



Thermal Spraying in Energy Generation in Thailand

Panadda Sheppard

National Metal and Materials Technology Center, National Science and Technology Development Agency,
Pathumthani, Thailand.

* Author for correspondence; e-mail: panaddn@mtec.or.th

Received: 24 July 2012

Accepted: 11 December 2012

ABSTRACT

Domestic demand for electricity in Thailand increases continuously as a result of economic expansion and the increasingly hot weather. The energy sector has a long-term plan to invest in new power plants in order to keep up with the growing demand. This plan includes both fossil fuel and alternative technologies such as nuclear and biofuel. However, in the short-term plan, natural gas-fired power plants dominate electricity generation in Thailand, both in terms of installed capacity and the amount of fuel consumption. Gas-fired combined cycle power plants have moderate fuel consumption efficiency. The efficiency is partly limited by the material technology of the engine components. Surface engineering, in particular thermal spraying, has a major role in increasing the plant efficiency by raising the operational temperature of the turbine engine thus making optimal use of the scarce fossil fuel.

Keywords: energy generation, thermal spraying, thermal barrier coating

1. INTRODUCTION

Demand for energy in Thailand, especially electricity, increases continuously every year. The current rate of increase is about 4-5% annually and is due to domestic usage as a result of population growth as well as industrial needs due to the country's development. At the current rate, the demand for electricity is reasonably expected to double within the next 15 years. Much has to be done in order to cope with this rapidly expanding demand including raising awareness and promoting energy saving practices both in household and in industrial uses, research and development in the areas of the effective

utilization of fossil fuels and in alternative renewable fuels.

Electricity generation in Thailand is managed solely by a state-owned utility known as EGAT (Electricity Generating Authority of Thailand). There are 4 groups of supplier as follows;

- EGAT power plants (state-owned)
- Independent power producer (IPP)
- Small power producer (SPP)
- Neighboring countries (Laos and Malaysia)

At the end of 2011, EGAT had about 130 power generators with a combined installed capacity of approximately

15,000 MW. Another 14-15,000 MW was provided by IPP and SPP and a small amount was purchased from Thailand's neighbors. These together provide a total installed capacity of approximately 30,000 MW [1].

Thailand is currently operating at 15-20% reserve margin of the total installed capacity. However, when the weather is very hot as it has been in the past years, the peak demand for electricity increases due to the use of air conditioning. It is estimated that an increase in the ambient temperature of 1°C in the current condition will roughly increase the electricity demand by about 250-300 MW [2], pushing down the reserve margin closer to 15%. Thus, more severe hot weather is another factor contributing to the rising demand in the electricity.

Thailand's plan within the next 5 years includes construction of new power plants. The immediate plan involves mostly gas-

fired combined cycle power plants totaling to about 3,000 MW. After this period, the focus broadens to include power from clean coal, nuclear and alternative green energies. But for the near future, the combined cycle system using natural gas as a fuel will remain a main source of energy in Thailand. Table 1 indicates that almost half of the total installed capacity from EGAT power plants is generated through the combined cycle plants. Hence, while it is essential to pursue the advanced renewable energy technology, it is equally important to strive to improve efficiencies of the existing generating facilities in particular the combined cycle plant. The benefit is not only realized in the slower rate of fossil fuel consumption but also in the reduction of green house gas emission. Continuous improvement of the power plant and the fuel usage will have a significant impact on Thailand's economy and security.

Table 1. System installed generating capacity in 2010 [3].

| Type of Power Plant | MW | Percentage |
|---------------------|------------------|------------|
| Combined Cycle | 6,866.00 | 45.8 |
| Thermal | 4,699.00 | 31.3 |
| Hydropower | 3,424.18 | 22.8 |
| Renewable energy | 4.55 | 0.05 |
| Diesel Oil | 4.40 | 0.05 |
| Total | 14,998.13 | 100 |

* The data covers the state-owned power plants only.

2. NATURAL GAS-FIRED POWER PLANT

Simple-cycle gas turbine power plant is known for its relatively low capital cost, high reliability, short delivery time and fast starting and loading [4,5]. In this cycle, cold air enters the compressor and is compressed to some higher pressure. The compression increases the air temperature and pressure.

The air is mixed with fuel gas in the combustion chamber when combustion occurs. During combustion, the gas volume expands whilst the pressure is constant (theoretically). The temperature and the entropy of the gas however increase rapidly. The gas then enters the turbine section where the energy of the hot gases

is converted into work that drives the compressor and the generator, see Figure 1. A large amount of energy is wasted through the turbine exhaust which is typically at a temperature of 400-600°C. A modern simple cycle gas turbine engine has an efficiency of 30-40% [6].

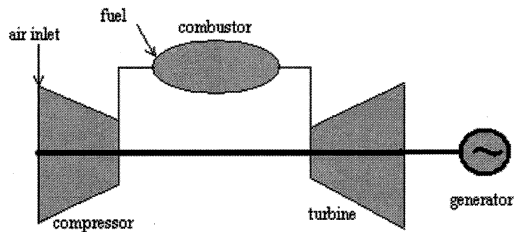


Figure 1. Schematic diagram of a simple-cycle gas turbine.

