium such as Nd, Gd, and Yb to create stable defect clusters (Ref 55, 56), varying the coating architectures, and

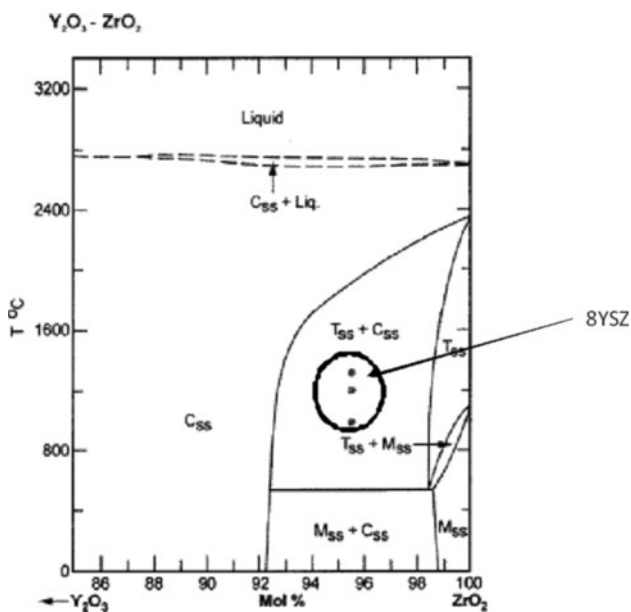


Fig. 6 The phase diagram for yttria and zirconia where typical 8YSZ composition is shown in the tetragonal+cubic solid solution phase region (Ref 34)

introduction of interfaces/density changes parallel to the top coat/bond coat interface (Ref 57). Zhu and Miller reported promising thermal conductivity and durability results in the laboratory performance of a 6 wt.% yttria, 7.6 wt.% gadolinia, and 8.3 wt.% ytterbia-stabilized ZrO₂ TBC compared to an APS 7YSZ TBC (Ref 58).

A summary of these low thermal conductivity oxides is presented by Pan et al. (Ref 59). Active research continues to overcome the limitations of these chemistries/coating structures, mainly in improving fracture toughness and erosion resistance when compared to the 7YSZ for equivalent microstructures.

3.2 High Temperature Oxidation Protection for Metallic Components

At temperatures over 900 °C (1650 °F), most superalloys show relatively rapid oxidation attack, since their compositions do not allow them to form a protective oxygen diffusion barrier in the early stages of oxidation (Ref 8). The most common metallic coatings used in gas turbines are overlay coatings or TBC bond coatings with high enough aluminum content to protect the superalloy components from high temperature oxidation and/or corrosion. Depending on the location in the turbine, oxidation-resistant coating compositions are selected to form stable, protective, slow growing, and adherent surface scales (TGO) to limit oxygen diffusion to the top surface. The coating surface also has to maintain resistance to deposits and subsequent fluxing to limit hot corrosion degradation. Coating chemistry and microstructure should also take into account the kinetics of the coating's protective element depletion to the surface as well as to the substrate. Chemical compatibility with the substrate material and wall consumption of hot section components should be designed for reparability considerations and life extension benefits. Coating should also be selected for good thermo-mechanical fatigue resistance and cracking tolerance as well as resistance to erosion and impact. The coating process should allow control of the desired chemistry, thickness, and provide the needed coverage on large parts with complex geometries.

As mentioned in section 3 and illustrated in Fig. 4, MCrAlY-type coatings where M can be Co, Ni, Fe, or combinations thereof and/or diffusion aluminides are most widely used for mitigating degradation in harsh environments. The diffusion aluminide coatings are based on β -NiAl phase and MCrAlY coatings are based on a mixture of β -NiAl, γ -fcc solid solution, and γ' -Ni₃Al phases (Ref 6). The equilibrium phase compositions are illustrated on a 1100 °C section of the Ni-Cr-Al phase diagram in Fig. 7 (Ref 60). MCrAlY coatings are thermally sprayed on the superalloy components by APS, low pressure plasma spray (LPPS), vacuum plasma spray (VPS), HVOF, and can also be deposited by EB-PVD (Ref 61).

