# PREPARATION AND CHARACTERIZATION OF CERAMIC THERMAL BARRIER COATINGS BY SOLVENT BASED SLURRY METHOD

Norhayati Ahmad*, Noor Liyana Mazeni

Department of Materials, Manufacturing and Industrial Engineering,
Faculty of Mechanical Engineering, Universiti Teknologi Malaysia,
81310 Johor Bahru, Johor, MALAYSIA.

**ABSTRACT**

*The use of thermal barrier coatings (TBCs) to increase the combustion temperature in diesel engines has received considerable attention where one of the most promising of coating materials is mullite. The objective of this study is to characterize and assess the mechanical properties of various compositions of titanium and mullite mixtures for application as thermal barrier coating materials in diesel engines piston crown. In the present study, functionally graded coatings (FG-TBC) were deposited by solvent based slurry method using a simple surface coating machine. The microstructure, phase composition, adhesion strength and micro-hardness were found to change gradually through the three-layer functionally graded coatings which was beneficial for the improvement of mechanical properties of the coatings. The microstructure formed in the functionally graded coating is attributable to the degree of firing of the feedstock powder. With an increase in the percentage of titanium (increment by 10wt.%) in the intermediate composite layer, the adhesion strength and hardness of the coatings increased. Both micro-hardness and adhesion strength values were in correlation with the microstructural analysis, proportional to the presence of unmelted particles and pores in these coatings.*

**Keywords :** *Thermal barrier coatings, mullite, solvent based slurry method, adhesion strength*

## 1.0 INTRODUCTION

Thermal barrier coatings (TBCs) are generally multilayer ceramic coatings, over metallic surfaces, subjected to extreme thermal and chemical environments. The aim of this coating is to provide thermal insulation and oxidation resistance at high temperatures. The main requirement of a TBC is the low thermal conductivity but high resistance to thermal shocks, corrosion, erosion and wear [1]. Numerous applications of TBCs can be found in aerospace and automotive industries. 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. Diesel engine parts which used coating materials are piston, cylinder head cylinder sleeve and exhaust valves.

Many investigations have been conducted on various aspects of applying TBCs to the metal components in the internal combustion engines. Various techniques of coating which have been in use for different applications in automotive industry involve pack cementation, chemical or physical

*Corresponding author: nhayatiahmad@utm.my

vapour deposition (CVD/PVD), directed vapour deposition (DVD), thermal spray (plasma spray), magnetron sputtering, and slurry-based coating. Out of these techniques, the commercialized process for ceramic coatings has been plasma spray technique. Although the coating by all the aforementioned techniques has been successfully employed and shows good quality performances, the fabrication costs are still expensive as these techniques involved complex and high-technology equipment. As an alternative to overcome the limitation, relatively simple and low-cost slurry and firing methods for fabricating thermal barrier coating was utilized. Even though there have been insufficient discussions about TBC of engine part by this technique, there is a growing need to determine its viability for high temperature application.

Zirconia-based coatings currently has received the most attention and found to be most suited among the several ceramic materials evaluated for TBCs applications. Unfortunately, the biggest problem is that they are expensive for practical usage. More research should be performed to reduce its cost. Thereby, this study will be dedicated to develop novel TBCs as alternates of zirconia-based ones for diesel engine components. To this purpose, mullite coating has considerable potentials in this respect with its properties of low thermal conductivity, low coefficient of thermal expansion (CTE), good thermal stability, high resistance in highly oxidative and corrosive environments, and importantly mullite are comparatively cheaper than zirconia. Some of these properties make it particularly promising as a coating material for metal parts in diesel engine.

In this study, the preparation of mullite coating by solvent based slurry method as well as the characterisation and quality of the as-prepared mullite coating were reported. The main emphasis of this study is placed on investigating parameter of the coating process and its respective coating quality of the selected ceramic for TBCs application. Furthermore, to determine the mechanical properties of the coatings by adhesion and hardness tests, and assessing the influence of composition of coating layers towards microstructure and mechanical properties. This study hopes to establish ceramic coating as a cost effective means to increase the efficiency of thermal barrier coated diesel engines components.