In part-load operation however its efficiency can significantly drop, resulting in a lower fuel economy. For example, it was estimated that at 50% load, the gas turbine achieves around 75% of its full-load efficiency, and at 30% load the efficiency is reduced by 50%. The part-load performance in terms of the work output and the efficiency can be increased through various machine designs and process improvement such as recuperation (heat exchanging) and intercooling. In order to increase the plant output further, a combined cycle such as the Brayton-Rankine cycle is employed. The combined Brayton-Rankine cycle power plant utilizes a steam turbine and a gas turbine thermodynamic cycles by using heat recovered from the gas turbine exhaust gases for steam production to supply the steam turbine as shown in Figure 2. First, the natural gas is burned in a combustion chamber of the gas turbine to produce a flow of hot gas which drives the turbine. The turbine is coupled to a generator

producing electricity. After the gas turbine, the hot exhaust gas is captured using a heat recovery steam generator to produce superheated steam. The steam expands and drives a steam turbine which is attached to a second generator, producing more electricity. By using the exhaust heat from the gas turbine engine to produce superheated steam via a complex heat recovery cycle, the overall efficiency of the combined cycle power plant is increased to 50-58% [6,7], significantly higher than that of the simple cycle.

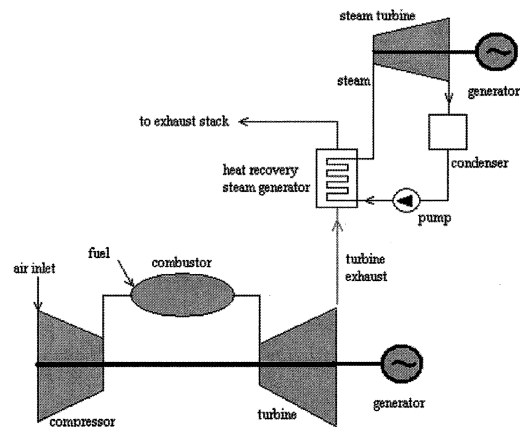


Figure 2. Schematic diagram of a combined cycle generation unit.

In order to increase the turbine efficiency further, the process conditions need to increase in severity, i.e. the firing temperature and the pressure of the gas need to be raised. Advanced high temperature material and cooling technique are therefore important factors limiting the performance of the modern gas turbine power plant.

3. THE USE OF THERMAL SPRAYING FOR GAS TURBINES

Many components in the simple cycle gas turbine plant and the combined cycle

plant work under high temperature environment, particularly in the gas turbine cycle where the maximum temperature is typically higher than 800°C. As a result components are prone to failures from creep, wear and corrosion at high temperature. The structure of the gas turbine engine's components is largely constructed from metals. High temperature creep-resistant Ni alloys such as Inconel and Hastelloy are the standard material for components operating in the hot gas path such as compressor, combustion basket/liner, transition piece and turbine blade and vanes. The use of Ni alloy components limits the maximum operating condition of the turbine to approximately 900°C. The critical components where the internal temperature is highest, and can be well above 900°C, are the combustion liner which forms a wall of the combustion zone

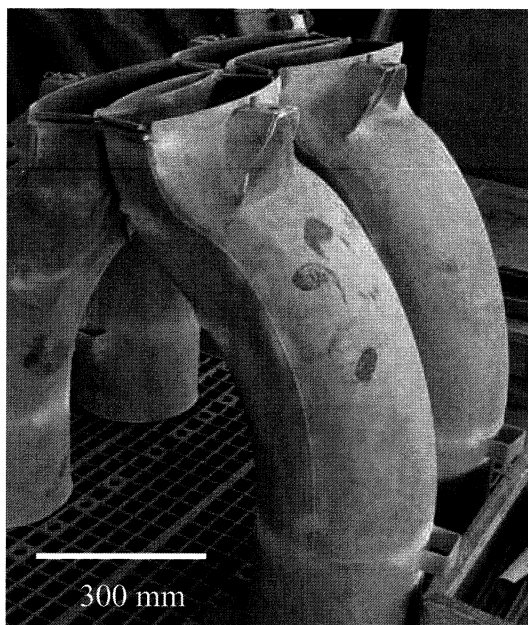


Figure 3. Example of a transition piece used in the gas turbine engine. The picture shows 4 transition pieces. The shape and size of the transition piece varies according to the engine model.

and the transition piece (see Figure 3) which transports and alters the shape of the hot gas going into the turbine zone. There are some newer designs where refractory ceramic tiles may be employed as the liner for the combustion chamber thus achieving a firing temperature above 1,200°C.