The two most commonly used slow growing TGOs for protection of high temperature commercial superalloys are α -alumina (Al₂O₃) and chromia (Cr₂O₃). Therefore, standard MCrAlY coatings for IGT use contain 8-12 wt.% aluminum which selectively oxidizes to insure formation of a continuous alumina layer during high temperature oxidation (Ref 8). Also, a significant amount of chromium (18-22 wt.%) can be added to the coatings for high temperature corrosion resistance and promoting formation of a continuous alumina layer at lower Al concentrations (Ref 62). It is important to note that chromia has higher growth rates than alumina and volatilizes into gaseous CrO₃ at temperatures above 900 °C (Ref 63). Yttrium as a reactive element ($Y \ll 1$ wt.%) promotes TGO adhesion by tying up impurities like sulfur in the coating. The amount, distribution, and solubility of reactive elements in the coating play an important role in degradation as over doping leads to localized oxidation (Ref 64, 65). The addition of Co to NiCrAlY is beneficial for low temperature hot corrosion resistance as well as coating phase stability during thermal cycling (Ref 62, 66).

The main degradation mechanism for the MCrAlY-type coatings is the loss of protective elements due to bi-directional diffusion, the rate of which increases exponentially with increase in temperature (Ref 67). For example, during turbine operation, aluminum continually diffuses toward the hot gases to protect the surface as well as diffuses to the aluminum-poor substrate to maintain thermodynamic equilibrium. The long-term oxidation

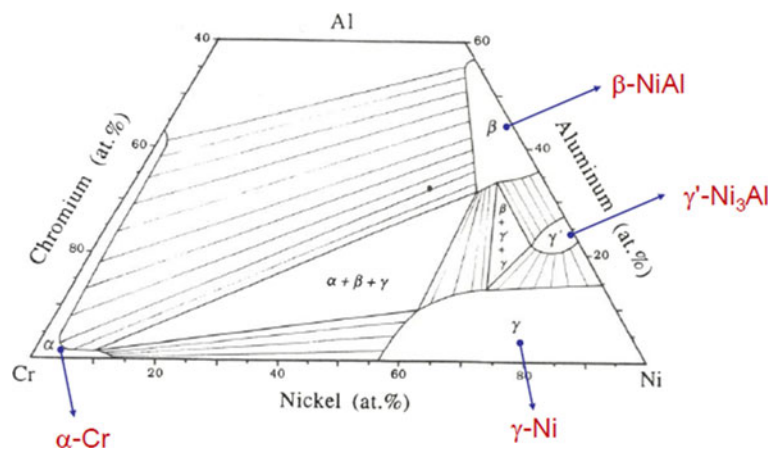


Fig. 7 1100 °C section of the Ni-Cr-Al equilibrium phase diagram (Ref 58)

behavior of the coating depends on the starting coating composition (Ref 68).

In order to accommodate the unavoidable increase in turbine inlet temperatures, proprietary metallic coatings that are capable of withstanding higher temperatures than the standard MCrAlYs have been developed by all the engine manufacturers over the past decade. The parameters to further improve the high temperature oxidation behavior of these coatings include the composition and size of the constituent phases; the initial distribution, chemical state, and reservoir of reactive elements in the coating; the composition and roughness at the coating surface; and the oxidation conditions during post-deposition heat treatment (Ref 62, 69-71). These more complex alloy systems are often generically known as M-Cr-Al-Y-X systems, where X refers to elements other than yttrium. In recent years, many activities have focused on finding the optimum Xs such as Si, Ti, Ta, Hf, Pd, Pt, Re, Ru, Ge, Zr, La, Sr, Sc, Mo, W, B, and C (Ref 72-76). These elemental additions may serve to slow down the diffusion of aluminum from the MCrAlY, reduce the beta to gamma phase transformation rate during thermal cycling, reduce the TGO growth rate and improve resistance to delamination of TBCs, and/or improve resistance to hot corrosion. As the design surface temperatures increase, another industry-wide concern is the load-bearing component wall property loss through interdiffusion of coatings and the substrate. Therefore, research is justified for higher temperature coatings in thermodynamic equilibrium with the substrate for reduced IDZ thickness at the interface (Ref 77).

