PERFORMANCE OF THERMAL BARRIER COATINGS PRODUCED BY SMART PLASMA PROCESSING

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Thermal barrier coating typically comprising of bondcoat and yttrium stabilized zirconium topcoat, has been used to improve the efficiency of turbine engine by providing the capability to sustain significant temperature gradient across the coating. Alumina and zirconia composite coating was proposed as a potential candidate to improve the qualities of thermal barrier coating system due to its low melting point and high hardness. The gas tunnel type plasma system, which has high energy density and also high efficiency, is useful for smart plasma processing. The characteristics of the obtained ceramic coatings such as Al_2O_3 and ZrO_2 coatings were superior to the conventional ones. The ZrO_2 composite coating has the possibility of the development of high functionally graded TBC (thermal barrier coating). In this study, the performance such as the mechanical properties, thermal behavior and high temperature oxidation resistance of the alumina/zirconia functionally graded TBCs produced by gas tunnel type plasma spraying was investigated and discussed. The results showed that the alumina/zirconia composite system exhibited the improvement of mechanical properties of thermal barrier coatings and oxidation resistance.

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1. INTRODUCTION

Zirconia sprayed coatings are widely used as thermal barrier coatings (TBC) for high temperature protection of metallic structures in gas turbine hot section components such as burners, transition ducts, vanes and blades. It allows the high temperature operation and results to increasing the efficiency of the engine and the durability of the critical components. However, their use in diesel engine combustion chamber components has been quite rare, because of the long run durability problems in such conditions. The main problem is the spallation at the interface between the coating and substrate due to the interface oxidation [1]. Although zirconia coatings have been used in many applications, the interface spallation problem is still waiting to be solved under the critical conditions such as high temperature and high corrosion environment. For that reason, there have been many investigations in developing proper TBCs for diesel engines [2,3].

It is reported that the spallation rate can be reduced but not completely by using suitable bond coats for the interface [4]. Nevertheless, it is difficult to find suitable bonding layers for all kind of substrate material. Alumina and zirconia composite coating was proposed as a potential candidate to improve the qualities of thermal barrier coating system due to its low melting point and high hardness. Also, extremely high porosity values (up to 25 vol%) of TBC s have been obtained by functionally graded layer of alumina. TBC failure occurs easily at the interface between the metallic bondcoat and topcoat. During high temperature service an oxide scale consisting mainly of α-alumina forms along bond/topcoat interface.

The resistance for thermal shock and high temperature corrosion are important properties in the high performance TBC. For TBC, the spalling of the coating is also very important problem as well as the coating quality. New type plasma spray methods are expected for using the excellent characteristics of ceramics such as corrosion resistance, thermal resistance, and wear resistance [5] by reducing the porosity and increasing the coating density.

The gas tunnel type plasma spraying developed by the author can make high quality ceramic coatings such as Al_2O_3 and ZrO_2 coating [6] compared to other plasma spraying method. A high hardness ceramic coating such as Al_2O_3 coating by the gas tunnel type plasma spraying, were investigated in the previous study in detail [7-10]. Usually, the Vickers hardness of this sprayed coating became 20…30% higher than that of conventional plasma spraying. And, the porosity was half of the value of the conventional ones.

The Vickers hardness of the zirconia (ZrO_2) coating was increased with decreasing spraying distance, and a higher Vickers hardness of about $Hv = 1200$ could be obtained at a shorter spraying distance of $L = 30$ mm [11]. This corresponds to the hardness of sintered ZrO_2: $Hv = 1{,}300$. ZrO_2 coating formed has a high hardness layer at the surface side, which shows the graded functionality of hardness [12,13]. With the increase in the traverse number of plasma spraying, the hardness distribution was much smoother, corresponding to the result that the coating became denser.

In this study, composite thermal barrier coatings (TBCs) of $Al_2O_3+ZrO_2$ were deposited on SS304 substrates by gas tunnel type plasma spraying. The performance such as the mechanical properties, thermal behavior and high temperature oxidation resistance of the alumina/zirconia functionally graded TBCs was investigated and discussed. The adhesive characteristics of such high hardness zirconia-alumina (ZrO_2-Al_2O_3) composite coatings were also investigated as well as its mechanical properties.

The resultant coating samples with different $Al_2O_3+ZrO_2$ mixing ratio and thickness are compared in their corrosion resistance with Al_2O_3 percentage and coating thickness as variables. Corrosion potential and deactivated corrosion current density are measured and analyzed corresponding to the microstructure of the coatings.

