Smart Coating Technology by Gas Tunnel Type Plasma Spraying

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Abstract. Nano-science & technology is one of the most important scientific fields, and the material processing using the nano-technology is now advanced towards more precise and controllable smart stage. Regarding thermal processing, plasma system with high precise, has been expected for smart thermal processing. The gas tunnel type plasma system developed by the author exhibits high energy density and also high efficiency. Among the applications to the various thermal processing, one practical application is plasma spraying of ceramics such as Al₂O₃ and ZrO₂. The characteristics of these ceramic coatings were superior to the conventional ones. The ZrO₂ 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 and oxidation resistance. Now, one of the advanced plasma application, a smart coating technology, is expected to obtain the desired characteristics of ceramics with improved corrosion resistance, thermal resistance, and wear resistance.

1. Introduction
In order to apply Nano-science & technology to Material Science, the material processing should be developed towards more precise and controllable smart processing stage. Regarding an applicable heat source, the most important key should be the performance of the applied heat source. A plasma is one of the most superior heat sources, because of high temperature, high energy density, easy controllable, etc. Therefore more precise plasma system has been expected in order to establish a smart thermal processing.

The gas tunnel type plasma system developed by the author has high energy density and also high efficiency [1-3]. The outline of this plasma system and the applications to the various thermal processing are described briefly in the following chapters. One of typical applications is plasma spraying of ceramics such as Al₂O₃ and ZrO₂ [4]. The characteristics of these ceramic coatings by the gas tunnel type plasma spraying were superior to that by the conventional ones. Usually, the Vickers hardness of this sprayed coating became 20-30% higher than that of conventional plasma sprayed coating. And, the porosity was only half of the value of the conventional ones [5].

Plasma sprayed zirconia coatings are widely used as thermal barrier coatings (TBC) for high temperature protection of metallic components in the hot section of gas turbine such as burners,
transition ducts, vanes and blades. It allows the high temperature operation and results to the increase in the efficiency of the engine and the durability of the critical gas turbine components. However, their use in diesel engine combustion chamber components has been quite rare, because of the durability problems in such conditions. The main problem is the TBC spallation at the interface between the coating and substrate due to the interface oxidation [6]. Although zirconia coatings have been used in many applications, the interface spallation problem is still waiting to be solved under the extreme conditions such as high temperature cycle and high corrosion environments. For that reason, there have been many investigations in developing high quality TBCs for diesel engines [7,8].

For TBC, the spalling of the coating is also a very important problem as well as the coating quality. It is reported that the spallation rate can be relatively reduced by using suitable bond coat for the interface [9]. Nevertheless, it is difficult to find suitable bonding layers for all kind of substrate material. Alumina / zirconia composite coating was proposed as a potential candidate to improve the properties of thermal barrier coating system due to alumina’s low melting point and high hardness. Also, extremely high porosity values (up to 25vol%) of TBCs 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 resistances for thermal shock and high-temperature corrosion are important properties of TBC. While the large porosity and the high melting point is advantage of ZrO2 coating, the porosity has disadvantage for the adoption under the critical conditions such as high temperature and high corrosion environment. New type plasma spray methods are expected for using the excellent characteristics of ceramics such as corrosion resistance, thermal resistance, and wear resistance [10] by reducing the porosity and increasing the coating density.

Now, a high hardness ceramic coating could be obtained by means of the gas tunnel type plasma spraying, which were investigated in the previous study in detail [5,11,12,13]. The Vickers hardness of the zirconia (ZrO2) coating was increased with decreasing spraying distance, and a higher Vickers hardness could be obtained at a shorter spraying distance. At \( L=30 \text{ mm} \), when \( P=33 \text{ kW} \), the Vickers hardness of ZrO2 coating was about \( H_v=1200 \) [14], which corresponds to the hardness of sintered ZrO2 \( (H_v=1,300) \). ZrO2 coating formed has a high hardness layer at the surface side, which shows the graded functionality of hardness [15,16]. 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. For TBC, the spalling of the coating is also a very important problem as well as the coating quality.

In this study, the mechanical properties, thermal behavior and high temperature oxidation resistance, of high hardness ZrO2 composite coating were investigated and the merit as TBC (thermal barrier coating) was clarified. The effect of alumina Al2O3 mixing ratio on the Vickers hardness of the ZrO2 composite coating was also clarified in order to develop high functionally graded TBC. Moreover the adhesive characteristics of such high hardness zirconia-alumina \( (\text{ZrO}_2-\text{Al}_2\text{O}_3) \) composite coatings were investigated as well as its mechanical properties. Especially, the influence on the thickness of the zirconia composite coating was discussed. Moreover, the corrosion potential and deactivated corrosion current density are measured and analyzed corresponding to the microstructure of the zirconia composite coatings. The corrosion resistance \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) was evaluated as a function of \( \text{Al}_2\text{O}_3 \) percentage and coating thickness.