In order for the turbine to operate at a higher temperature, thermal barrier coatings (TBC) have been extensively employed to protect the Ni alloy components from high temperature corrosion. There are various techniques and materials used for the fabrication of TBC. In this paper, the focus is given to a thermal-sprayed type TBC as it is widely used in the gas turbine engine in Thailand. Conventional TBC consists of 2 layers of coating; an outer topcoat and an intermediate bondcoat, see Figure 4. The partially-stabilized ZrO_2 topcoat acts as a thermal insulator for the metallic component under heat flux conditions and can withstand an operating condition above 1,200°C. ZrO_2 partially-stabilized with 7-10wt.% Y_2O_3 is a standard material used for the TBC topcoat for land-based gas turbine applications. Its popularity is due to its low thermal conductivity, relatively high

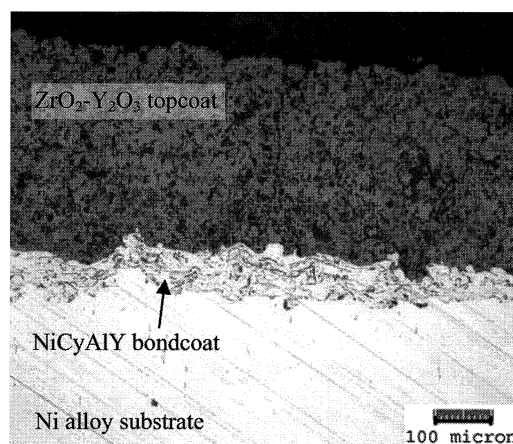


Figure 4. Typical plasma-sprayed TBC for land-based gas turbine components.

thermal expansion coefficient, ease of fabrication and low material cost. This insulating layer coupled with effective cooling can reduce the maximum temperature of the Ni alloy component by a few hundred degrees Celsius thus allowing it to operate at temperatures above 1,000°C. The intermediate bondcoat layer of MCrAlY alloy, where M is Ni and/or Co, is also an essential part of TBC. The bondcoat has 2 functions;

1. It provides a barrier to oxidation. The relatively large amount of Al in MCrAlY (6-10 wt.%) can diffuse to the bondcoat/topcoat interface and forms an Al_2O_3 layer via selective oxidation. Thermally-grown Al_2O_3 scale is a protective oxide which means it hinders diffusion of elements such as O and Al. Once a continuous scale is formed on the bondcoat, the rate of oxygen diffusion through to the bondcoat reduces. Thus it can reduce the oxidation rate of the bondcoat and prolong the service life of NiCrAlY coating [8].
2. It acts as a bonding layer for the ceramic topcoat by dispersing the thermal stress within the bondcoat. The thermal stress is induced during a cooling cycle of the turbine engine. By reducing the stress at interfaces, delamination of the ZrO_2 coating can be prevented [9].

TBC can be economically applied onto the gas turbine components using an atmospheric plasma spraying (APS) technique, see Figure 5 and 6. A plasma-sprayed $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coating may exhibit a reduction in the thermal conductivity depending on its microstructure, possibly to as low as 2.0 to 2.2 W/mK at 1,000°C [10]. The reduction in the thermal conductivity is mostly due to the cracks and pores typically present in the as-

sprayed coating. The size and shape of these defects govern the heat transfer rate through the coating [11-14]. Other factors such as the coating thickness dictate the maximum temperature the component can endure.

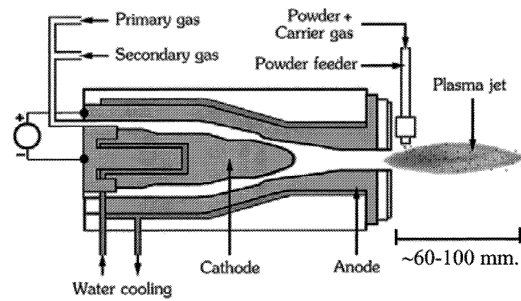


Figure 5. Atmospheric plasma spraying setup.

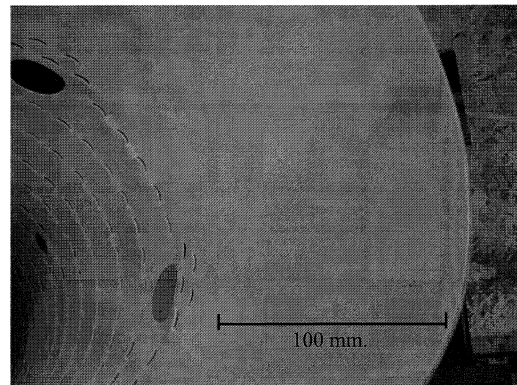


Figure 6. Combustion liner coated with TBC.

Apart from TBC, other thermal sprayed coatings used in the gas turbine plant are wear-resistant coatings such as CoCrMoSi and NiCr-Cr₃C₂, which can be applied using APS or high velocity oxy fuel (HVOF) techniques, see Figure 7. These coatings, although they can only operate at a temperature below 800°C, possess good resistance against metallic sliding wear. Thus they are employed at the connections between components such as the seal for the transition piece, the seal for

the cross fire tube, combustion nozzle and the retainer plate. These components are not in direct contact with the hot gas but are subjected to strong vibration from the combustion which can result in rapid wear damage, see Figure 8.