2. EXPERIMENTALS

2.1. CHARACTERISTICS OF GAS TUNNEL TYPE PLASMA SPRAYING

Figure 1 shows the gas tunnel type plasma spraying torch [4,6,7,8,9]. The spraying powder is fed inside plasma flame in axial direction from center electrode of plasma gun. So, the spraying powder was molten enough in the plasma, and the plasma spraying for high melting point ceramics is available. The coating is formed on the substrate traversed at the spraying distance: *L*. In this case, the gas divertor nozzle diameter was *d*=20 mm. It can be easy to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying.

2.2. EXPERIMENTAL PROCEDURE

The gas tunnel type plasma spraying torch used was shown in Fig. 1. The experimental method to produce the ceramic coatings by means of the gas tunnel type plasma spraying is as follows. After igniting plasma gun, the main vortex plasma jet is produced in the low pressure gas tunnel. The spraying powder is fed from center inlet of plasma gun. The coating was formed on the substrate traversed at the spraying distance of *L*.

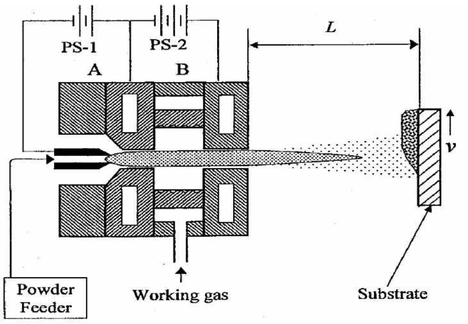

Fig.1. Schematic of the gas tunnel type plasma spraying torch

The experimental conditions for the plasma spraying are shown in Table 1. The power input to the plasma torch was about $P = 25$ kW, and the power input to the pilot plasma torch, which was supplied by the power supply PS-1, was turned off after starting of the gas tunnel type plasma jet. The spraying distance was short distance of $L = 40$ mm.

Table 1. Experimental conditions

Powder:	ZrO_2+Al_2O_3 Mixture
Traverse number: N	1~30
Power input, *P* (kW):	25~28
Working gas flow rate, *Q* (l/min):	180
Powder feed gas, *Q feed* (l/min):	10
Spraying distance, *L* (mm):	40
Traverse speed, *v* (cm/min):	25~1000
Powder feed rate: *w* (g/min):	20~35
Gas divertor nozzle dia., d (mm)	20

The working gas was Ar gas, and the flow rate for gas tunnel type plasma spraying torch was $Q = 180$ l/min, and gas flow rate of carrier gas was 10 l/min. The powder feed rate of zirconia/alumina mixed powder was $w = 20$~35 g/min. The traverse speed of the substrate was changed the value from *v*=25 to 1000 cm/min. Also the traverse number was changed 1…30 times. The thickness of the coating was 50~250 μm.

The chemical composition and the particle size of Zirconia (ZrO_2) and/or alumina (Al_2O_3)powder used in this study was respectively shown in Table 2. This ZrO_2 powder was commercially prepared type of K-90 (PSZ of 8% Y_2O_3), and Al_2O_3 powder was the type of K-16T. The substrate was SUS304 stainless steel (3x50x50), which was sand-blasted before using.

2.3. ANALYSIS OF COATING PROPERTIES

Micro-structural characterization of thermal sprayed coatings involves quantitative measurements of geometrical features such as porosity (in the form of voids, cracks and other defects) and analysis of material aspects in the coatings such as splat structure, interfaces, phases, etc. The microstructure of the cross section of zirconia composite coating was observed by an optical microscope in this research. The microscope is equipped with a CCD camera for image acquisition. Micrographs with two magnifications (200 X and 400 X) taken on polished cross sections are used for determining the total porosity and coating thickness by using image analysis software.

Table 2. Chemical composition and size of zirconia and alumina powder used (20~80% Al_2O_3 Mixture)

	Composition (wt%)					Size (μm)
ZrO_2	ZrO_2	Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	
	90.78	8.15	0.38	0.20	0.11	10…44
Al_2O_3	Al_2O_3	Na_2O	SiO_2	Fe_2O_3		
	99.8	0.146	0.01	0.01		10…35

The Vickers hardness Hv_{50}, Hv_{100} of the sprayed coatings was measured at the non-pore region in those cross sections under the condition that the load weight was 50 g, 100 g and its load time was 15s, 25 s. The Vickers hardness: Hv_{100} was calculated as a mean value of 10 point measurements. The distribution of the Vickers hardness in the cross section of the coating was measured at each distance from the coating surface in the thickness direction.