3.3 Protection of Ceramic Components

In next generation turbine applications where the component surface temperatures exceed the melting point of Ni-based superalloys, components made of ceramic matrix composites (CMCs) are an alternative. CMCs, particularly those reinforced with continuous fibers, have been developed for structural applications where conventional ceramics have unacceptable fracture toughness and thermal shock resistance or in which metal components have limited lifetimes due to high temperature degradation. Silicon carbide fiber-reinforced silicon carbide matrix composites, so-called SiC/SiC composites, are more attractive for turbine engine applications than oxide fiber/oxide matrix composites such as alumina, zirconia, and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) because of the availability of high temperature fibers and better thermal shock and creep resistance of SiC (Ref 78, 79). CMCs are also lighter than metallic turbine alloys. This allows the design to not only be one-third of the weight when using CMC components but also impacts the entire rotor architecture; therefore, fuel efficiency rates could be dramatically improved in engines (Ref 80).

In terms of environmental resistance, pure silicon carbide is one of the most atmospheric corrosion-resistant materials. The reaction with oxygen in clean, dry air above about 800 °C forms CO_2 and a surface layer of protective SiO_2 which slows down subsequent oxidation (passive oxidation) (Ref 81). However, in high gas velocity environments containing water

vapor, a combustion reaction product, the silica scale, reacts with the water vapor and forms gaseous $\text{Si}(\text{OH})_4$, causing rapid loss of SiC (Ref 82-84). These materials also suffer from severe hot corrosion in environments contaminated by molten salt (Ref 85). Therefore, protective coatings (referred as environmental barrier coatings or EBCs) are required for SiC/SiC composites (Ref 86).

APS is the most successful and widely used thermal spray process to apply EBCs (Ref 87). Current EBCs have multiple layers designed in such a way that the system satisfies all the key requirements for a successful EBC, mainly (i) environmental stability, especially in water vapor, (ii) coefficient of thermal expansion (CTE) match, (iii) chemical compatibility, (iv) phase stability, and (v) low thermal conductivity. Multilayer EBCs consist of a silicon bond coat, mainly for adhesion and oxidation resistance, and a ceramic top coat comprising at least two ceramic layers for protection from water vapor and for thermal insulation (Ref 88). The reported current state-of-the-art environmental barrier coating comprises three layers: a silicon bond coat, a mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)-based intermediate coat, and a BSAS ($\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{Si}_2\text{O}_8$ where $0 \leq x \leq 1$) top coat (Ref 89). For applications over 1400 °C, where Si bond coat would melt, the next ceramic layer, such as a mullite-based coating, may become the bond coat. Additional top coat candidates are other silicates containing rare earth (RE) elements like Y, Sc, Er, Yb in the form of RE_2SiO_5 , $\text{RE}_2\text{Si}_2\text{O}_7$, and Ta_2O_5 (Ref 90). For gas turbine applications requiring long-term, high velocity, and high gas pressure exposures at temperatures above 1300 °C, EBC durability issues related to the volatilization of the BSAS top coat and the formation of a detrimental low melting glass phase chemical reaction between BSAS and the thermally grown silica on the Si bond coat were reported (Ref 91).

In the CMC product realization area, GE has successfully designed, developed, and tested stationary and rotating CMC turbine components in a working engine for commercial and military applications (Ref 80). Melt infiltrated (MI) SiC/SiC composites were made by the infiltration of silicon into a preform containing BN-coated silicon carbide fibers embedded in a matrix of SiC and/or carbon (Ref 92, 93). The fiber coating provided the damage tolerance to the (MI) SiC/SiC composite which showed excellent high temperature fracture, creep, wear, corrosion, and thermal shock resistance at temperatures exceeding 1200 °C (Ref 80, 94).