A major advantage of thermal spraying is its ease in recoating. This allows a component to be refurbished by stripping off the used coating and resupplied with a fresh one. The component can be repaired in this way until material degradation (usually creep or thermo mechanical fatigue in the case of high temperature applications) occurs. This is particularly important in the gas turbine engine due to the use of expensive Ni-based alloys as the component materials.

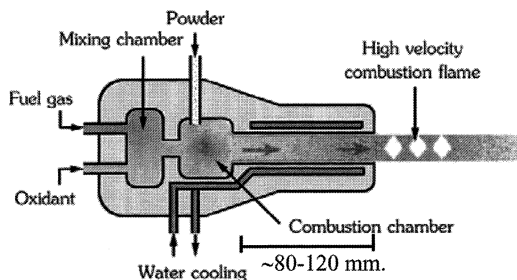


Figure 7. High velocity oxy fuel (HVOF) spraying setup.

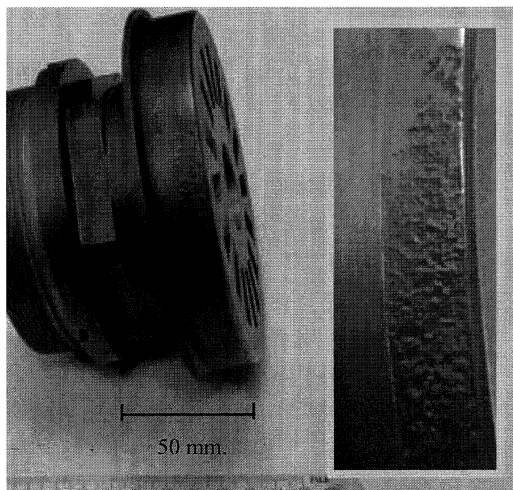


Figure 8. Wear damage on a fuel nozzle in a combustor.

4. HIGH TEMPERATURE FAILURE IN THERMAL-SPRAYED TBC

The conventional TBC is typically employed at temperatures between 800-1,200°C. At this temperature range, the topcoat can reduce the temperature of the bondcoat by 150-250°C depending on the coating thickness and the amount of cooling used [15]. The coating may have a lifetime of 3,000-6,000 hours during which period failure can occur in the form of cracking spalling and/or delamination of the topcoat. The coating failure may be as a result of;

1. Thermal expansion mismatch during cooling between the bondcoat, the thermally-grown oxide and the topcoat.

During cooling, the coatings and the substrate contract in volume according to their thermal expansion coefficients (CTE). The difference in the volume change causes stress at the material interface. This thermal stress can be large enough to cause cracking in the topcoat and the thermally-grown oxide (TGO) at the bondcoat/topcoat interface [16]. High thermal stress can also result in delamination of the topcoat.

2. Diffusion of Al into the substrate.

At high temperature, Al can diffuse into the Ni alloy substrate causing Al reduction in the bondcoat. This Al is a reservoir for the formation of the slow-growing, protective Al_2O_3 TGO. Once the Al is near depleted in the bondcoat, other less protective oxides in particular Ni-oxide spinels can form at the interface at a faster rate resulting in excessive oxidation of the bondcoat. Cracks can initiate in these oxides easier than in Al_2O_3 , leading to the spallation of the topcoat, see Figure 9 and 10.

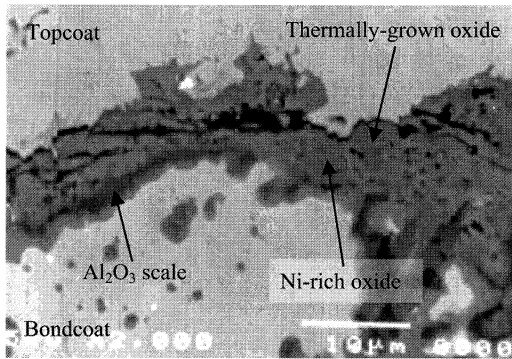


Figure 9. Scanning electron microscopy (SEM) micrograph in secondary electron mode showing cracks in the thermally grown oxide.

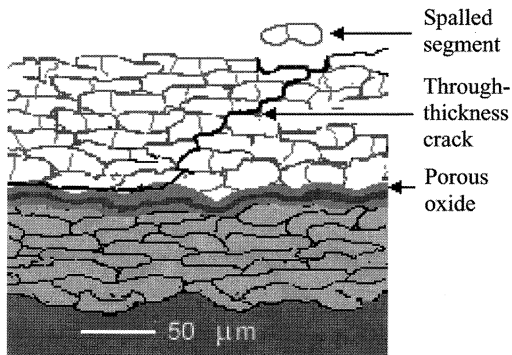


Figure 10. Spallation of topcoat.

3. Phase transformation of the topcoat.

The Y₂O₃ partially-stabilised ZrO₂ topcoat has a metastable tetragonal phase but prolonged operation at high temperature can destabilize this tetragonal phase causing it to transform to a monoclinic phase. The phase transformation is accompanied by a volume change, thus inducing residual stress in the coating [17].