## 2.0 METHODOLOGY

Stainless steel, with chemical composition 10 wt.% nickel, 16 wt.% chromium and 2 wt.% manganese, was used as substrate material. Substrate was cut into the dimension of 60 mm (length) x 30 mm (width) x 4 mm (height). Finally the substrate was sand blasted by silica with a grit size of 80-120 μm to enhance the surface roughness and guarantee the mechanical interlocking between the coating and substrate by using sand blasting machine (Growell Manufacturing). Average surface roughness (Ra), after blasting was about 3 µm. Stylus profilometer (MitutoyoSurftest SJ-301) was used in the measurement of surface roughness. Finally, steel substrate was degreased ultrasonically in ethanol. Commercial powders of mullite ($3Al_2O_3$-$2SiO_2$) and titanium were used as starting coating materials. The two powders were then pre-mixed with the percentage weight propotion of 60 wt.% Ti-40 wt.% M, 50 wt.% Ti-50 wt.% M and 40 wt.% Ti-60 wt.% M pre-mixed to form three powder blends. The compositions considered in the study are summarized in Table 1 and the employed TBC system is illustrated in Figure 1.

All coats were applied using solvent based slurry method. The TBC system considered in this study was prepared with the same individual and overall thickness of 100 µm and 300 µm respectively. Initially, a volume of distilled water solvent was added to the powder mixture and agitated using a magnetic stirrer. A dispersant was slowly added to the agitated solvent and allowed to mix before the poly(vinyl) alcohol binder was added to the slurry mixture. The mixture was stirred for four hours at 200 rpm to produce the required coating slurry. Typically the slurry mixture composes of a ceramic and metal powder (mullite and titanium powder), binder and dispersant, with the remaining percentage being distilled water.

In manufacturing the three-layer FG-TBC, the titanium powder was coated on to the substrate directly to form a bond coat (BC) about 100 µm thick. An automatic film applicator

(Sheen Instruments) was used for coating the stainless steel 316L substrate with the FG-TBC slurry composition. The coated sample was then allowed to dry under atmospheric condition for 48 hours. The coating was further dried in an oven at a temperature of 100°C for 2 hours. The sample was subjected to a heating rate of approximately 10°C/min up to the time the temperature reached 650°C where it was hold at that point for 30 minutes in order to effectively remove the binder present in the coating before the temperature in the muffle furnace was raised to 1000 °C. The sample was hold at that point for 3 hours to ensure the firing of the powder contained in the FG-TBC composition as to enhance the interdiffusion between adjacent lamellae and between adjacent layers.

Table 1 : Compositions of coating layers

| **Sample** | **Layer-1** | **Layer-2** | **Layer-3** |
|---|---|---|---|
| | wt.% Ti | wt.% Ti : wt.% M | wt.% M |
| **A** | 100 | 60 : 40 | 100 |
| **B** | 100 | 50 : 50 | 100 |
| **C** | 100 | 40 : 60 | 100 |


Figure 1 : Thermal barrier coatings (TBCs) systems

The same procedure in fabrication the first layer was repeated for the next layer according to Table 1 until a coated three-layer FG-TBC sample was obtained. The slurry mixture of metal-ceramic composite powders was coated successively to form intermediate layer (second layer), with the same thickness as the first one, 100 µm thick and finally, the mullite powder was coated as the top coat (TC). The thickness of the entire three-layer FG-TBC was about 300 µm.

The ceramic coatings were deposited on to the stainless steel substrate by solvent based slurry coating method. The samples were characterized by Field Emission Scanning Electron Microscope (FESEM) to determine the microstructure, Energy Dispersive X-ray (EDX) to analyse element distribution in the coating, and X-ray Diffractometer (XRD) were employed to investigate the phase of both mullite feedstock and as-prepared mullite coating sample. Mechanical properties of the coating were determined through the adhesion and Vickers micro-hardness tests.

## 3.0 RESULTS AND DISCUSSION

The surface and cross-sectional images of the feedstock powder and coated samples were observed by FESEM. Fig. 2 shows FESEM micrograph for thermal barrier coatings of mullite top coat (sample A). The micrograph shows the surface of the coating which is quite smooth but still exhibits some protrusions, pores and as well as a few unmelted mullite powders. Surface of this coating did provide some information regarding pore healing as a result of firing. Mullite coating is fired below the suggested firing temperature (at temperatures between 60 and 90% of the melting-point of mullite) and it still possesses some un-molten and semi-molten powders. To sum up, the temperature of 1000°C was not sufficient for the ceramic to be completely sintered. The mullite coating prepared in this study shows relatively good coverage over intermediate composite layer of titanium-mullite of any composition with some rises and dimples. As can be seen from the cross-sectional micrographs (Fig. 3), as-prepared mullite coating shows a good coated layer with uniform interface of all layers.

