

APPLICATION OF FUNCTIONALLY GRADED MATERIALS AS THERMAL INSULATOR IN HIGH TEMPERATURE ENGINEERING COMPONENTS

Debasish Das*

A. K. Saini*

M. K. Pathak*

Sachin Kumar**

ABSTRACT

The future predicted scenario of energy crisis is emphasizing today on the development in the area of energy saving, particularly in the high temperature engineering components such as gas turbines and Internal Combustion engines. Higher the operating temperature more is the efficiency of the system. However, increase in the operating temperature strictly affects the longevity of material. Use of certain ceramic layers as thermal barrier coatings (TBCs) over such high temperature components sufficiently reduces the heat penetration into the substrate and hence increases the efficiency and performance of the system. Further, high temperature stability is one of the key issues in this regard, which restricts the use of as such coating of ceramic layers and necessitates the use of some functionally graded materials (FGMs). This paper presents the need, status and effects of coatings of such functionally graded materials in improving performance of gas turbine systems and diesel engines. Certain coating techniques suitable in this context have also been discussed.

Keywords: Diesel engine, Gas turbine, Thermal barrier coating, Functionally graded material, Partially stabilized zirconia (PSZ), Plasma spray technique.

*Department of Mechanical Engineering, N.I.T. Hamirpur, H.P.

**Assistant Professor, Department of Mechanical Engineering, N.I.T. Hamirpur, H.P.

1. INTRODUCTION

The engineering devices such as internal combustion engines and gas turbines have to deal with sufficiently high operating temperatures. That is why these devices are usually termed as high temperature engineering devices. Increasing this operating temperature of the system or decreasing the heat loss from the system is bound to increase its thermal efficiency. However any increase in the operating temperature puts a significant thermal load on the substrate, which deteriorates the material of the substrate. Ultimately, it results into the extra cooling load on the system, which further decreases the thermal efficiency of the system. In general, it is necessary to prevent the distortions and deformations that the maximum temperature of any point in an alloy must not exceed more than 66% of its melting point temperature [1]. Ceramic coatings are developed for these high temperature applications in the form of thermal barrier coatings (TBCs). Providing a thin layer of such ceramic coating over the substrate restricts the penetration of heat into the substrate and lowers the temperatures within the material. Thus, mechanical efficiency of the system also goes up because of significant decrease in the cooling load. In other words, working temperature of the system can be raised or it can be said that heat loss through conduction within the substrate, which had to be otherwise taken away by the coolant, can be reduced. However, in the case of thermal loading, it is well known that the thermal stresses are generated at the interfaces when dissimilar materials are bonded together [2]. As a result, there happens to be failure of these coatings in the form of debonding and spalling from the substrate [3-4]. Huang et al. [5] and Hu et al. [6] suggested through experiments that the cracks have further a strong tendency to extend into the substrate and they propagate parallel to the interface. The concept of using graded transition in composition across an interface of two materials (for instance, metal and ceramics or polymer) has come into picture because of such aspects only and it can essentially reduce the thermal stresses and stress concentration at intersection with free surfaces. Such materials are known as functionally graded materials (FGMs). The thermo-mechanical behavior of these materials having spatial gradients in the microstructure and composition has been of considerable interest in a number of technical areas like tribology, optoelectronics, biomechanics, nano-technology and of course, the high temperature technology also. A reviewing study has been presented in this article on these materials, particularly in context with their prominent application as thermal barrier coatings in the engineering devices operating at elevated temperatures. Further, of a number of techniques

available to coat FGMs or TBCs over the substrate, a worldwide being adopted process of plasma spray has been discussed.

