Deposition and characterization of plasma sprayed Ni-5Al/magnesia stabilized zirconia based functionally graded thermal barrier coating

M N Baig¹ and F A Khalid
Faculty of Materials Science & Engineering, GIK Institute of Engineering Sciences & Technology, Pakistan
E-mail: mnbaig8167@gmail.com

Abstract. Thermal barrier coatings (TBCs) are employed to protect hot section components in industrial and aerospace gas turbine engines. Conventional TBCs frequently fail due to high residual stresses and difference between coefficient of thermal expansion (CTE) of the substrate & coatings. Functionally graded thermal barrier coatings (FG-TBCs) with gradual variation in composition have been proposed to minimize the problem. In this work, a five layered functionally graded thermal barrier coating system was deposited by atmospheric plasma spray (APS) technique on Nimonic 90 substrates using Ni-5Al as bond coat (BC) and magnesia stabilized zirconia as top coat (TC). The coatings were characterized by SEM, EDS, XRD & optical profilometer. Microhardness and coefficient of thermal expansion of the five layers deposited as individual coatings were also measured. The deposited coating system was oxidized at 800°C. SEM analysis showed that five layers were successfully deposited by APS to produce a FG-TBC. The results also showed that roughness (Ra) of the individual layers decreased with an increase in TC content in the coatings. It was found that microhardness and CTE values gradually changed from bond coat to cermet layers to top coat. The oxidized coated sample revealed parabolic behavior and changes in the surface morphology and composition of coating.

1. Introduction
Thermal barrier coatings (TBCs) are widely used to protect internally cooled hot section components of gas turbine engines for both power generation and propulsion. These coatings are applied to provide a temperature drop (∼170-200 °C) between the coating surface and the load-bearing alloy component underneath thus increasing the Turbine Entry Temperature (TET) and consequently turbine engine’s efficiency. The eventual target of TBCs application is to achieve an enhancement in fuel efficiency by increasing the operating temperature (∼100-300 °C) thereby increasing the engine thrust and efficiency up to 5 % and 1 %, respectively. TBCs are also meant to extend the life of turbine components and hence to improve engine reliability [1-8].

A TBC system is a multilayered coating structure having a complex geometry and usually consists of four layers, (1) a superalloy substrate, (2) an oxidation & corrosion resistant bond coat (BC), (3) a thermally grown oxide (TGO) and (4) a low thermal conductivity ceramic top coat (TC) [9]. It has been reported that most superalloys oxidize rapidly at temperatures above 900 °C as they are unable to form a protective oxygen diffusion barrier during early stages of oxidation [10]. The use of an approximately 100-150 µm thick layer of a metallic BC has now been a norm to protect the superalloy...
substrate from high temperature oxidation and corrosion [11]. The typical BC materials used in TBCs are NiCrAlY/CoCrAlY/NiCoCrAlY alloys, Ni-Cr-Al, Ni-Cr and Ni-Al with or without Pt modification [8, 11-13]. The Ni-Al type bond coats such as Ni-20Al and Ni-5Al are recognized for their enhanced bond strengths attributed to an exothermic reaction apparently resulting from an extra heat of solidification associated with the partial oxidation of Ni and Al during spraying [14-16]. It has also been reported that Ni-5Al coatings develop a protective and adherent oxide scale when cyclically oxidized at 900 °C resulting in a reduction in weight gains of the superalloy substrates thus lowering the rate of oxidation [16].

The TC is characterized by a high melting point, excellent thermal stability, good erosion resistance, comparatively high coefficient of thermal expansion (CTE), and low thermal conductivity and is usually 200-250 µm thick layer attached directly to the BC [8,10-11]. Partially or fully stabilized zirconia by adding various oxides like Y₂O₃, CeO₂, CaO, Al₂O₃, Gd₂O₃ and MgO as stabilizers is used as TC material because of its low thermal conductivity and relatively good mechanical properties [8, 17-18]. Among these, ZrO₂-Y₂O₃ (7-8 % YSZ) has been documented as an outstanding TC material for last few decades due to its high thermal shock resistance, low thermal conductivity, and a higher melting point than most oxides [10]. However, it is more expensive as compared to CaO and MgO-stabilized zirconia [8, 19-20]. Zirconia stabilized with 15-24 % MgO (magnesia stabilized zirconia) is comparatively cheaper and is utilized in those regions where the temperature intensity is relatively low such as in the exhaust nozzle of the jet engines [20-21]. Recently, magnesia stabilized zirconia has been investigated for its hot corrosion behavior in LiCl-Li₂O molten salt owing to its excellent chemical stability [21]. Moreover, magnesia stabilized zirconia has low thermal conductivity (1.0-1.5 W/mK), fairly comparable to YSZ, which suggests that it has a huge potential to be used as TC material for suitable applications.