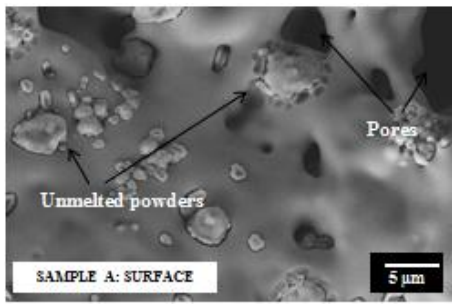



Figure 2 : Surface morphology of mullite top coat by FESEM

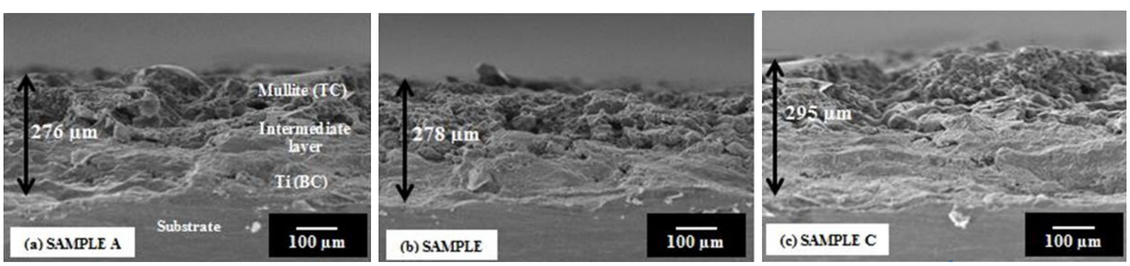
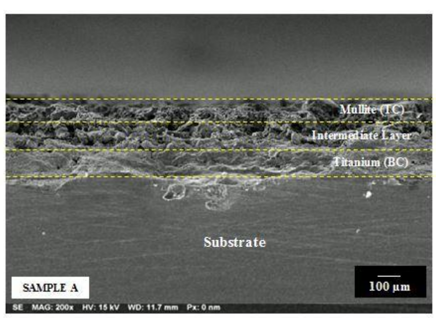



Figure 3 : FESEM cross-sectional micrographs for thermal barrier coatings for (a) sample A, (b) sample B and (c) sample C

(a)



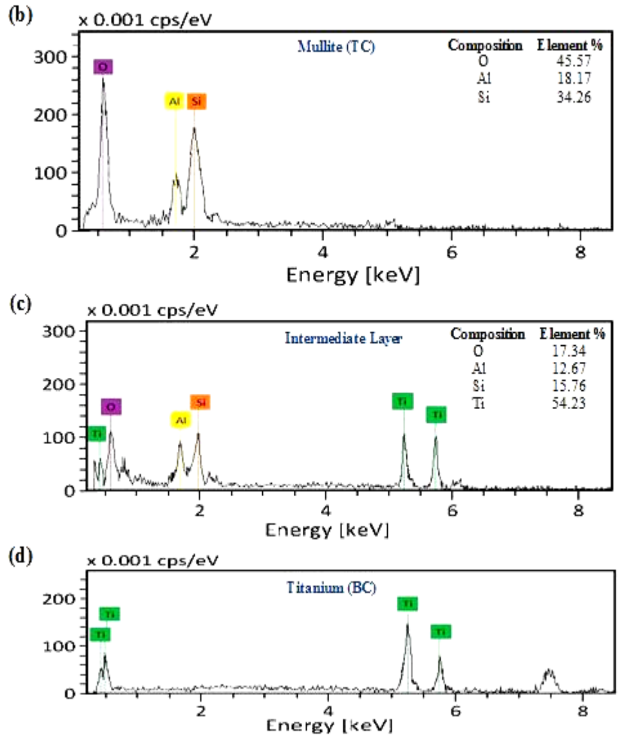



Figure 4 : Cross-section morphology and EDX analysis of FG-TBC (sample A)

From Fig. 3 , coating with the highest amounts of titanium for sample A (60 wt.%) obtained the lowest coating thickness which seems to be approximately 276 µm (Fig. 3a) compare to sample C (highest thickness of 295 um, Fig. 3c). If we focus on the cross-sectional image of the titanium coating sitting on the substrate, it shows a dense and compacted structure. The cross section indicates a smooth interface at the substrate and bond-coat junctions and suggests good adherence to each other. No apparent microcracks appear implying that good adhesion is reached between the bond coating and stainless substrate and between the bond coating and composite intermediate layer, though it is hard to distinguish the intermediate layer from bond coat layer from the micrograph. It is likely that complete melting of feedstock powder during firing process result in good integrity and homogeneity of the titanium coatings.