2. Gas Tunnel Type Plasma System

The schematic of gas tunnel type plasma torch developed by the author is shown in Figure 1. The working gas makes a strong vortex flow in the chamber, and forms low pressure gas tunnel along the torch center axis. This makes plasma production easier, and the strong vortex constrains and stabilizes the plasma jet. The feature of gas tunnel type plasma is shown in Table 1 as compared to the conventional ones. The gas tunnel type plasma system has high energy density and also high efficiency. [1,2,3]
Figure 1. Schematic of the gas tunnel type plasma spraying torch.

Table 1. Comparison between gas tunnel type plasma jet and conventional ones.

|                         | Gas tunnel type plasma jet | conventional ones |
|-------------------------|----------------------------|-------------------|
| Temperature             | 15000 K                    | 10000 K           |
| Energy density          | $10^5$ W/cm²               | $10^5$ W/cm²      |
| Heat efficiency         | 80%                        | 50%               |

One example of application of the gas tunnel type plasma is the thermal spraying. Figure 1 shows the gas tunnel type plasma spraying torch. The experimental method to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying have been described in the previous papers [4,5,11,12,13].

The spraying powder is fed inside plasma flame in axial direction from center electrode of plasma gun. So, the spraying powder flying around central axis was molten enough in the plasma, and the plasma spraying for high melting point ceramics is available.

This plasma system has many possibilities for the industrial applications to the various thermal processing, such as plasma spraying, surface modification. The typical applications are:

1. Plasma spraying of ceramics (Al₂O₃ and ZrO₂ etc.)
2. Surface modification of Ti materials (Nitridation)
3. Other Applications such as nano-science, functional materials processing technology
4. Application to environmental problems, such as CO₂ decomposition by plasma jet.

Moreover, the development of new type of smart plasma system is planned in order to apply to thermal processing of materials and so on.

3. Gas Tunnel Type Plasma Spraying

3.1. Characteristics of gas tunnel type plasma spraying

The gas tunnel type plasma spraying can make high quality ceramic coatings compared to conventional plasma spraying systems. The gas tunnel type plasma spraying torch [4, 5,11,12,13] is shown in Figure 1. 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. Table 2 shows the properties (hardness, porosity, etc.) of the Al₂O₃ coating by gas tunnel type plasma spraying [5,11]. The hardness was similar to sintered alumina: $Hv=1,200$ and high density, porosity was half of the value of the conventional ones. Even when the working gas is argon and low input of 20 kW, we can obtain enough high Vickers hardness of $Hv=800$.

Thus it can be easy to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying.
Table 2. Comparison between gas tunnel type plasma spraying and conventional type for Al₂O₃ coating. (Input = 45kW, Distance = 65-100mm)

|                        | Gas tunnel type plasma spraying | Conventional ones |
|------------------------|--------------------------------|-------------------|
| Vickers hardness       | 1200                           | 800               |
| Porosity               | 10%                            | 20%               |

3.2. Experimental procedures
The gas tunnel type plasma spraying torch used was shown in Figure 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.

Table 3. Experimental conditions.

| Powder: ZrO₂ + Al₂O₃ Mixture | Traverse number: N     | 1~30            |
|-------------------------------|------------------------|-----------------|
| Traverse number: N            | 1~30                   |                 |
| Power input, P (kW):          | 25~28                  |                 |
| Working gas                   |                        |                 |
| Working gas flow rate, Q (l/min): | 180                  |                 |
| Power 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 experimental parameters for the plasma spraying are shown in Table 3. 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.

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=20~35g/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 (: high speed traverse of v=1000cm/min, 30times).

The chemical composition and the particle size of Zirconia (ZrO₂) and/or alumina (Al₂O₃)powder used in this study was respectivel y shown in Table 4. This ZrO₂ powder was commercially prepared type of K-90 (PSZ of 8% Y₂O₃), and Al₂O₃ powder was the type of K-16T. The substrate was SUS304 stainless steel (3x50x50), which was sand-blasted prior to plasma spray.