The main problem in using a conventional TBC system is its premature failure because of the delamination or spallation of the ceramic TC from the metallic BC due to large residual stresses generated during cooling from the spraying temperature at or near the interface and poor bond strength between the coating and the substrate. These residual stresses are induced due to mismatch in CTEs of the substrate and BC & TC and can have a considerable effect on the properties of the deposited coating system [22-25].

In order to reduce the thermal expansion mismatches and to enhance the service life of the TBC system, the introduction of one or more intermediate layers with compositional gradient between the bond and top coats has been proposed. These thermal barrier systems are usually referred to as functionally graded-thermal barrier coatings (FG-TBCs). FG-TBCs may consist of several intermediate layers whose composition changes gradually from substrate metal to ceramic coating [24-29].

In this study, a five layer FG-TBC system and five individual layers comprising of the coating system were prepared by APS to study their characteristic properties. The coatings were characterized by SEM, EDS, XRD and optical profilometer. CTEs and microhardness of the individual coatings were also measured. Oxidation of the coating system was also performed at 800 °C.

2. Materials and methods
The substrate used in this study were discs of a nickel-based alloy, Nimonic 90, 12.8 mm in diameter and approximately 3 mm in thickness from Goodfellow Cambridge Limited, UK ([nominal composition Ni-20Cr-18Co-2.5Ti-1.5Al-1.5Fe & 3.5-others (in weight %)]. Two types of commercial feedstock powders from Sulzer Metco, USA, namely Metco 450NS (Ni-5Al, will be referred as Ni) and Metco 210NS-1 (ZrO₂-24MgO, will be referred as MSZ) were used as BC and TC materials, respectively. The two powders were also pre-mixed with each other in three different ratios (by weight) to form three powder blends, i.e., 75 Ni/25 MSZ, 50 Ni/50 MSZ, and 25 Ni/75 MSZ. These powders were then used to prepare five layer FG-TBC system. The coatings were deposited by APS using a Metco 9MB plasma spray gun (Sulzer Metco, USA). Prior to deposition, the substrates were grit blasted with Corundum 500 particles to a surface roughness of ~4.0 µm followed by ultrasonic
cleaning. Deposition parameters are summarized in table 1 and the coating architecture is shown in figure 1.

| Parameter                    | Limits used                      |
|------------------------------|----------------------------------|
| Primary gas type/pressure/flow rate | Ar/100±5Psi/100+5 ft³/min         |
| Auxiliary gas type/pressure/flow rate | H₂/56+5Psi/15+5 ft³/min          |
| Powder carrier gas/flow rate   | Ar/37 ft³/min                    |
| Powder feed rate               | 51, 60, 68 g/min                 |
| Arc current                   | 500 Amps                         |
| Arc voltage                   | 70 ± 5 V                         |
| Spray distance                | 75, 100, 125 mm                  |
| Gun to work angle             | 90 degree                        |
| Atmosphere                    | Ambient                           |

The powders and coatings were characterized by an analytical low vacuum scanning electron microscope (JEOL-Japan, Model JSM 6490 LA) operated at 20 kV and coupled with an energy dispersive spectrometer (EDS). Roughness profiles of the individual coatings were recorded by a 2D optical profilometer (Nanovea-USA, Model PS 50). The distance scanned was 1 mm and a scan velocity of 0.1 mm/sec with a scan step of 0.1 µm was used. The coating in as sprayed and oxidized conditions was analyzed by using X-ray diffractometer (STOE-Germany, Model Theta/Theta) with CuKα radiation at 40 kV and 40 mA. Microhardness profiles of the polished surfaces of individual coatings were obtained utilizing a Vickers Indenter (Wilson Instruments-USA, Model 401MVD) with a 300gf load and 15 sec. dwell time (loading time). The CTEs of the two individual freestanding coatings (bond and top coats) were measured as a function of temperature using a dilatometer (Netzsch Germany, Model 402E). CTE of the remaining three types of coatings representing composite layers was calculated using Vegard’s rule of mixture. Approximately 03 mm thick individual coatings were deposited onto a 05 mm thick steel plate (SS 304L). The specimens for CTE measurements were then removed from the SS substrate by an automatic diamond cutter. The approximate sample size was 03x03x25 mm. The coating system was oxidized at 800 °C in a tube furnace in still laboratory air for 100 hours. For measuring weight gain during oxidation, the heating cycle consisted of 11 hours in furnace at 800 °C followed by cooling in still laboratory air to room temperature for 30 minutes. The coated discs were then weighed by a precise weight balance.