The microstructures of the FG-TBC layers appear to be affected by the firing temperature and sinterable particles. This is important as the optimal firing temperature is not yet finalized as a lot of consideration need to be taken. Thus, further research need to be carried to look at optimization of the firing conditions. It is believed that varying the firing parameters will significantly affect the mechanical properties of the coatings, and further tests are expected to be performed to confirm this.

Fig. 4 shows the EDX result of a three layer FG-TBC for sample A. From EDX spectrum, the titanium bond coat, intermediate layer and mullite top coat can be distinguished easily (Fig. 4). Three areas were analysed by EDX: bond coat, intermediate and top coat layer. The application of EDX analysis confirmed the presence of elements in each of the coating layers. EDX spectrum reveals that the component of the top coat layer is mainly composed of O, Al and Si elements which is consistent with their being composed of a mixture of mullite ($3Al_2O_3.2SiO_2$) and alumina. The X-ray diffraction spectrum shown in Fig. 5 confirms that mullite and α phase of $Al_2O_3$, are present, being the main crystalline constituents. From Fig. 4c, it can be seen that the second intermediate layer mainly contains Ti element, as well as elements in mullite; O, Al, and Si. The ratio of Ti and mullite almost reaches 60:40. It illustrates that the major element is Ti in the second coating layer.

As the first layer was deposited by pure titanium as the bond coat, it composed of Ti only. Fig. 5 shows the XRD patterns of mullite powders and as-sprayed mullite coating obtained recorded in the 2θ range of 20-90˚. It can be seen that the mullite powder contain mullite ($3Al_2O_3.2SiO_2$) as the main crystalline phase as well as $\alpha$-$Al_2O_3$ and $SiO_2$ (cristobalite) as the minor constituent.Formation of SiO phase is weakly evidenced in the general shape of the background in the XRD pattern of mullite powder. As-prepared mullite coating contains the XRD signals of the crystalline phases of mullite and $\alpha$-$Al_2O_3$. The crystallinity of the material is evident from the fairly sharp diffraction peaks.Crystalline $\alpha$-$Al_2O_3$ in the coating is associated with unmelted or semimolten particles.

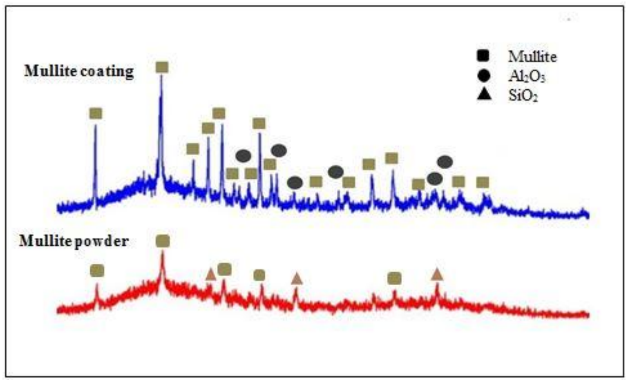



Figure 5 : XRD patterns of mullite powders and as-prepared mullite coatings

Fig. 6 shows the result of the adhesion test conducted on the three coated FG-TBC samples, tested on each coating layer. In this study, the lowest coating thickness (276 µm) which was obtained by sample A (Fig. 3a) showed the highest adhesion strength whereas sample C with the highest coating thickness (295 µm), showed the lowest strength of adhesion. Coating with lower thickness show higher adhesion due to lesser internal stress. Barely visible interface in Fig. 3a was found in this study between the adjacent layer of bond coat and intermediate layer suggesting an almost continuous microstructure. All these factors attributed to the increment of adhesion strength as the coating layer increase.

Regarding the adhesion strength of second layer; titanium and mullite composite coatings which decreased with an increase in the mullite-mixing ratio, the adherence of the intermediate composite coating was minimum when the ratio of mullite to titanium was 60:40 (sample C). It is noted that the adherence improved when the titanium content was higher. Sample A shows the highest adhesion strength amongst the three coated samples. It can be due to the higher composition of titanium to mullite in the second layer.