4. Sintering of the topcoat.

As-sprayed ZrO₂ topcoat is full of microcracks and pores. These defects are an essential characteristic of TBC. The cracked and porous structure has been shown to be able to tolerate thermal stress by relieving the stress through strain

relaxation. Long periods of operation at temperatures above 1,000°C inevitably result in sintering and densification of the topcoat. This involves reduction in microcracks and porosity and coalescence of the pores. While the strength and hardness of the topcoat increase slightly as a result, the coating becomes less compliant making coating delamination more likely [18,19]. Sintering can also cause phase transformation in the partially-stabilized ZrO₂ and changes in the thermal conductivity of the coating [14,20-22].

5. AREAS FOR IMPROVEMENT AND DEVELOPMENT

As well as improving TBC for better reliability and longer lifetime, the diminishing natural gas resources also drive the need for turbine cycles with higher fuel efficiency. One way this can be done effectively is by increasing the turbine inlet temperature. It is estimated that a turbine efficiency of over 60% can be achieved with the turbine inlet temperature of about 1500°C [23]. Research efforts to improve thermal-sprayed TBC are underway. Examples are given below.

Thick TBC

The conventional plasma-sprayed TBC is usually employed with ZrO₂ thickness of up to 500 μm due to their limited reliability. A thicker TBC has an obvious advantage of a greater reduction in temperature of the underlying metallic substrate. Applying a thick ZrO₂ coating however results in a greater thermal stress at the bondcoat/topcoat interface which can cause premature spallation of the TBC. If sintering occurs during operation, the risk of failure becomes more pronounced. In order to successfully employ the thick TBC, its durability particularly in term of

the strain tolerance must be improved. This has been shown by increasing the porosity level and segmentation cracks in the ZrO_2 coating thus allowing an easier and more even strain relieve [24-27]. Plasma-sprayed TBC of thickness greater than $1,000\ \mu\text{m}$ can be achieved, see Figure 11. Increasing the porosity of ZrO_2 also has the benefit of lowering its thermal conductivity rendering it a more effective insulator [11-13].

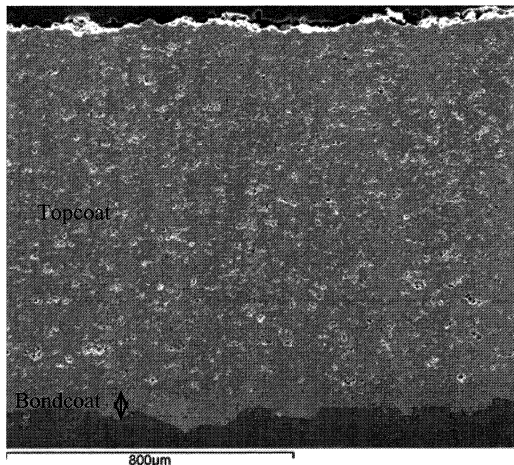


Figure 11. SEM micrograph in secondary electron mode showing the microstructure of plasma-sprayed thick TBC.

Functionally graded TBC

Normally as-sprayed ZrO_2 topcoat can adhere reasonably well to its underlying bondcoat, however when it is subjected to a sudden drop in temperature thermal stress due to a large difference in CTE of the bondcoat and the topcoat can induce large stresses near the bondcoat/topcoat interface. This problem becomes more pronounced when a thicker ZrO_2 topcoat is employed leading to spallation or a large-scale delamination of the ZrO_2 topcoat. One method to reduce the effect of the CTE mismatch is to apply a functionally-graded TBC. Functionally-graded TBC consists of the MCrAlY bondcoat and the

partially-stabilised ZrO_2 topcoat, and an intermediate layer or layers in between the bondcoat and the topcoat, see Figure 12. The intermediate layer is a physical mixture of the bondcoat and the topcoat. When more than one intermediate layer is used, a compositional gradient can be created. The functionally-graded TBC works by spreading out the thermal stress over the thickness of the intermediate layers thus reducing the stress at the topcoat interface where cracking often initiates [28-30].

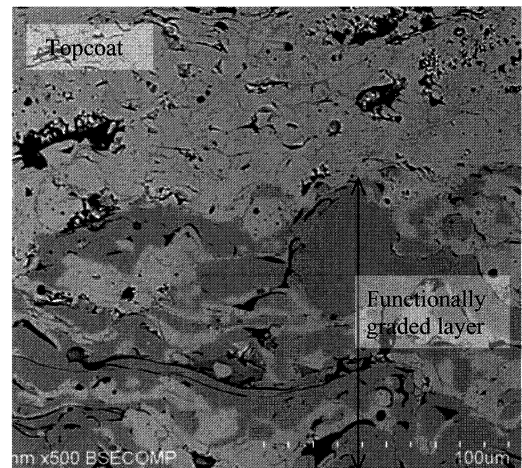


Figure 12. SEM micrograph in backscattered electron mode showing the microstructure of plasma-sprayed, functionally-graded TBC. The functionally graded layer consists of two major phases; partially-stabilised ZrO_2 and MCrAlY.