3. Results and discussions

3.1. Characterization of powders and coating morphology

SEM micrographs showing the morphology and particle size distribution of the two powders used as BC and TC materials are shown in figure 2 (a) & (b), respectively. Both the powders showed a spheroidal morphology however MSZ powder particles showed a perfectly round spherical

Figure 1. Schematic diagram showing architecture of the five layer FG-TBC system.
morphology as compared to Ni powder particles. Surface morphologies of the single particles of both the powders at higher magnification showed that Ni particle has an irregular and rough surface whereas MSZ particle has a very smooth surface. Furthermore, SEM micrographs of both the powders showed that MSZ has a higher range of finer size particles as compared to Ni powder.

![SEM micrographs of the two feedstock powders showing surface morphology and particle size distribution, (a) Ni powder and (b) MSZ powder.](image)

**Figure 2.** SEM micrographs of the two feedstock powders showing surface morphology and particle size distribution, (a) Ni powder and (b) MSZ powder.

SEM micrograph of polished cross section of the five layered TBC system is shown in figure 3 (a). The microstructure showed that there were no sharp boundaries formed between the layers and the structure was continuous. EDS line scan analysis for each element comprising the TBC system is shown in figure 3 (b). It can be seen from the figure that there were no clear boundaries formed between the deposited layers resulting in a relatively continuous microstructure and the distribution of elements comprising the TBC was relatively unbroken. Three graded layers of different compositions as shown in figure 1 were deposited between the bond and top coats thus giving rise to a microstructure having a gradient in composition. The introduction of such graded layers between the bond and top coats in a TBC system is believed to be an important factor in ensuring a sound bonding between them and thought to offer a great potential for increased service life due to microstructural and compositional stability at the interface [28].

![SEM micrograph of the polished cross section of the five layered coating system showing typical plasma sprayed microstructure and (b) EDS line scan analysis of the elements comprising the five layered FG-TBC system.](image)

**Figure 3.** (a) SEM micrograph of the polished cross section of the five layered coating system showing typical plasma sprayed microstructure and (b) EDS line scan analysis of the elements comprising the five layered FG-TBC system.

3.2. Surface Roughness

Surface roughness profiles of the five individual coatings were recorded by a 2D optical profilometer and are shown in figure 4. The results showed that coating C-1 (100% Ni) has the maximum Ra value whereas coating C-5 (100% MSZ) has the minimum Ra value. Furthermore, Ra values of the intermediate layers were found to be decreasing with an increasing amount of MSZ content in the cermets, respectively. The surface morphology of the sprayed coatings is thought to be strongly
dependent on the size and shape of the starting powder particles. The decrease in surface roughness of the coatings with an increasing amount of MSZ content is due to the fact that MSZ powder particles have a perfectly round morphology as compared to BC powder. Furthermore, MSZ powder has a particle size smaller than Ni powder and has a larger range of finer particles as compared to Ni powder [29].

![Image]

**Figure 4.** Surface roughness profiles of the as sprayed five individual coatings.

### 3.3. Microhardness measurements

Vickers microhardness (HV0.3) of the polished surfaces of five individual coatings were measured and drawn in order to simulate the coating system as shown in figure 5. It was observed that the microhardness changed gradually through the five layers of the coating in such a way that a sharp mismatch could be avoided. Therefore, it is expected that the absence of a sharp mismatch in microhardness due to the presence of compositionally gradient layers might cause suppression in the development of otherwise high residual stresses at the coating layers interfaces thus increasing the expected life of the TBC system [30-31].