Table 4. Chemical composition and size of zirconia and alumina powder used. (20~80% Al₂O₃ Mixture)

| Composition (wt%) | Size (μm) |
|-------------------|-----------|
| ZrO₂              | 90.78     | 8.15 |
| Zr₂O₃             | 8.15      | 0.38 |
| Y₂O₃              | 8.15      | 0.38 |
| Al₂O₃             | 99.8      | 0.146|
| Na₂O              | 0.01      | 0.01 |
| SiO₂              | 0.146     | 0.01 |
| Fe₂O₃             | 0.11      | 0.11 |
| 10-44              | 10-35     |      |
3.3. Analysis of Coating Properties

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. The microstructure of the cross section of zirconia composite coating was observed by an optical microscope.

The Vickers hardness $H_{V_{50}}, H_{V_{100}}$ of the sprayed coatings was measured at the non-pore region in those cross sections under the condition that the load weight was 50g, 100 g and its load time was 15s, 25 s. The Vickers hardness: $H_{V_{100}}$ 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 fixed 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 load for the tester could be changed 0~200kg. The kgf/cm$^2$ was used as a unit for the adhesive strength of the composite coating. The adhesive strength of the ZrO$_2$ composite coatings was mainly measured in the case of different coating thickness.

The schematic of anodic polarization corrosion system is shown in Figure 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 500ml corrosion media of 0.5M 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$_4$.

The sample surfaces were firstly degreased by ultrasonic process in acetone for 5 minutes then were washed by 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 galvanical contact with the solution, then the sample potential was set to -0.5V and was swept to +0.5V at a rate of 10mV/s. All the tests were carried out at room temperature.

Figure 2. Anodic Polarization Corrosion Tester.
4. Results and Discussion

4.1. Microstructure and Vickers hardness of zirconia composite coating

Typical optical cross sectional micrographs for thermal barrier coatings are shown in Figure 3. Those are the zirconia composite coatings of 20% and 50%Al2O3 mixture, respectively. The coatings are porous and lamellar structure which is typical characteristic for as-sprayed coatings. The thickness was about 150μm.

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 (ZrO2) and gray was alumina (Al2O3). Pores appear to be dark, which permit them to be distinguished and quantified by image analysis.

![Figure 3. Micrographs of the cross-section of coating samples.](image)

![Figure 4. Dependence of Vickers hardness of zirconia composite coating on the alumina mixing rate. 2 times traverse at L=40mm when P=25kW.](image)
4.2. Effect of alumina mixing ratio on the Vickers hardness of zirconia composite coating

Figure 4 shows the relationships between Vickers hardness and porosity of the ZrO$_2$ composite coatings and the alumina Al$_2$O$_3$ mixing ratio $R$ (wt%), at the same spraying time. In this case, the coating thickness was approximately 200 $\mu$m at $P=25$ kW, $L=40$ mm, when the traverse number was two times.

The average Vickers hardness over the cross section of ZrO$_2$ composite coatings is increased with the increase in the Al$_2$O$_3$ mixing ratio. The increment of coating hardness corresponds to attendance of alumina particles with hardness higher than that of ZrO$_2$. The Vickers hardness of Al$_2$O$_3$ coating was $Hv_{50}=1360$.

The hardness distribution of the ZrO$_2$ composite coating has remarkable graded functionality in the case of large Al$_2$O$_3$ mixing ratio. Because, the part near the substrate did not change so much, but the Vickers hardness near the coating surface became much higher. This leads to the development of a high functionally TBC.

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

4.3. Graded Functionality of zirconia composite coating

The hardness distribution of the ZrO$_2$ composite coating has remarkable graded functionality in the case of large Al$_2$O$_3$ 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 Figure 3 (coating thickness: about 150$\mu$m). 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 the coating surface of $l=40$ $\mu$m, and decreased linearly like towards the substrate side.

While, the porosity profile over the coating cross-section (Figure 6) gives an almost linearly graded distribution, increasing from the surface of the coatings towards the surface of the substrate. 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 present in the coatings is the origin of the improved hardness because higher mixing ratio of alumina results in lower porosity.

![Figure 5](image1.png)

**Figure 5.** Dependence of Vickers hardness of zirconia composite coating on the alumina mixing rate. 2 times traverse at L=40mm when P=25kW.

![Figure 6](image2.png)

**Figure 6.** Porosity distribution over coating cross-section.
4.4. Influence of plasma thermal process on the coating
For an increase in the traverse number, the surface temperature of the coating during spraying became higher. Therefore it would be expected that coating density would be increased when the traverse number increases. The maximum Vickers hardness of ZrO$_2$ composite coating was almost the same when the coating thickness was the same. But the graded functionality became much better, and the distribution of Vickers hardness was much smoother as the traverse number was increased. This means that the structure at the surface of the coating was denser by the thermal process of the high energy plasma.