3.4 Life Extension of Engine Components and Efficiency Upgrades

Thermal spray coatings are also employed in the turbine aftermarket to extend life of components as well as to improve overall unit efficiencies. Fairly recent coatings applications include sound absorption, vibration damping, surface sealing, and clearance control in gas turbines.

3.4.1 Damping Coatings. Turbine components such as stator vanes, inlet guide vanes, combustor cans, and turbine and compressor airfoils are known to have vibrational resonance challenges induced by the engine

environment. Component vibration levels may be controlled even at high temperatures if the appropriate damper materials are designed into the component (Ref 95). A vast majority of damping mechanisms involve stress-induced movement of crystal defects such as point, line, and/or planar defects (Ref 96). The damping behavior of various steels and nickel alloys is reported by Matveev et al. up to 950 °C (Ref 97). Analytical models of vibration behavior of magnetic Fe-Cr coatings predict significant dissipation of mechanical energy due to the irreversible movement of magnetic domain boundaries of the coating material (Ref 98).

Thermal spray coating microstructures naturally contain many defects which may be engineered to reduce vibrational stresses and extend the life of components. One example of a HVOF-deposited damping coating microstructure is shown in Fig. 8a where the oxide (dark phase) dispersed in an oxidation-resistant matrix (light phase) changes its properties with heat to absorb vibration (Ref 99). Figure 8b shows the dependence of relative damping capacity, for two vibration modes, on temperature and microstructure where coatings F19-21 vary in

their oxide content as well as thickness as compared to uncoated baseline.

3.4.2 Abradable Coatings. Reducing the physical distance between rotating and stationary parts in industrial turbines can significantly increase turbine operating efficiencies. Some turbine and aircraft engine manufacturers now offer a series of compressor and hot section upgrades that are primarily composed of enhanced abradable sealing features and modified clearance control techniques to minimize hot gas bypass (i.e., leakage) around the turbine (Ref 100). Abradable coatings are applied on the compressor casings and stationary shrouds opposite the rotating blade tips to reduce clearances with minimum risk to compressor and turbine blade wear during rubs, as illustrated in Fig. 1 (see also Ref 101).

Figure 9 lists the various types of abradable materials deposited by thermal spray processes for applications in the compressor (up to 550 °C) or turbine section (up to 1350 °C) (Ref 101). Abradability of the coatings is enhanced by having large pores created by the fugitive polyester (about 15 wt.%) in the thermal spray powder mix, as illustrated in Fig. 10. Commercial SM2043 is an

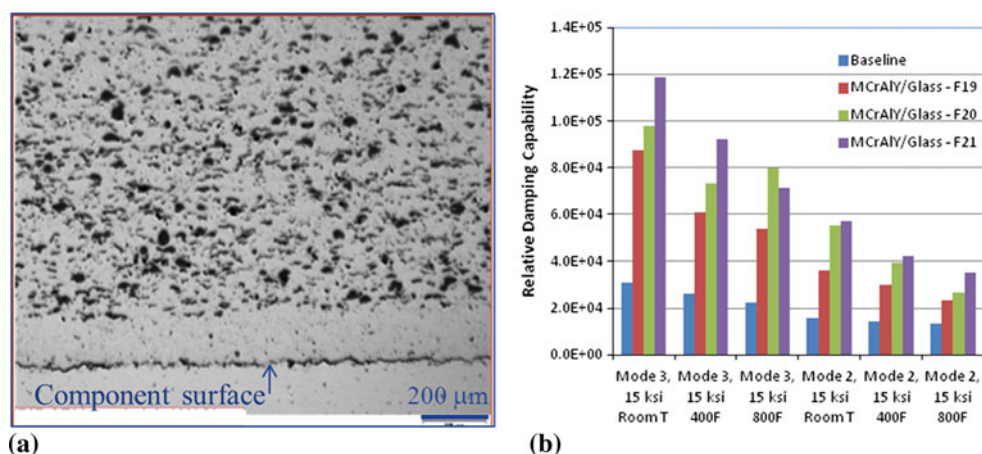


Fig. 8 (a) An example of a vibration damping microstructure created by HVOF and (b) relative damping capacity varying with surface temperature and microstructure characteristics