![Image]

**Figure 5.** Microhardness distributions of the five individual layers comprising the TBC system

**Figure 6.** CTE values plotted as a function of temperature for five layered TBC system.
3.4. Measurement of CTE
Linear CTEs of the five individual freestanding coatings as a function of temperature from room temperature to 800°C on heating were plotted against temperature in order to simulate the conditions of the coating system as shown in figure 6. It was observed that coating C-5 exhibited the lowest linear expansion rates whereas coating C-1 exhibited the largest linear expansion rates. While for the cermet coatings, there was a gradual increase in the linear expansion rates with the reduction of MSZ content in the coatings (C-4, C-3, & C-2, respectively). It can also be seen from figure 6 that the CTE values of the five coated layers gradually increased thus steadily reducing the difference between their thermal expansion coefficients. This gradual variation in thermal expansion coefficients between the five deposited layers is expected to further reduce the level of residual stresses within the FG-TBC system.

3.5. Oxidation Behavior
SEM micrographs in as sprayed and oxidized conditions of the coating system after 100 hours at 800°C are shown in figure 7. As can be seen from figure 7 (b), a network of continuous cracks was formed on the surface of the coating after oxidation. These multiple cracks were formed because the top zirconia layer became thinner as the graded layers were introduced and this top layer started behaving like a thin single-layered zirconia coating. Such behavior has been reported for single layered zirconia coatings [32]. During oxidation, sintering, healing or bridging of these microcracks as marked by arrows can be seen as shown in figure 7 (c) [33]. Cross sectional SEM micrograph of the coating system within the top zirconia layer is shown in figure 7 (d). Both horizontal and vertical cracks were seen within the top zirconia layer.

![Figure 7. SEM micrographs of the coating system, (a) in as-sprayed condition, (b) after oxidation showing multiple surface cracks, (c) sintering of inter-splat microcracks and (d) cross section showing vertical and horizontal cracks within the top MSZ layer.](image-url)
Weight gain per unit area (mg/cm²) as a function of oxidation time of the TBC system is shown in figure 8 (a). The oxidation kinetic curve showed a sharp increase in weight gain for the initial 11 hours followed by an extensive period of slower weight gain rate throughout the oxidation period. The oxidation rate was calculated to be 0.0676 mg/cm²/hour. Oxidation kinetics was further examined to find out what oxidation rate law is more relevant to be followed by the coating. The relationship between the specific weight gain and the square root of time is shown in figure 8 (b). It was observed that the data almost fell along a straight line indicating that the oxidation kinetics obeyed a parabolic rate law according to the equation [34]:

\[ \Delta m/A = (k_p t)^{1/2} + C \]

where \( \Delta m/A \) is the weight gain per unit surface area (mg/cm²) at anytime t (h), \( k_p \) is the parabolic rate constant (mg²cm⁻⁴h⁻¹) and C is a constant.

![Figure 8](image1.png)
Figure 8. Oxidation kinetics after 99 hours at 800 °C, (a) weight gain as a function of time and (b) weight gain as a function of square root of time.

XRD patterns of the coating system oxidized at 800 °C for 99 hours and in as sprayed condition are shown in figure 9. Both the as sprayed coating and after oxidation treatment consisted of cubic zirconia (c-ZrO₂), monoclinic zirconia (m-ZrO₂) and cubic magnesia (c-MgO) phases. However, the intensity of the c-ZrO₂ peaks in the oxidized coating was found to be higher than those in the as sprayed coating. This may be due to the fact that at high temperature, through diffusion of the stabilizer (MgO), the metastable c-ZrO₂ phase transformed to the stable c-ZrO₂ phase [35].

![Figure 9](image2.png)
Figure 9. XRD patterns of the five layer coating system in as sprayed condition and after oxidation at 800 °C for 99 hours.

4. Conclusions
Microhardness changed gradually across the coating layers indicating no distinctive boundaries across the coating. There was a gradual increase in the CTE of the five coated layers thus steadily reducing the difference between their thermal expansion coefficients. Multiple surface cracks were formed in
oxidized coating. Oxidation kinetics was found to follow a parabolic rate law. No phase change was observed after oxidation however intensity of the c-ZrO$_2$ peaks was found to be increasing after oxidation as compared to as-sprayed condition.