2. FUNCTIONALLY GRADED MATERIALS (FGMs)

The concept of functionally graded material (FGM) was first originated in 1984 in Japan during a space plane project in which a combination of materials was used to act as thermal barrier capable of withstanding a surface temperature of 2000 K and a temperature gradient of 1000 K across a 10 mm section. Since 1984, FGM thin films have been comprehensively researched, and are almost a commercial reality. In the recent years, this concept has become more popular in Europe, particularly in Germany. Basically, a functionally graded material is a multi-component composite material characterized by a compositional gradient from one component to the other. Unlike a traditional composite material which is basically a homogeneous mixture and is a throughout compromise between the properties of individual materials, the composition and/or function of FGM is designed to change continuously within the solid. This way there is full utilization of the properties of individual materials. For example, the toughness of a metal can be mated with the refractoriness of a ceramic, without any compromise in the toughness of the metal side or the refractoriness of the ceramic side. The gradual transition between the heat resistant outer ceramic layer and the tough metallic base material increases the longevity of the component. The bamboo, bones and teeth are the natural examples of FGMs. In each case, there is a smooth transition of hard and wear-resistant exterior to a soft interior. Thus, a functionally graded material varies in composition and structure gradually over the volume, resulting in corresponding changes in the properties of the material. FGMs have great utilization in the applications such as wear-resistant linings for handling large heavy abrasive ore particles, rocket heat shields, heat exchanger tubes, thermoelectric generators, heat-engine components, plasma facings for fusion reactors, armour protection for military applications, high density magnetic recording media, optical applications as graded refractive index materials in audio-video discs, bioengineering applications as dental and orthopaedic implants, electrically insulating metal/ceramic joints, structural applications as fire retardant doors and penetration resistant materials for armour plates and bullet-proof vests. Since, they are also capable of minimizing thermo-mechanical mismatch in metal-ceramic bonding, FGMs find significant interest in a wide range of applications as thermal barrier coatings for gas turbine blades in power and aerospace sectors, thermal barrier coatings for combustion zone parts of diesel engine such as piston in automobile sector.

3. FUNCTIONALLY GRADED MATERIALS AS THERMAL BARRIER COATINGS

Among the components working in the environment of high temperatures, gas turbine blades and combustion zone parts of a diesel engine have been of core interest in regard to application of thermal barrier coatings. The TBCs consist of a top layer of thermally insulating ceramic layer and an intermediate oxidation resistant metallic bond coat [7]. Further, zirconia based ceramics have always been a forefront focus of attention for TBC applications [8-10]. Zirconia has a monoclinic crystallographic structure at ambient temperatures but at elevated temperature of about 1170°C, monoclinic phase undergoes transformation to tetragonal one. Further, there occurs phase transformation from tetragonal to cubic at 2370°C. At 2680°C, the melting of the material is there. But, during cooling from elevated temperatures at 1170°C, disruptive phase transformation occurs from tetragonal to monoclinic associated with 6.5% of volumetric expansion [11]. This change causes failure of the ceramic coating. This problem is generally eliminated by stabilizing either partially or fully, the high temperature cubic/tetragonal phase by doping monoclinic ZrO₂ with CaO, MgO or Y₂O₃ [12-14]. 8 wt% Y₂O₃-ZrO₂ (AMDRY-6610), 18-26 wt % MgO-ZrO₂ (AMDRY-333) and 5 wt % CaO-ZrO₂ (AMDRY-6700) are most commercially available and extensively studied compositions [15-17]. Apart from this phase transformation, there are two more reasons of failure of ZrO₂ based coatings at high temperatures, one being the oxidation of intermediate bond coat [18] and another being the mismatch between coefficient of thermal expansion between substrate and ceramic layers.

The interlayer, usually known as bond coat, basically provides sufficient adhesive strength between ceramic layer and the substrate and to aid to that, it also acts as a protection barrier for oxidation and corrosion. Initially, simple NiAl coatings used to be this bond coat but now MCrAlY (M = Ni, Co, Fe or their combinations etc.) coatings or Pt modified NiAl coatings are in use as bond coats. Oxidation of bond coat itself gives alumina (Al₂O₃). Originally, it was considered that TBC failure is the result of this Al depletion in the bond coat giving rise to the formation of faster growing spinels [19-20]. However, Clarke et al. [21] and Tolpygo et al. [22] have shown the stresses development during the growth of alumina and also rumpling of the surface of alumina scales due to enhanced grain boundary growth rates. Faster growing grain boundary regions of oxide push the TBC away from the flatter regions of oxide. Zirconia has also been found to possess a good compatibility with Al₂O₃. Further, the thermal cycle life of Y₂O₃ stabilized zirconia TBCs has also been improved by interposing a 2-5