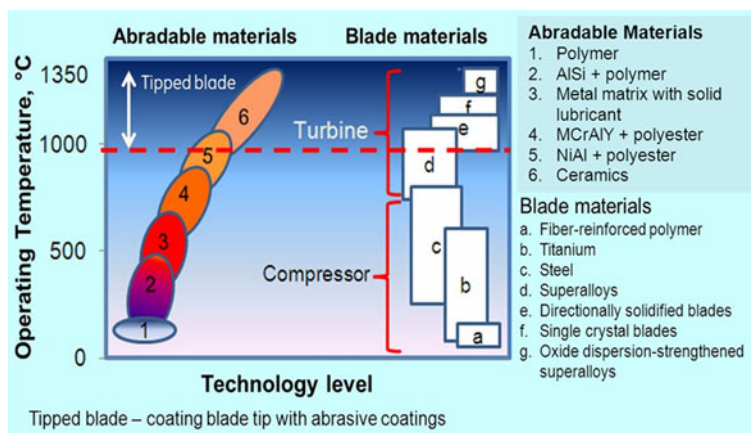


Fig. 9 Characteristics of thermal spray abradable materials

example of a MCrAlY + polyester abrasible for use in compressor and turbine applications at temperatures less than 850 °C (Ref 102). For temperatures between 850 and 1000 °C, oxidation-resistant aluminides were developed as abrasible materials (Ref 101, 103). For higher temperatures, ceramic materials such as 7YSZ blended with polyester are most often used for abrasibles (Ref 104). Typically, the use of ceramic abrasible coating requires a hard tipping of the blade, i.e., coating the blade tip with an abrasive coating for cutting into the abrasible materials. Standard tipping systems include silicon carbide and cubic boron nitride in a metal matrix (Ref 105, 106); however, blade tipping is expensive with short life at high operating temperatures (Ref 104). Therefore, an abrasible system that can be cut by untreated, bare blades is of great interest to the end user.

Recently, dysprosium oxide-stabilized zirconia blended with polyester was shown to possess the necessary abrasibility to be cut by untreated blades when sprayed to certain porosity (Ref 104, 107). Air plasma-sprayed non-stoichiometric magnesia alumina spinel coatings have also been tested for abrasibility as well as resistance to high thermo-mechanical loading for temperatures up to 1200 °C (Ref 108).

Instead of a continuous ceramic abrasible coating which requires high porosity and tipped blades, an alternative approach is to use patterned ceramic abrasibles (Ref 104, 109-112). Figure 11 shows such an example of a ceramic shroud abrasible where a ceramic coating such as 7YSZ TBC is deposited onto a brazed or cast grid struc-

ture to form a honeycomb-like patterned surface (Ref 104). This patterned abrasible structure enhances the abrasibility as the effective coating area that has to be rubbed away by the contacting blade tip is substantially reduced. This allows the use of blades without coated tips even at high operation temperatures.

3.5 Future Developments in Thermal Spray Technologies for Energy Generation

Thermal spray technologies will continue to be utilized for new applications in energy generation. Some examples are provided below.

3.5.1 Solid Oxide Fuel Cell. A solid oxide fuel cell (SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing fuel (Ref 113). SOFCs are characterized by the periodic stacking of hundreds of unit cells, each of which is about a few millimeters thick and is composed of four layers, three of which are ceramics (hence the name “solid oxide”). These ceramics which are thermally sprayed do not become electrically and ionically active until they reach 500-1000 °C. The high operating temperatures result in mechanical and chemical compatibility issues and longer start-up times. Fuel cell companies have been developing APS for creating high quality coatings at an affordable total manufacturing cost (Ref 94, 114-116).