It can be seen that the adhesion strength of the coating increase with an increase in the coating layer. According to S. Zhang et al. (2008), the adhesion strength between the coating and substrate comes from two aspects, the mechanical interlocking and the chemical bonding. In current study, since the substrate was sand blasted before coating with average surface roughness of 3 µm, it enables the mechanical interlocking between the stainless steel and Ti powder. Furthermore, the increase in the adhesion strength as the coating layer increase is attributed to the stronger chemical bonds, which were developed at the coating-substrate, bond coat-intermediate coat, and intermediate coat-top coat interface during coating deposition process, especially at the firing stage.
According to E. Altuncuet al. (2012), the residual stress is believed to be an important effective factor on the adhesion properties of coatings. In the FG-TBC system, the composition of layers changed gradually from purely metallic (BC) to metallic/ceramic mixtures (intermediate layer) to purely ceramic (TC) resulted in reduced levels of residual stresses which otherwise might be quite high in case of duplex TBC due to compositional mismatch at the interface (M.N. Baiget al., 2014).

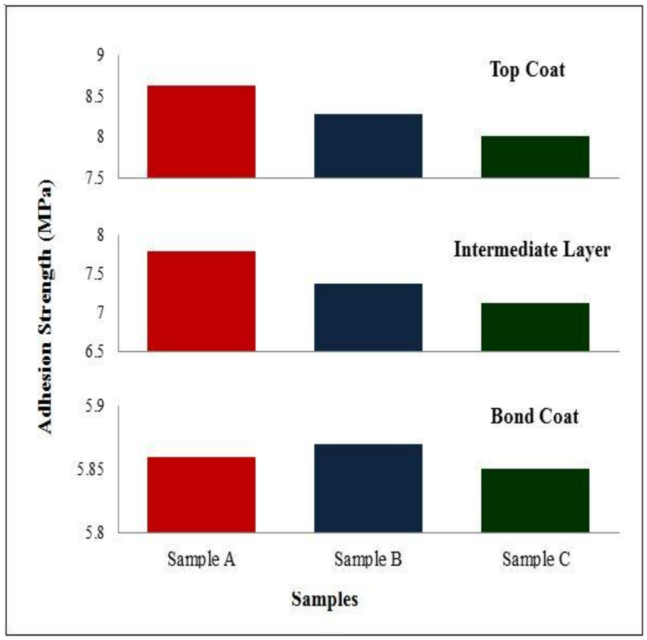



Figure 6 : The adhesion strength of the FG-TBC samples

The residual stress is believed to be an important effective factor on the adhesion properties of coatings and may be affected by some factors such as coating thickness, substrate temperature, process parameters and others. According to A.M. Khoddamiet al. (2007), the fracture toughness of bond coat is much higher due to its metallic nature as compared to the ceramic coat. Consequently, the presence of metallic Ti in the functionally graded layer might improve overall fracture toughness of the coating system and the crack growth rate maybe decreased. These factors are believed to be the major contributors in improving the adhesion strengths of the FG-TBC especially sample A which have the highest composition of Ti in the second intermediate layer other than pure Ti in the bond coat. This also explained why the metallic bond coat has the highest individual adhesion strength when compared to the intermediate and ceramic top coat layer for the three coated sample. Adherence of coatings also depends on the amount of un-melted particles and pores in the coating. In other word, un-melted particle ratio affects the porosity. Presence of any porosity generally decreases adhesion test values since a pore of critical size can induce a macroscopic failure with the stress applied (A. Venclet al., 2011). Sample C showed the lowest values of adhesion strength (8.01 MPa). These results are in correlation with the cross-section microstructure (Fig. 3c) since the presence of un-melted particles and pores of mullite were the highest in this coating compared to the other two coatings. Therefore, the improvement in the adhesive properties of the coatings can mainly be achieved by decreasing the volume fraction of porosity and reducing un-melted areas.

The overall results of Vickers micro-hardness distribution for three coated FG-TBC samples, determined at indentation load 3N, are depicted in Fig. 7. Based on the observation in the figure, the Vickers hardness of the as-prepared mullite coatings are far below that of bulk mullite (1256 Hv). This phenomenon can be understood and related by the fact that the indentation response of coating is governed not only by the intrinsic hardness of the material but also by the special microstructure of the deposited coating, such as a certain amount of pores. Mullite top coat had a very low hardness value due to high levels of porosity. Hence, the measured hardness value is a little lower than actual hardness. The decrease in micro-hardness for the coated samples is due to the increase in porosity along the cross-section that might be explained by incomplete firing of mullite ceramic during heat treatment at 1000˚C where the suggested firing temperature for mullite should be at least around 1200˚C.