Regarding the microphotograph of ZrO$_2$/Al$_2$O$_3$ coating (Figure 7) produced by the gas tunnel spraying on the fixed substrate for 3s spraying time, the coating thickness was about 250 μm, and white and gray layers were deposited alternatively as the same as Figure 3.

The graded functionality of the structure is remarkable, and small pores are distributed disparately in the whole coating while large pores existed near the substrate. The surface side has fewer pores and dense, compared to the coating near the substrate. This was caused by the thermal process of the high energy plasma from the surface side of the coating.

In this case, the Vickers hardness was linearly decreased in the thickness direction towards the substrate side (Figure 8). The dense microstructure led to the suppression of the deviation of the hardness distribution.

![Microphotograph of cross section of zirconia composite coating. The traverse number was 30 time traverse. Sprayed at L=40mm when P=25 kW.](image)

**Figure 7.** Microphotograph of cross section of zirconia composite coating. The traverse number was 30 time traverse. Sprayed at L=40mm when P=25 kW.

![Distribution of Vickers hardness of zirconia composite coating sprayed by 30 times traverse at P=25kW, L=40 mm.](image)

**Figure 8.** Distribution of Vickers hardness of zirconia composite coating sprayed by 30 times traverse at P=25kW, L=40 mm.

4.5. Adhesive strength of ZrO$_2$ composite coating
Figure 9 shows the dependence of the adhesive strength between coating and substrate on the coating thickness of ZrO$_2$ composite coating sprayed by 2-4 times traverse. The adhesive strength of the ZrO$_2$ composite coatings was decreased when the thickness was large. In the case of small coating thickness (100μm), the adhesive strength was large: more than 140 kgf/cm$^2$ for the coating thickness below 100μm. While, the value was $F = 100 \sim 120$ kgf/cm$^2$ when the thickness was more than 200μm.
Therefore the thick coating was much easier to break than thin coating, but the adherence was improved when the traverse number was large.

4.6. Oxidation of ZrO\textsubscript{2} composite coating
After heat treatment at 1050 °C for 5 Hr, the ZrO\textsubscript{2} coating system showed spallation from the substrate. But the Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}. Analytical model showed that plasma sprayed Al\textsubscript{2}O\textsubscript{3} layer should be very thin since thicker layer would generate larger residual tensile stress.
To evaluate phase transformation of Al₂O₃ due to plasma spray process, free standing Al₂O₃ layer was oxidized at 1050 ºC for 5 Hrs. X-ray diffraction was conducted to examine phases of the sprayed layers. A comparison of diffraction patterns of the as-sprayed and heat-treated Al₂O₃ is summarized in Figure 10. The α-Al₂O₃ that was formed during plasma spray undergoes a phase transformation to a more stable α-Al₂O₃ during heat treatment, although some fraction of γ phase was retained in the coating. Other phases, namely δ-, θ- Al₂O₃ 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.

4.7. Anodic corrosion polarization characteristics of ZrO₂ composite coating
Figure 11 presents the anodic corrosion polarization characteristics of the samples coated with different thickness of 80% ZrO₂ + 20%Al₂O₃ 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. Figure 12 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.

Figure 11. Corrosion curves of ZrO₂ composite coatings.

Figure 12. Corrosion potential versus thickness.
5. CONCLUSIONS
The following results were obtained during the application of the gas tunnel type plasma system to smart coating processing. The performance such as the mechanical properties, thermal behavior and high temperature oxidation resistance of the ZrO$_2$/Al$_2$O$_3$ composite coating produced by gas tunnel type plasma spraying was clarified.

(1) The gas tunnel type plasma system has high energy density and also high efficiency as compared to the conventional ones, and can be applied to the various thermal processing. One typical application is plasma spraying of ceramics such as Al$_2$O$_3$ and ZrO$_2$. And the characteristics of these ceramic coatings were superior to the conventional ones.

(2) The ZrO$_2$/Al$_2$O$_3$ 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). 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. The $\alpha$-Al$_2$O$_3$ that was formed during plasma spraying undergoes a phase transformation to a more stable $\alpha$-Al$_2$O$_3$ during heat treatment, although some fraction of $\gamma$ phase was retained in the coating. The high temperature oxidation behavior of the functionally graded TBCs showed the effectiveness of Al$_2$O$_3$ layer functioning as an oxidation barrier.

(4) 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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