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6. References

[1] Zhang Y Y, Deng H X, Shi H J, Yu H C and Zhong B 2012 Surf. Coat. Technol. 206 2977-85
[2] Okazaki M, Yamagishi S, Yamazaki Y, Ogawa K, Waki H and Arai M 2013 Int. J. Fatigue 53 33-39
[3] Wang X, Tint S, Chiu M and Atkinson A 2012 Acta Mater. 60 3247-58
[4] Bargraser C, Mohan P, Lee K, Yang B, Suk J, Choe S and Sohn Y H 2012 Mater. Sci. Eng. A 549 76-81
[5] Ramachandran C S, Balasubramanian V, Ananthapadmanabhan P and Viswabaskaran V 2012 Ceram. Int. 38 4081-96
[6] Yugeshwaran S, Kobayashi A and Ananthapadmanabhan P V 2012 J. Eur. Ceram. Soc. 32 823-34
[7] Kumar S and Cocks A C F 2012 J. Mech. Phys. Solids. 60 723-49
[8] Bhatti M B, Khalid F A and Khan A N 2012 J. Therm. Spray Technol. 21 121-31
[9] Liang J J, Matsumoto K, Kawagishi K and Harada H 2012 Surf. Coat. Technol. 207 413-20
[10] Hardwicke C U and Lau Y-C. 2013 J. Therm. Spray Technol. 22 (5) 564-76
[11] Song S-H, Xiao P and Weng L-Q 2005 J. Eur. Ceram. Soc. 25 1167-73
[12] Pan C and Xu X 2003 Surf. Coat. Technol. 162 194-201
[13] Darzens S and Karlsson A M 2004 Surf. Coat. Technol. 177-178 108-12
[14] Khor K A, Chia C T and Gu Y W 2000 Mater. Sci. Eng. A 279 166-71
[15] Sampath S, Jiang X Y, Matejicek J, Prchlik L, Kulkarni A and Vaidya A 2004 Mater. Sci. Eng. A 364 216-31
[16] Mahesh R A, Jayaganthan R and Prakash S 2008 Mater. Sci. Eng. A 475 327-35
[17] Choi H, Yoon B, Kim H, Lee C 2002 Surf. Coat. Technol. 150 297-308
[18] Portinha A, Teixeira V, Carneiro J, Martins J, Costa M F, Vassen R and Stoever D 2005 Surf. Coat. Technol. 195 245-51
[19] Khan A N and Qureshi I N 2009 J. mater. Process. technol. 209 488-96
[20] Khan A N, Khan S H, Ali F and Iqbal M A 2009 Comput. Mater. Sci. 44 1007-12
[21] Cho S H, Park S B, Lee J H, Hur J M and Lee H S 2012 Mater. Chem. Phys. 131 743-51
[22] Begley M R and Wadley H N G 2012 Acta. Mater. 60 2497-2508
[23] Khoddami A M, Sabour A and Hadavi S M 2007 Surf. Coat. Technol. 201 6019-24
[24] Kawasaki A and Watanabe R 2002 Eng. Frac. Mech. 69 1713-28
[25] Khor K A and Gu Y W 2000 Mater. Sci. Eng. A 277 64-76
[26] Schulz U, Peters M, Bach Fr-W and Tegeder G 2003 Mater. Sci. Eng. A 362 61-80
[27] Khor K A, Dong Z L and Gu Y W 1999 Mater. Lett. 38 437-44
[28] Kwon J-Y, Jung S-I, Lee S Y, Lee P H, Lee J H, Jung Y G, Paik U, Cho H and Chang J C 2010 Prog. Org. Coat. 67 95-101
[29] Demirkıran A S and E. Avcı 1999 Surf. Coat. Technol. 116–119 292-95
[30] Khor K A, Dong Z L and Gu Y W 2000 Thin Solid Films 368 86-92
[31] Khor K A and Gu Y W 2000 Mater. Sci. Eng. A 277 64-76
[32] Kokini K, Dejonge J, Rangaraj S and Beardsley B 2002 Surf. Coat. Technol.154 223-31
[33] Eriksson R, Brodin H k, Johansson S, Östergren L and Li X-H 2012 Surf. Coat. Technol. xxx
[34] Khor K A and Gu Y W 2000 Thin Solid Films 372 104-13
[35] Prawara B, Yara H, Miyagi Y and Fukushima T 2003 Surf. Coat. Technol. 162 234-41