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Performance of Zirconia Composite Coatings Produced by Gas Tunnel Type Plasma Spraying as a Thermal Barrier Coating †

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Abstract

Zirconia (ZrO_2) formed by the plasma spray method is widely used industrially as a thermal barrier coating (TBC). But it still has problems such as spallation and cracking inside the coating. The solution may be found through the development of new spraying processes. The zirconia-alumina (ZrO_2-Al_2O_3) composite coating formed by gas tunnel type plasma spraying at short spraying distances, also has a high hardness layer at the surface side of the coating, which shows a graded functionality of hardness. In this paper, the performance of such high hardness ZrO_2-Al_2O_3 composite coatings under different spraying conditions was investigated and their merits as TBC clarified. For the enhancement of the graded functionality of such composite coatings, the Vickers hardness of the high hardness layer near the coating surface increased as a result of the thermal process of the high energy plasma, and corresponded to the result that the coating became denser. Also, the effect of alumina mixing on the microstructure of this composite coating was examined. The combination of high hardness of Al_2O_3 with the low thermal conductivity of ZrO_2 resulted in the development of high functionally graded TBC. By a calculation using laminate theory, the thermal conductivity of such ZrO_2-Al_2O_3 composite coatings in the thickness direction was proved to be much smaller than in the longitudinal direction. Moreover the adhesive strength of such high hardness zirconia composite coatings was investigated as well as their mechanical properties. The adhesive strength of such high hardness coatings to the substrate was weakened with an increase in the alumina content of the spraying powder.

Keywords: (Zirconia-alumina composite coating) (Gas tunnel type plasma spraying) (Graded functionality) (Microstructure) (High Vickers hardness) (Thermal barrier coating) (Heat transfer model) (Adherence of the coating) (Mixing ratio of alumina)

1. Introduction

The ceramic coatings produced by plasma spraying are effective as thermal barrier coatings (TBC) for high temperature protection of metallic structures because of having high temperature resistance. For example, TBC are used in hot sections of gas turbine engines and/or diesel engine and in high temperature parts of detonation furnaces. They allow operation at high temperature and increase the efficiency of the engine and the durability of the critical components [1]. Zirconia (ZrO_2) coating in Particular has been widely used as TBC because of the large porosity and the high melting point. On the other hand, the porosity has disadvantages for adoption under critical conditions such as high temperature and highly corrosive environments.

Research to overcome this problem of zirconia coating has been conducted by many institutions. For use in more severe environments, the high temperature performance should be much greater than at present. In particular, the resistance to thermal shock and high temperature corrosion are important properties for high performance TBC. New plasma spray methods are expected to introduce the excellent characteristics of ceramics such as corrosion resistance, thermal resistance, and wear resistance [1] by reducing the porosity and increasing the coating density.

The gas tunnel type plasma spraying developed by the author [2] has superior properties compared with the conventional plasma spray method. A high hardness ceramic coating could be obtained by means of the gas tunnel type plasma spraying, and were investigated in the previous studies in detail [3,4,5,6]. For example, the Vickers hardness of the zirconia (ZrO_2) coating increased with decreasing spraying distance, and a higher Vickers hardness could be obtained at a shorter spraying distance ($L< Lp$). At L=30 mm, when P=33 kW, the Vickers hardness of the zirconia coating was about Hv=1200 [7]. This corresponds to the hardness of sintered zirconia. Usually, the Vickers hardness of such a sprayed coating became 20-30% higher than that of conventional plasma spraying.

A zirconia (ZrO_2) coating formed by gas tunnel type plasma spraying has a high hardness layer at the surface side of the coating, and shows a graded functionality of hardness [8,9]. With an increase in the number of traverses, the hardness distribution was much smoother, corresponding to the fact that the coating became denser.

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The combination of high hardness of Al_2O_3 with the low thermal conductivity of ZrO_2 will contribute to the development of high functionally graded TBC (thermal barrier coating) with higher wear resistance. In TBC, the spalling of the coating is a very important problem, as well as the coating quality such as high density of the coating. But a study of the adherence between the coating and the substrate has not been carried out for these coatings produced by the gas tunnel type plasma spraying.

In this paper, the performance of such high hardness ZrO_2 and composite coatings in the case of different spraying conditions was investigated and the merit as TBC was assessed. The effect of alumina mixing was also examined and the effect of plasma energy discussed. Specifically, the graded functionality in hardness characteristics and effects of alumina mixing ratio on the Vickers hardness of the zirconia composite coatings were investigated in detail. The combination of high hardness of Al_2O_3 with the low thermal conductivity of ZrO_2 was discussed to develop high functionally graded TBC (thermal barrier coating), and the thermal conductivity of such ZrO_2-Al_2O_3 composite coatings was calculated.