micron thick continuous alumina diffusion barrier between the top coat and the bond coat which suppresses the oxidation rate of bond coat [23-24]. As far as effectiveness and longevity of FGMs as TBCs is concerned, a number of experiments and numerical modelling and simulations have been carried out by the researchers worldwide. For instance, thermo-mechanical experiments were conducted over the cylindrical specimens by Perrin et al. to visualize and analyze the crazing in TBCs [25] in which the substrate was an aluminium alloy, containing 12% silicon, which is currently used for making pistons in internal combustion engines. The magnesium zirconate (76% ZrO_2 , 24% MgO) coating was plasma-sprayed on one end of the aluminium cylinder, the isolating layer being bonded to the substrate using an intermediate layer. This last one constituted two different layers: one of pure metal (95% Ni, 5% Al) close to the substrate and one of a mixture of magnesium zirconate and NiAl (50% ponderal each). This has been illustrated in Fig.1.

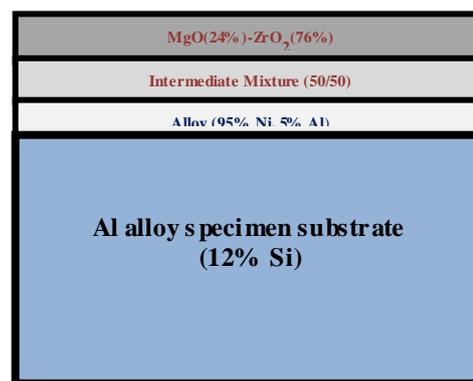


Fig. 1. Schematic representation of FGM as TBC over Al alloy substrate

The main difference in loading TBCs in turbines and diesel engines is the thermal cycle characteristic. Thermo-mechanical fatigue life is the most important life-time limiting factor in diesel engines since the thermal cycle lasts for just a fraction of seconds and maximum temperature is about 800°C. While in an aircraft turbine application, thermal loading cycle is of several hours and maximum temperature is also much higher. Therefore, bond coat oxidation becomes more important and in fact, it together with thermo-mechanical fatigue life decides the life-time of TBC coatings [26]. Kim et al. [27] showed that the type of thermal cycle testing and therefore service condition is important with respect to TBC life. This work shows that for longer cycle times (>1 h), Pt modified NiAl bond coats work in a better way while for shorter cycle times (about 10 min), MCrAlY bond coats behave in a superior manner.

4. COATING TECHNIQUES SUITABLE FOR FGMs AS TBCs

The different techniques which are in use for coating applications are thermal spray processes (plasma sprayed metal matrix composite coating, high-velocity oxy-fuel coating etc.), diffusion coating processes (pack cementation, chemical vapor deposition etc.), physical vapor deposition (PVD) processes, magnetron sputtering coating, Ni-dispersion coating and electric arc wire spray coating [28]. Besides there are, reactive ion coating, hot isostatical press coating, detonation gun coating etc.

Plasma spray technique which is further of two types viz. atmospheric plasma spray (APS) and vacuum plasma spray (VPS), has been of immense use to obtain ceramic coatings because of its ease of application and versatility. The technique involves a plasma torch consisting of an anode in the form of a nozzle and a cathode. The plasma is generated in the torch on ionization of a mixture of two or more of the gases like Ar, H₂, He or N₂ by an electric arc discharge. The ionized gas heats up to over 15000 K, expands enormously, and leaves the anode exit with high velocity [29]. The powder particles varying in the size from 5–200 μm are injected in the plasma just from outside the anode. There the particles are heated to a semi-plastic or even molten state and accelerated towards the work piece to be coated. The particle velocities vary between 80 to 300 m/s depending on the plasma properties and particle size [29-30]. Fig. 2 [31] shows a schematic for plasma spray process.