Alternative insulating topcoat material

Plasma-sprayed ZrO_2 -8% Y_2O_3 , even though having many thermal properties suitable for high temperature insulator applications, has a tendency to undergo phase transformation when operating at a temperature higher than $1,250^\circ\text{C}$ for a long duration, resulting in higher residual stress in the coating [17]. Sintering of this coating at temperatures above $1,400^\circ\text{C}$ also cause changes in the properties of the coating

leading to failure [31]. Alternative refractory materials, e.g. $\text{CeO}_2\text{-Y}_2\text{O}_3\text{-ZrO}_2$, SiO_2 , $\text{Nd}_2\text{O}_3\text{-ZrO}_2$, rare earth oxide-doped $\text{La}_2\text{Zr}_2\text{O}_7$ and other zirconates, have been suggested [32-36]. Balance still needs to be reached between low thermal conductivity, high durability and economical processing route.

Diffusion barrier

The lifetime of TBC can be lengthened by hindering the degradation of the bondcoat, i.e. by slowing down the growth rate of the protective Al_2O_3 TGO. The growth rate of Al_2O_3 is highly dependent on the oxygen diffusion rate in the oxide which is much slower than the oxygen permeation through the plasma-sprayed TBC [37]. Thus in order to reduce the oxide growth rate even more, a diffusion barrier between the bondcoat and the topcoat is required (Diffusion barrier 1 in Figure 13). Previous work has explored the possibility of applying Pt and/or Ni aluminide on the bondcoat using electrolytic techniques, pack cementation, spark plasma sintering etc. [38-43]. It is generally agreed that the aluminide layers can provide a better resistance to oxidation for TBC. The adhesion of the topcoat is also improved as a result of a reduction in TGO thickness due to the improved oxidation resistance of TBC.

Apart from the growth rate of the protective Al_2O_3 , the amount of Al available for the selective oxidation is equally important since the depletion of Al in the bondcoat results in the formation of other oxides contributing to failure of TBC. At temperatures above $1,000^\circ\text{C}$ however, alloying elements including Al can diffuse from the bondcoat into the substrate thus reducing the amount of Al available for the oxide formation [44]. In

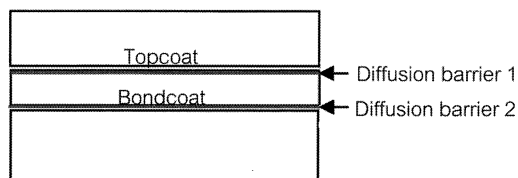


Figure 13. Diffusion barrier.

order to reduce the interdiffusion of Al, a diffusion barrier may be applied between the substrate and the bondcoat (Diffusion barrier 2 in Figure 13). Various types of barrier have been studied, e.g. AlON, CrON, $\alpha\text{-Al}_2\text{O}_3$ and TiN using methods such as chemical vapor deposition, thermal spraying, arc ion-plating and anodizing [45-49]. The diffusion barriers were shown to be partially effective at reducing the interdiffusion of the alloying elements but investigations on their long-term stabilities and their effects on the durability of TBC are still limited.

6. CONCLUSIONS

The natural gas-fired turbine power plants contribute a large amount of output towards electricity generation in Thailand. In order to increase the fuel efficiency further thus reducing the rate of fossil fuel consumption, the temperature of the turbine engine needs to be raised. Development on high temperature materials is one of the key technologies required to achieve this goal. The current technology involves the use of TBC on Ni-alloy gas turbine components. At high temperatures and/or prolonged operation periods, failure mechanisms such as CTE mismatch, diffusion of alloying elements and sintering of the ZrO_2 topcoat can take place resulting in premature spallation and delamination of TBC. Research is being conducted on various topics including coating materials and fabrication techniques in order to increase the reliability of the coating, the

lifetime and the operational temperature of the components.

ACKNOWLEDGEMENT

The author would like to thank Dr. John T.H. Pearce for his invaluable advice and input towards the writing of this paper.