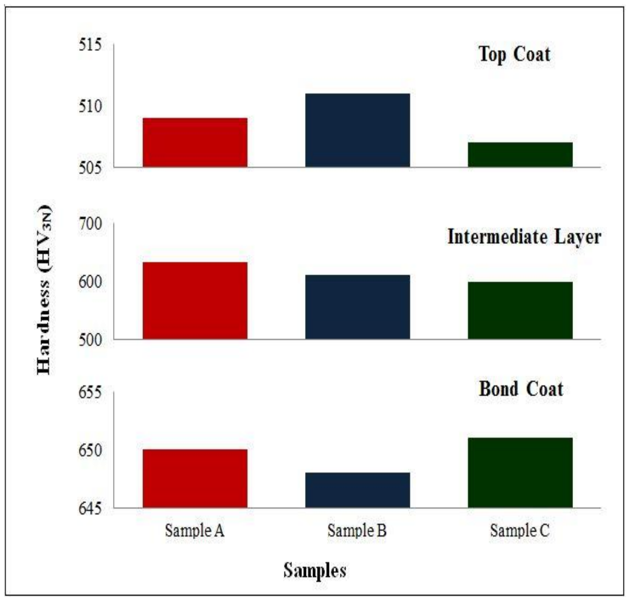



Figure 7 : Micro-hardness measurements of the FG-TBC samples

The mullite top coat is mechanically weakened with increasing pores and residual stresses. To put differently, the reduction in the porosity contributes to an increase of the hardness within coatings. Sample A has a less decrease in hardness value among the three coated samples because the variation in porosity is minor too. As the intermediate composite layer consists of higher percentage of titanium, the sinterable particle is higher than sample B and C which consist of lower titanium constituent. The higher hardness values for the coating are due to the effective firing of titanium powder. After firing, all of the first coating layer show higher values for the micro-hardness. In addition, the micro-hardness of the titanium bond coat was measured and gave constant values along the cross-section (about 650 Hv).

## 4.0 CONCLUSIONS

Functionally graded thermal barrier coatings (FG-TBC) for diesel engine piston crown have been obtained through solvent based slurry method. The coatings were compositionally graded with different titanium/mullite ratio. These composite powders (were used as feedstock to form the gradient intermediate layer). The microstructure, phase composition, adhesion strength and micro-hardness were found to change gradually through the three-layer functionally graded coatings which was beneficial for the improvement of mechanical properties of the coatings. The microstructure formed in the functionally graded coating is attributable to the degree of firing of the feedstock powder. With an increase in the percentage of titanium (increment by 10wt.%) in the intermediate composite layer, the adhesion strength and hardness of the coatings increased. Both micro-hardness and adhesion strength values were in correlation with the microstructural analysis, proportional to the presence of un-melted particles and pores in these coatings.

## ACKNOWLEDGEMENT

Special thanks to Malaysian Government through Ministry of Higher Education Malaysia for Fundamental Research Grant Scheme (FRGS) Vot No 4F552/4F808 and contract research grant Vot No 4C044 to enable the research being conducted.


## REFERENCES


[1] A.M. Khoddami, A. Sabour, S.M.M. Hadavi (2007). Microstructure formation in thermally-sprayed duplex and functionally graded NiCrAlY/yttria-stabilized zirconia coatings, Surface and Coatings Technology, 201, 6019-6024.

[2] A.Vencl, S. Arostegui, G. Favaro, F. Zivic, M. Mrdak, S. Mitrovic, V. Popovic (2011). Evaluation of adhesion/cohesion bond strength of the thick plasma spray coatings by scratch testing on coatings cross-sections, Tribology International, 44, 1281-1288.

[3] E. Altuncu, F. Ustel (2012). Adhesion Properties of The Plasma Spray Coatings, Metal, 23, 25-31.

[4] M.K. Pathak, K.K.S. Mer, P.K. Pant, S.S. Samant (2013). Applications of Thermal Barrier Coatings on the Performance Parameters of Diesel Engines, International Journal of Research in Mechanical Engineering & Technology, 68-72.

[5] M.N. Baig, F.A. Khalid, F.N. Khan, K. Rehman (2014). Properties and residual stress distribution of plasma sprayed magnesia stabilized zirconia thermal barrier coatings, Ceramics International, 40, 4853-4868.

[6] S. Zhang, Y.S. Wang, X.T. Zeng, K.A. Khor, WenjianWeng, D.E. Sun (2008). Evaluation of adhesion strength and toughness of fluoridated hydroxyapatite coatings, Thin Solid Films, 516, 5162-5167.