3.5.2 Nanostructured Coating Applications. In recent years, significant advancement has been made in the field of plasma-sprayed nanomaterials and nanostructured

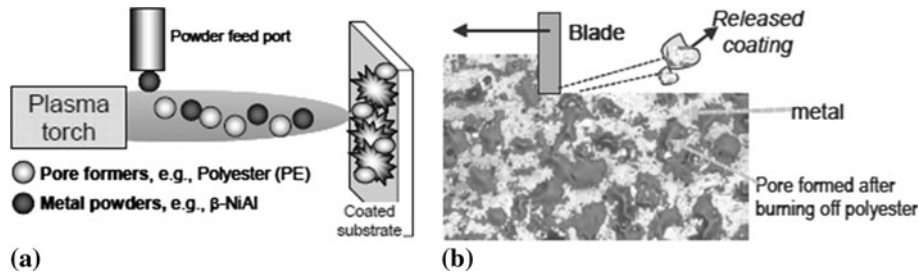


Fig. 10 (a) Abrasible coating applied by air plasma spray process where the spray powder is a mixture of metal powders and fugitive pore formers and (b) post-heat treatment coating microstructure that is abrasible when cut by a rotating blade tip

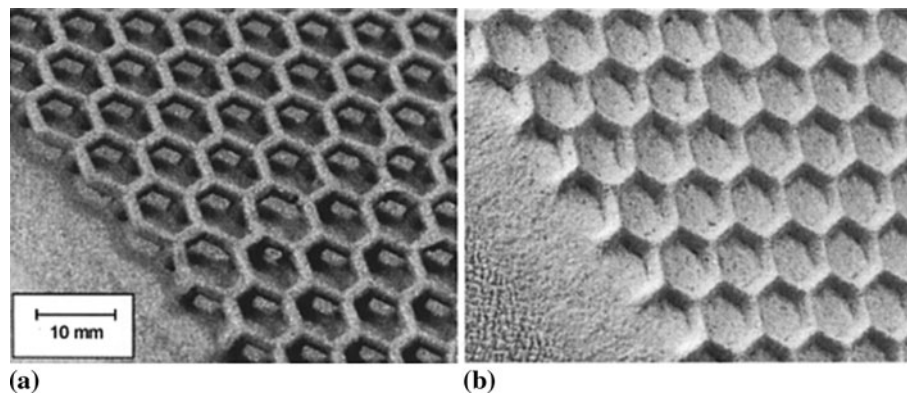
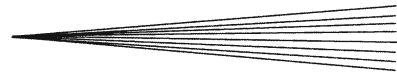


Fig. 11 (a) Cast hexagonal grid on substrate surface and (b) grid sprayed with YSZ to provide a patterned abrasible surface (Ref 104)



coatings for applications including better conductivity TBCs (Ref 117-119), lower friction coatings (Ref 120), better wear, and hot corrosion resistance (Ref 121, 122). However, more process development for improved efficiency and better coating properties is needed to realize any applications in the industry.

3.5.3 Combined Cycle Power Plant Combinations.

Today's combined cycle power plants use gas and steam turbines working in tandem to make efficient use of fuel. Recent power generation company announcements centered on integrating renewable resources onto the power grid for cleaner, more efficient energy generation. For example, GE's FlexEfficiency™ 50 (FlexEfficiency is a trademark of General Electric Company) plant rated at 510 MW combines wind and solar power fields, therefore burns less fuel, and starts in less than 30 min, all at 10% less footprint than existing combined cycle plants with equivalent output (Ref 123). These technical breakthroughs can certainly utilize the new developments in the thermal spray industry to achieve the highly integrated combined cycle efficiencies.

4. Summary

Thermal spray coatings will continue to be applied in industrial turbine applications. The need for improved reliability of existing coatings for life extension and development of new materials and processes for higher temperature applications will drive future research. New coatings will enable more efficient, fuel flexible operation. The industry will have to respond to the global challenges such as a shortage of "rare" materials (Y, He) by developing higher material utilization techniques and processes.

Acknowledgments

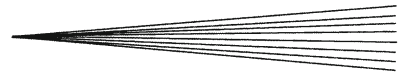
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