REFERENCES

- [1] www.egat.co.th
- [2] www.thaipost.net/news/230412/55823.
- [3] EGAT 2010 annual report, the Electricity Generating Authority of Thailand, 2010.
- [4] Najjar Y.S.H., Efficient use of energy by utilizing gas turbine combined systems, *Appl. Therm. Eng.*, 2001; **21**: 407-438.
- [5] Kaupang B.M., Combined cycle economics, 33rd GE Turbine State-of-the-Art Seminar, Paper No. GER 3584A, 1989.
- [6] Poullikkas A., An overview of current and future sustainable gas turbine technologies, *Renew. Sust. Energ. Rev.*, 2005; **9**: 409-443.
- [7] Farmer R., 227 MW frame 9FA will power Epon's 1.7 GW combined cycle, *Gas Turbine World*, 1992; **June**: 15-22.
- [8] Koomparking T., Damrongrat S. and Niranatlumpong P., Al-Precipitation in NiCoCrAlY bondcoat at High Temperature, *J. Therm. Spray Techn.*, 2005; **14**: 264-267.
- [9] Taylor M.P., Niranatlumpong P., Evans H.E. and Ponton C.B., Observations of the Spallation Modes in an Overlay Coating and the Corresponding Thermal Barrier Coating System, *Mater. High Temp.*, 1999; **17**: 219-224.
- [10] Liu H., Li S., Li Q., Li Y. and Zhou W., Microstructure, phase stability and thermal conductivity of plasma sprayed Yb₂O₃, Y₂O₃ co-stabilized ZrO₂ coatings, *Solid State Sci.*, 2011; **13**: 513-519.
- [11] Klemens P.G. and Gell M., Thermal conductivity of thermal barrier coatings, *Mater. Sci. Eng. A*, 1998; **245**: 143-149.
- [12] Cernuschi F., Ahmaniemi S., Vuoristo P. and Mäntylä T., Modelling of thermal conductivity of porous materials: application to thick thermal barrier coatings, *J. Eur. Ceram. Soc.*, 2004; **24**: 2657-2667.
- [13] Zhao H., Yu F., Bennett T.D. and Wadley H.N.G., Morphology and thermal conductivity of yttria-stabilized zirconia coatings, *Acta Mater.*, 2006; **54**: 5195-5207.
- [14] Zhang J. and Desai V., Determining thermal conductivity of plasma sprayed TBC by electrochemical impedance spectroscopy, *Surf. Coat. Tech.*, 2005; **190**: 90-97.
- [15] Sadowski T. and Golewski P., Multidisciplinary analysis of the operational temperature increase of turbine blades in combustion engines by application of the ceramic thermal barrier coatings (TBC), *Comp. Mater. Sci.*, 2011; **50**: 1326-1335.
- [16] Evans A.G., Mumm D.R., Hutchinson J.W., Meier G.H. and Petit F.S., Mechanisms controlling the durability of thermal barrier coatings, *Prog. Mater. Sci.*, 2001; **46**: 505-553.
- [17] Ilavsky J. and Stalick J.K., Phase Composition and its changes during annealing of plasma-sprayed YSZ, *Surf. Coat. Tech.*, 2000; **127**: 120-129.
- [18] Zhu D. and Miller R.A., Sintering and creep behavior of plasma-sprayed

- zirconia- and hafnia-based thermal barrier coatings, *Surf. Coat. Tech.*, 1998; 108-109: 114-120.
- [19] Rahaman M.N., Gross J.R., Dutton R.E. and Wang H., Phase stability, sintering, and thermal conductivity of plasma-sprayed ZrO₂-Gd₂O₃ compositions for potential thermal barrier coating applications, *Acta Mater.*, 2006; 54: 1615-1621.
- [20] Schulz U., Phase Transformation in EB-PVD Yttria Partially Stabilized Zirconia TBCs During Annealing, *J. Amer. Ceram. Soc.*, 2000; 83: 904-910.
- [21] Allen A.J., Ilavsky J., Long G.G., Wallace J.S., Berndt C.C., Herman H., Microstructural characterization of yttria-stabilized zirconia plasma-sprayed deposits using multiple small-angle neutron scattering, *Acta Mater.*, 2001; 49: 1661-1675.
- [22] Dutton R., Wheeler R., Ravichandran K.S. and An K., Effect of heat treatment on the thermal conductivity of plasma-sprayed thermal barrier coatings, *J. Therm. Spray Techn.*, 2000; 9: 204-209.
- [23] ATS: the countdown continues, *Power Engineering International*, 1998; 57-61.
- [24] Helminiak M.A., Yanar N.M., Pettit F.S., Taylor T.A. and Meier G.H., The behavior of high-purity, low-density air plasma sprayed thermal barrier coatings, *Surf. Coat. Tech.*, 2009; 204: 793-796.
- [25] Steffens H. D., Babiak Z. and Gramlich M., Some aspects of thick thermal barrier coating lifetime prolongation. *J. Therm. Spray Techn.*, 1999; 8: 517-522.
- [26] Schwingel D., Taylor R., Haubold T., Wigren J. and Gualco C., Mechanical and thermophysical properties of thick PYSZ thermal barrier coatings: correlation with microstructure and spraying parameters. *Surf. Coat. Tech.*, 1998; 108-109: 99-106.
- [27] Ahmaniemi S., Vippola M., Vuoristo P., Mantyla T., Cernuschi F. and Lutterotti L., Modified thick thermal barrier coatings: Microstructural characterization, *J. Eur. Ceram. Soc.*, 2004; 24: 2247-2258.
- [28] Rangaraj S. and Kokini K., Estimating the fracture resistance of functionally graded thermal barrier coatings from thermal shock tests, *Surf. Coat. Tech.*, 2003; 173: 201-212.
- [29] Chen X., Gu L., Zou B., Wang Y. and Cao X., New functionally graded thermal barrier coating system based on LaMgAl₁₁O₁₉/YSZ prepared by air plasma spraying, *Surf. Coat. Tech.*, 2012; 206: 2265-2274.
- [30] Tsukamoto H., Design against fracture of functionally graded thermal barrier coatings using transformation toughening, *Mater. Sci. Eng. A*, 2010; 527: 3217-3226.
- [31] Zhu D. and Miller R.A., Thermal conductivity and elastic modulus evolution of thermal barrier coatings under high heat flux conditions. *J. Therm. Spray Techn.*, 2000; 9: 175-180.
- [32] Clarke D.R. and Phillpot S.R., Thermal barrier coating materials, *Materials Today*, 2005, 22-29.
- [33] Ingo G.M., Combined use of XPS, XAES and SIMS for the characterization of fracture surfaces of CeO₂-Y₂O₃-ZrO₂ coatings, *Appl. Surf. Sci.*, 1993; 70-71: 235-239.
- [34] Khor K.A. and Yang J., Rapidly solidified neodymia-stabilised zirconia coatings prepared by DC plasma spraying, *Surf. Coat. Tech.*, 1997; 96: 313-322.