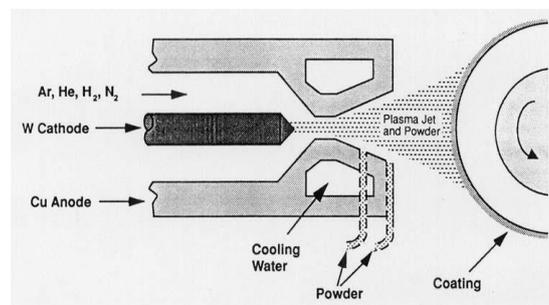


Fig. 2. A schematic for plasma spray process

The adherence of coating to substrate occurs mainly through mechanical locking and not through metallurgical bonding via inter-diffusion. This is because substrate surface to be sprayed is to be first cleaned and roughened. This roughened surface causes the molten material to solidify around the asperities and coating gets as such locked. Moreover, no appreciable melting of surface occurs due to higher cooling rate of small mass of powder particles as compared to that of substrate. The structure obtained from plasma technique is highly porous due to low velocity of spray process as shown in Fig. 3. This high porosity is in fact intentionally introduced to reduce thermal conductivity of ceramic layer [32] and make the TBC more effective but it is undesirable in the sense that it decreases the ability of bond

coating to protect substrate from oxidation. It is because, oxygen from the high temperature working environment penetrates through these pores and it reacts with aluminium usually present in the bond coat forming a layer of alumina which gradually goes on developing. This thermally grown oxide (TGO) layer results into separation of coating from the substrate.

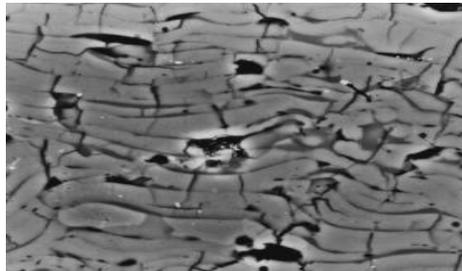


Fig. 3. Porous structure from plasma spray process

5. CONCLUSION

The high temperature engineering devices like gas turbines and IC engines experience sufficient heat loss from the working medium. Providing a thin layer of certain ceramic material over the surface as thermal barrier coating has significant effect in reducing this heat loss and improving the efficiency and performance of the system. Partially stabilized zirconia has been of great interest as TBC due to its suitable properties. However, an appreciable difference in the values of coefficient of thermal expansion for the two materials viz. substrate and the coating affects adhesive strength. The concept of using functionally graded material has attracted the focus of researchers in this context, which is basically the concept of making a composite material by varying the microstructure from one material to another material with a specific gradient. This enables the material to have the best of both materials. Further, plasma spray system is one of the widely accepted techniques to put ceramic coatings of FGMs as TBCs due to its versatility in ceramic-substrate combinations. But the structure obtained from plasma spray is associated with micropores, which are beneficial in the sense that they decrease thermal conductivity of the coating material but are undesirable since they decrease longevity of the coating.

6. REFERENCES

1. Properties and Selection: Irons, steels and high performance alloy, ASM Handbook, vol. 1, ASM International, 1990.
2. Boley, B. and Weiner, J. H., *Theory of Thermal Stresses*. Kreiger Publishing, Florida, 1985.