The adhesive strength between the ZrO_2 composite coating and the substrate was measured by using the tension tester original designed. The test piece for adhesive strength was 10mm square and the coating surface side and substrate side was respectively attached to each holder by polymer type glue. The kgf/cm^2 was used as a unit for the adhesive strength of the composite coating.

The schematic of anodic polarization corrosion system is shown in Fig. 2, which is a normal potentiostatic polarization corrosion tester, which is using a Hokuto Denko, HA303 power source. An Ag/AgCl reference electrode (SCE) was inserted in saturated KCl solution and was connected galvanically to the test cell by a self-made salt-bridge. A platinum wire used as the counter electrode was immersed in the reaction cell containing 500 ml corrosion media of 0.5 M HCl solution. HCl solution was chosen as corrosion media because Cl^- ions are assumed passing through the coating layer more easily than another commonly-used anodic oxidant SO_4^{2-}

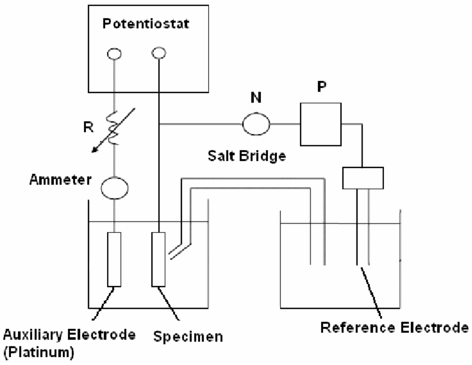

Fig.2. Anodic Polarization Corrosion Tester

The sample surfaces were degreased by ultrasonic process in acetone for 5 minutes then were washed by

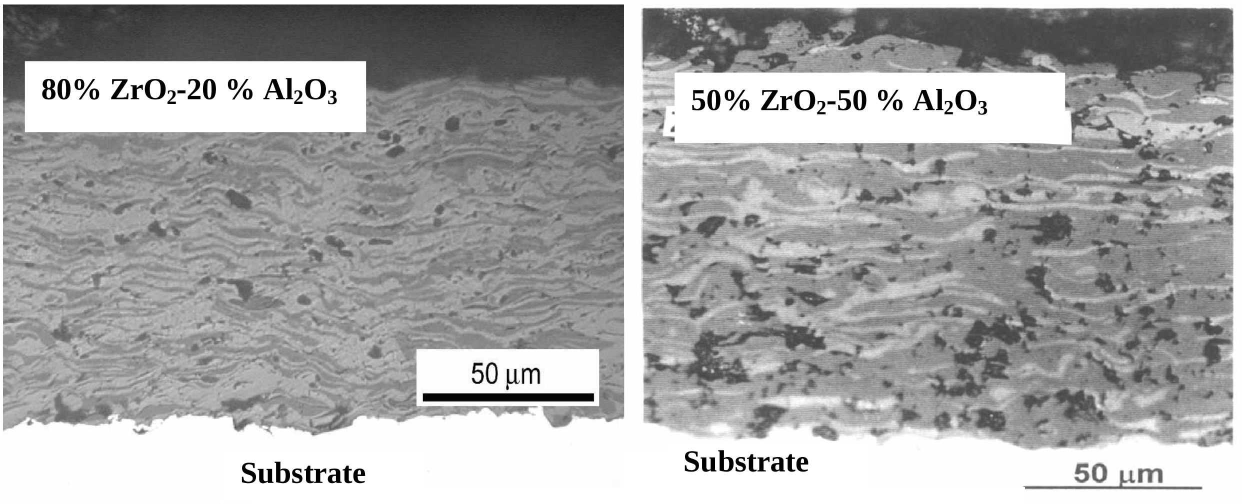

Fig. 3. Micrographs of the cross-section of coating samples

distilled water before putting into test. The cleaned sample was held by a well-designed sample holder and immersed in the testing media for 15 min to stabilize its galvanic contact with the solution, then the sample potential was set to -0.5V and was swept to +0.5V at a rate of 10 mV/s. All the tests were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. MICROSTRUCTURE AND VICKERS HARDNESS OF ZIRCONIA COMPOSITE COATING

Typical optical cross sectional micrographs for thermal barrier coatings are shown in Fig 3. Those are the zirconia composite coatings of 20% and 50%Al_2O_3 mixture. The coatings have a porous and lamellar structure which is characteristic for this kind of coatings. The thickness was about 150 µm.