- [35] Zhou H. and Yi D., Effect of rare earth doping on thermo-physical properties of lanthanum zirconate ceramic for thermal barrier coatings, *J. Rare Earths.*, 2008; **26**: 770-774.
- [36] Moskal G., Swadzba L., Hetmanczyk M., Witala B., Mendala B., Mendala J. and Sosnowy P., Characterization of microstructure and thermal properties of $Gd_2Zr_2O_7$ -type thermal barrier coating, *J. Eur. Ceram. Soc.*, 2012, **32**: 2025-2034.
- [37] Fox A.C. and Clyne T.W., Oxygen transport by gas permeation through the zirconia layer in plasma sprayed thermal barrier coatings, *Surf. Coat. Tech.*, 2004; **184**: 311-321.
- [38] Schmitt-Thomas Kh.G. and Hertter M., Improved oxidation resistance of thermal barrier coatings, *Surf. Coat. Tech.*, 1999; **120-121**: 84-88.
- [39] Nicholls J.R., Advances in coating design for high performance gas turbines, *MRS Bulletin*, 2003; **28**: 659-670.
- [40] Orru R., Licheri R., Locci A.M., Cincotti A. and Cao G., Consolidation/synthesis of materials by electric current activated/assisted sintering, *Mater. Sci. Eng. R*, 2009; **63**: 127-287.
- [41] Murakami T., Sasaki S., Ito K., Inui H. and Yamaguchi M., Microstructure of Nb substrates coated with $Mo(Si,Al)_2-Al_2O_3$ composite and B-doped Mo_5Si_3 layers by spark plasma sintering, *Intermet.*, 2004; **12**: 749-754.
- [42] Taylor T.A. and Bettridge D.F., Development of alloyed and dispersion-strengthened MCrAlY coatings, *Surf. Coat. Tech.*, 1996; **86-87**: 9-14.
- [43] Monceau D., Oquab D., Estournes C., Boidot M., Selezneff S., Thebault Y. and Cadoret Y., Pt-modified Ni aluminides, MCrAlY-base multilayer coatings and TBC systems fabricated by Spark Plasma Sintering for the protection of Ni-base superalloys, *Surf. Coat. Tech.*, 2009; **204**: 771-778.
- [44] Cremer R., Witthaut M., Reichert K., Schierling M. and Neuschütz D., Thermal stability of Al-O-N PVD diffusion barriers, *Surf. Coat. Tech.*, 1998; **108-109**: 48-58.
- [45] Müller J., Schierling M., Zimmermann E., Neuschütz D., Chemical vapor deposition of smooth $\alpha-Al_2O_3$ films on nickel base superalloys as diffusion barriers, *Surf. Coat. Tech.*, 1999; **120-121**: 16-21.
- [46] Widjaja S., Limarga A.M. and Yip T.H., Modeling of residual stresses in a plasma-sprayed zirconia/alumina functionally graded-thermal barrier coating, *Thin Solid Films*, 2003; **434**: 216-227.
- [47] Wang Q.M., Wu Y.N., Guo M.H., Ke P.L., Gong J., Sun C. and Wen L.S., Ion-plated Al-O-N and Cr-O-N films on Ni-base superalloys as diffusion barriers, *Surf. Coat. Tech.*, 2005; **197**: 68-76.
- [48] Jagminas A., Kurtinaitiene M., Angelucci R. and Valinčius G., Modification of alumina barrier-layer through re-anodization in an oxalic acid solution with fluoride additives, *Appl. Surf. Sci.*, 2006; **252**: 2360-2367.
- [49] Xu Z., He L., Mu R., Zhong X., Cao X., Formation of diffusion barrier on the Ni-based superalloy by low-pressure pre-oxidation, *Vacuum*, 2008; **82**: 1251-1258.