3. Miller, R. A. and Lowell, C. R., Failure mechanism of thermal barrier coatings exposed to elevated temperatures. *Thin Solid Films*, 1982, 95, 265-273.
4. Miller, C. C. and Berndt, R. A., The performance of thermal barrier coatings in high heat flux environment. *Thin Solid Films*, 1984, 119, 173-184.
5. Huang, Y. and Zhang, H. W., *Acta Metallurgica*, 1995, 43, 1523-1530.
6. Hu, M. S., Thouless, M. A. and Evans, A. G., *Acta Metallurgica*, 1988, 36, 1301-1307.
7. Bratton, R. J. and Lau, S. K., in "Advances in Ceramics", Vol. 3 "Science and Technology of Zirconia", edited by Heuer, A. H. and Hobbs, L. W., (American Ceramic Society, Columbus, OH, 1981) p. 226.
8. Bennett, A., *Material Science Technology*, 2(3) (1986) 257.
9. Alperine, S. and Lelait, L., *J. Eng. Gas Turbines Power Trans ASME* 116(1) (1994) 258.
10. Porter, D. L. and Heuer, A. H., *J. Amer. Ceram. Soc.* 62 (1979) 298.
11. Chan, S. H. and Khor, K. A., The effect of thermal barrier coated piston crown on engine characteristics. *Journal of Materials Engineering and Performance*, 2000, 9, 103-109.
12. Hannink, R. H. J., *J. Mater. Sci.* 18 (1983) 457.
13. Vanvalzah, J. R. and Eaton, H. E., *Surf. Coat. Technol.* 46 (1991) 289.
14. Curtis, C. L., Gawne, D. T. and Priestnall, M., *J. Mater. Sci.* 29 (1994) 3102.
15. Scardi, P., Lutterotti, L. and Galvanetto E., *Surf. Coat. Technol.* 61 (1993) 52.
16. Joshi, S. V. and Srivastava, M. P., *ibid.* 56 (1993) 215.
17. Miller, R. A., Smialek, J. L. and Garlick, R. G., in "Advances in Ceramics", Vol. 3 "Science and Technology of Zirconia", edited by Heuer, A. H. and Hobbs, L. W., (American Ceramic Society, Columbus, OH, 1981) p. 241.
18. Wu, B. C., Chang, E., Chao, C. H. and Tsai, M. L., The oxide pecking spalling mechanism and spalling modes of ZrO₂ 8 wt % Y₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings under various operating conditions. *J. Mater. Sci.*, 25 (1990) 1112-1119.
19. Sohn, Y. H., Biederman, R. R. and Sisson, Jr. R. D., Microstructural development in physical vapour-deposited partially stabilized zirconia thermal barrier coatings. *Thin Solid Films*. 250(1-2),1-7, 1994.
20. Shillington, E. A. G. and Clarke, D. R., Spalling failure of a thermal barrier coating associated with aluminum depletion in the bond-coat. *Acta Mater.* 47(4), 1297-1305, 1999.

21. Clarke, D. R., Christensen, R. J. and Tolpygo, V., The evolution of oxidation stresses in zirconia thermal barrier coated superalloy leading to spalling failure. *Surf Coat Technol.* 94-95(1-3), 89–93, 1997.
22. Tolpygo, V. K. and Clarke D. R., Surface rumpling of a (Ni, Pt) Al bond coat induced by cyclic oxidation. *Acta Mater.* 48(13), 3283–93, 2000.
23. Schmitt-Thomas, Kh. G. and Dietl, U., Thermal barrier coatings with improved oxidation resistance. *Surf. Coat. Technol.*, 68/69 (1994) 113-115.
24. Sun, J. H., Chang, E., Chao, C. H. and Cheng, M. J., ZrO₂-8 wt % Y₂O₃ CVD-Al₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings. *Oxidation of Metals*, 40 (1993) 465-481.
25. Perrin, N., Burlet, H., Boussuge, M. and Desplanches, G., Thermomechanical experiments and numerical simulation of ceramic coatings. *Surface & Coatings Technology*, 1993;56:151-156.
26. Stover, D. and Funke, C., Directions of the development of thermal barrier coatings in energy applications. *Journal of Materials Processing Technology*, 92-93, 195-202, 1999.
27. Kim, G. M., Yanar, N. M., Hewitt, E. N., Pettit, F. S. and Meier, G. H., The effect of the type of thermal exposure on the durability of thermal barrier coating. *Scr Mater*, 46(7), 489–95, 2002.
28. Friedrich, C., Berg, G., Bras, EZ, Rick, F. and Holland, J., PVD Cr_xN coatings for tribology application on piston rings. *Surf. Coat. Technol.*, 97, 661-668, 1997.
29. Fauchais, P., Vardelle, M., Vardelle, A., and Coudert, J. F., Plasma Spraying of Ceramic Particles in Argon-Hydrogen D.C. Plasma Jets: Modeling and Measurements of Particles in Flight Correlation with Thermophysical Properties of Sprayed Layers. *Met. Trans. B*, Vol. 20B, 1989, pp. 263-276.
30. Diessen, van, S.L.M., 1998, *Mechanical Measuring Method for Plasma Sprayed Particle Velocities*, Master's Thesis, WOC/GTS/98-001, Eindhoven University of Technology, The Netherlands (in Dutch).
31. Tucker, R. C., "Thermal Spray Coatings", ASM Handbook Ninth Ed. 5 (1994).
32. Beardsley, M. B. and Larson, H. J., Thick Thermal Barrier Coatings for Diesel Components. DOE/NASA/0332-1, NASA CR-190759 (1992).