The composition of the microstructure is represented by gray level variation. It consisted of 2 different layers, white and gray layers were deposited alternatively. The analysis by EPMA revealed that white was zirconia (ZrO_2) and gray was alumina (Al_2O_3). Pores appear to be dark, which permit them to be distinguished and quantified by image analysis.

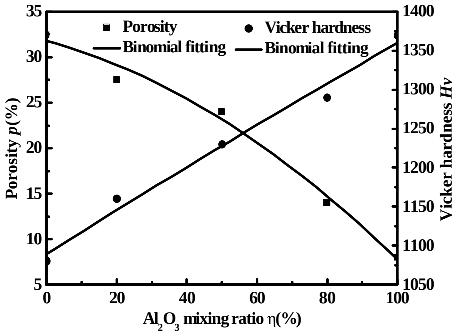

Fig.4. Dependence of Vickers hardness of zirconia composite coating on the alumina mixing rate; 2 times traverse at L=40 mm when P=25 kW

Fig. 4 shows the relationships between Vickers hardness and porosity of the ZrO_2 composite coatings and the alumina Al_2O_3 mixing ratio *R* (wt%), at the same spraying time. In this case, the coating thickness was approximately 200 µm at P = 25 kW, L = 40 mm, when the traverse number was two times.

The average Vickers hardness over the cross section of zirconia composite coatings is increased with the increase of the alumina mixing ratio. The increment of coating hardness corresponds to attendance of alumina particles with hardness higher than that of zirconia the Vickers hardness of Al_2O_3 coating was Hv_{50} = 1360.

The average porosity over the coating layer shows a decrease tendency with increasing alumina mixing ratio. In the meanwhile, the porosity profile (shown in Fig. 6) over the coating cross-section gives an almost linearly graded distribution.

3.2. GRADED FUNCTIONALITY OF COMPOSITE COATING

The hardness distribution of the ZrO_2composite coating has remarkable graded functionality in the case of large Al_2O_3 mixing ratio. Because, the part near the substrate did not change so much, but the Vickers hardness near the coating surface became much higher.

Figure 5 shows the distribution of Vickers hardness: Hv_{50} of the zirconia/alumina composite coating shown in Fig. 3 (coating thickness: about 150 µm). The distribution of this composite coating has a highest value in the coating at the surface side. The maximum hardness was near to $Hv_{50} = 1300$ at the coating surface of $l = 40$ µm, and decreased linearly like towards the substrate side.

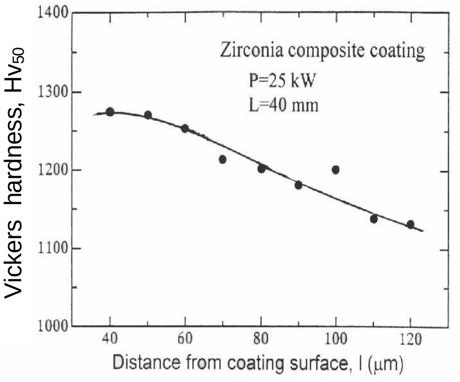

Fig. 5. Distribution of Vickers hardness: Hv_{50} of the zirconia/alumina composite coating

While, the porosity profile (shown in Fig. 3) over the coating cross-section gives an almost linearly graded distribution, increasing from the surface of the coatings towards the surface of the substrate, as shown in Fig.6. In as-sprayed condition the porosity variation ranges from 18.95 to 33.23% from the surface of the coatings to the surface of the substrate. Although lower porosity can increase the average hardness of the coatings, alumina presence in the coatings is the origin of the improved hardness because higher mixing ratio of alumina results in lower porosity.

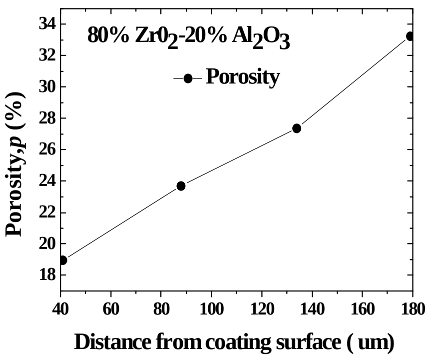

Fig. 6. Porosity distribution over coating cross-section

3.3 OXIDATION OF ZrO_2 COMPOSITE COATING

After heat treatment at 1050 °C for 5 h, the ZrO_2 coating system showed spallation from the substrate. But the Al_2O_3 coating showed no spallation even failure occurred after exposure at the same heat treatment condition. The delamination failure is due to large thermal stresses developing within the coating and the phase transformation of Al_2O_3. Analytical model showed that plasma sprayed Al_2O_3 layer should be very thin since thicker layer would generate larger residual tensile stress.

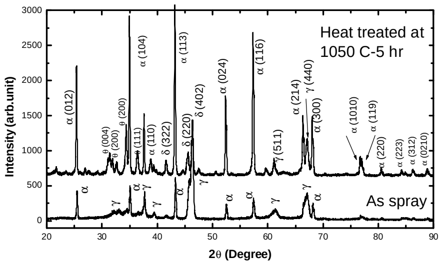

Fig.7. XRD patterns of as sprayed coating and coating after heat treatment

To evaluate phase transformation of Al_2O_3 due to plasma spray process, free standing Al_2O_3 layer was oxidized at 1050 °C for 5 h. X-ray diffraction was conducted to examine phases of the sprayed layers. A comparison of diffraction patterns of the as-sprayed and heat-treated Al_2O_3 is summarized in Fig.7. The α-Al_2O_3 that was formed during plasma spray undergoes a phase transformation to a more stable α-Al_2O_3 during heat treatment, although some fraction of γ phase was retained in the coating. Other phases, namely δ-, θ- Al_2O_3 were also identified. It is noted that the transformation of γ to α had never been direct such that δ and θ phases can be regarded as the intermediate phases, suggesting that the transformation of γ to (δ,θ) to α occurred in the annealed coating. The phase transformation of α to γ involves a volume change, resulting in additional residual stresses. Density values of coated samples believed that an additional volume change could be attributed to the porosity closing during heating.

3.4 ANODIC CORROSION POLARIZATION CHARACTERISTICS OF ZrO_2 COMPOSITE COATING

Figure 8 presents the anodic corrosion polarization characteristics of the samples coated with different thickness of 80% ZrO_2+ 20%Al_2O_3 mixture coating. All the curves are obtained from their first polarization scan. From the curves, their corrosion potentials increase clearly with the coating thickness. However, their corrosion current shows a complicated tendency with the coating thickness, which is possibly due to the complex bonding states of the coatings to the substrates because the effective area of the substrate exposed to the corrosion media is responsible for the corrosion current.

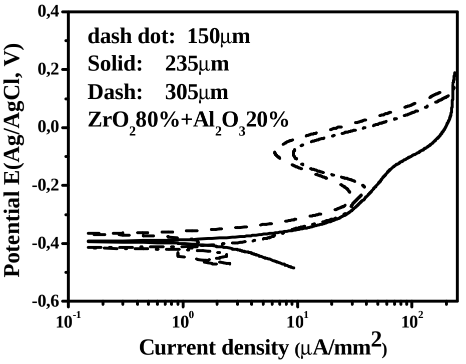

Fig.8 Corrosion curve of coatings with different thickness

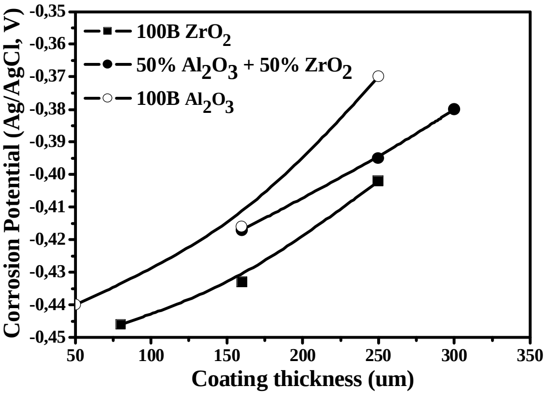

Fig.9. Corrosion potential versus thickness and composite

Figure 9 displays the relationships of the corrosion potential of the tested samples to the alumina mixing ratios and thickness. As expected, the trends show that the corrosion potential goes up slightly with both the alumina content ratio and coating thickness. Theoretically, high corrosion potential means lower electrochemical activity and higher oxidation resistance. So, in conclusion, higher thickness and lower porosity sprayed coatings lead to increase of corrosion resistance because both higher thickness and lower porosity provide stronger diffusion resistance to prevent the anodic oxidants of the corrosion solution from accessing the interface of the coated samples.

CONCLUSIONS

The performance such as the mechanical properties, thermal behavior and high temperature oxidation resistance of the ZrO_2/Al_2O_3 composite coating produced by gas tunnel type plasma spraying was investigated, and the following results were obtained.

1)The ZrO_2 Al_2O_3 composite coating has graded functionality on the hardness and the porosity, and has a possibility of the development of high functionally graded TBC (thermal barrier coating).

2)The effect of alumina mixing on the Vickers hardness of the ZrO_2 composite coating was also clarified in order to develop high functionally graded TBC.

3) The ZrO_2 composite system exhibited the improvement of mechanical properties of thermal barrier coatings and oxidation resistance.

4)The α-Al_2O_3 that was formed during plasma spraying undergoes a phase transformation to a more stable α-Al_2O_3 during heat treatment, although some fraction of γ phase was retained in the coating. The high temperature oxidation behavior of the functionally graded TBCs showed the effectiveness of Al_2O_3 layer functioning as an oxidation barrier.

5)The higher alumina content and thicker coatings, the better the corrosion resistance, which is attributed to the diffusion resistance of the coating layers to corrosion reaction.

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ИСПОЛЬЗОВАНИЕ ТЕРМИЧЕСКИХ БАРЬЕРНЫХ ПОКРЫТИЙ, ПОЛУЧЕННЫХ ТОНКОЙ ПЛАЗМЕННОЙ ОБРАБОТКОЙ

А. Кобаяши

Термическое барьерное покрытие (ТБП), обычно состоящее из связывающего слоя и верхнего покрытия из окиси иттрия, стабилизированного окисью циркония, используется для улучшения эффективности двигателя турбины благодаря способности выдерживать значительные поперечные градиенты температуры. Покрытие, состоящее из окиси алюминия и циркония было предложено как возможный кандидат для улучшения качества сложного ТБП из-за его низкой точки плавления и высокой твердости. Плазменная система газо-тоннельного типа, имеющая высокую плотность энергии и высокую эффективность, является удобной для тонкой плазменной обработки. Характеристики полученных керамических покрытий, таких как Al_2O_3 и ZrO_2, оказались лучше обычных. Сложное покрытие ZrO_2 оказалось пригодным для разработки высоко-функционального ступенчатого ТБП. Настоящее сообщение посвящено изучению и обсуждению ряда свойств, полученных с помощью газо-тоннельного плазменного распыления ступенчатых Al_2O_3 / ZrO_2 функциональных ТБП, таких, как механические свойства, поведение при высоких температурах, стойкость к окислению при высокой температуре. Результаты свидетельствуют о том, что покрытия Al_2O_3 / ZrO_2 обеспечивают улучшение механических свойств ТБП и их стойкость к окислению.

ВИКОРИСТАННЯ ТЕРМІЧНИХ БАР'ЄРНИХ ПОКРИТТІВ, ОТРИМАНИХ ЗА ДОПОМОГОЮ ТОНКОЇ ПЛАЗМОВОЇ ОБРОБКИ

А. Кобаяши

Термічне бар'єрне покриття (ТБП), що звичайно складається із зв’язуючого шару і верхнього покриття з окислу ітрію, стабілізованого окислом цирконію, використовується для поліпшення ефективності двигуна турбіни завдяки здатності витримувати значні поперечні градієнти температури. Покриття, що складається з окислу алюмінію і цирконію було запропоновано як можливий кандидат для поліпшення якості складного ТБП, завдяки його низькій точці плавлення і високій твердості. Плазмова система газо-тунельного типу, що має високу густину енергії і високу ефективність, є зручною для тонкої плазмової обробки. Характеристики отриманих керамічних покриттів, таких як Al_2O_3 і ZrO_2, виявилися краще звичайних. Складне покриття ZrO_2 виявилося придатним для розробки високо-функціонального ступінчастого ТБП. Дане повідомлення присвячено вивченню й обговоренню ряду властивостей, отриманих за допомогою газо-тунельного плазмового розпилення ступінчастих Al_2O_3 / ZrO_2 функціональних ТБП, таких, як механічні властивості, поводження при високих температурах, стійкість до окислювання при високій температурі. Результати свідчать про те, що покриття Al_2O_3 / ZrO_2 забезпечують поліпшення механічних властивостей ТБП і їхню стійкість до окислювання.