Moreover the adhesion characteristics of such high hardness zirconia-alumina ZrO_2-Al_2O_3 composite coatings for the case of different mixtures of alumina were investigated as well as their mechanical properties, in order to develop a high performance thermal barrier composite coating. In particular, the influence of the alumina mixture the spraying powder on the thickness of the zirconia composite coating was discussed.

2. Experimental Procedure

Figure 1 shows the gas tunnel type plasma spraying torch used in this study. The experimental method to produce high hardness ceramic coatings by means of the gas tunnel type plasma spraying has been described in previous papers [3,4,5,6]. The spraying powder is fed inside the plasma flame in an axial direction from the center electrode of the plasma gun. The coating was formed on the substrate traversed at the spraying distance: L. In this case, the gas divertor nozzle diameter was d=20 mm.

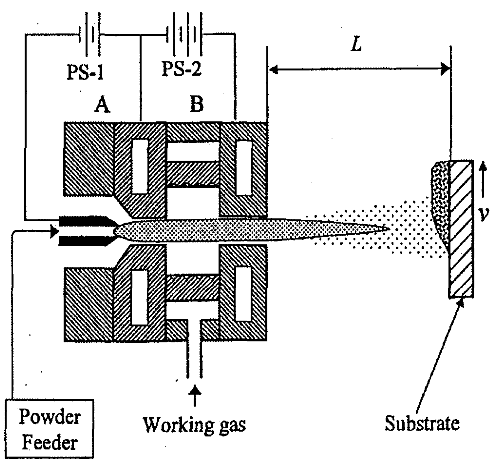

Fig.1 Gas tunnel type plasma spraying apparatus used in this study; L: spraying distance. Gas divertor nozzle was 20 mm.

Table 1 Experimental condition.

Powder: Mixture	$ZrO_2+Al_2O_3$
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

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 experimental conditions for this 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 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 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 over values from v=25 to 1000 cm/min. Also the traverse number was changed 1-30 times.

The chemical composition and the particle size of Zirconia and/or alumina powder used in this study are respectively shown in **Table 2**. This zirconia powder was a commercially prepared type of K-90 (PSZ of 8% Y_2O_3), and alumina powder was of the type K-16T. The mixing ratio of alumina to zirconia powder was changed from, 20~80 weight-% in this study. The substrate was SUS304 stainless steel (3x50x50), which was sandblasted before use.

Zirconia composite coatings were formed at L=40mm by changing the traverse speed and traverse number, with the conditions of P=25kW, L=40mm. 50~

250 μm Also, high speed traverses of v=1000cm/min, 30times, and Non traverse spray formed deposit for the spraying time of 3 sec were made.

The Vickers hardness Hv_{50}, Hv_{100} of the sprayed coatings was measured at the non-pore region in those cross sections with a load weight of 50g, 100 g and a load time of 15sec 25 s. The Vickers hardness: Hv_{100} was calculated as a mean value of 10point measurements. The distribution of the Vickers hardness in the cross section of the zirconia composite coating was measured at each distance from the coating surface in the thickness direction. The microstructure of the cross section of zirconia composite coating was observed using an optical microscope.

The adhesive strength between the zirconia composite coating and the substrate was measured by using the tension tester of original design and/or a commercial type of autograph. The test piece for adhesive strength was 10mm square and the coating surface side and substrate side was attached to each holder by polymer glue. The load for the tester was changed between 0～200kg. The value of kgf/cm^2 was used as a unit for the adhesive strength of the composite coating. The adhesive strengths of composite coatings in the case of different coating thickness and in the case of different alumina mixing rate, were investigated as well as their mechanical properties.

From the experimental results, a simple heat transfer model for the ceramic composite coatings was considered theoretically. By a calculation using laminate theory, the thermal conductivity of such ZrO_2-Al_2O_3 composite coatings in the thickness direction was proved to be much smaller than that in the longitudinal direction.

3. Results and Discussion

3.1 Distributions of Vickers hardness in the cross sections of zirconia composite coatings and the effect of alumina mixing ratio

Figure 2 shows the distributions of Vickers hardness in the cross sections of zirconia composite coatings produced by the gas tunnel type plasma spraying at the same spraying time of about 10 seconds. These coatings were formed by single or double traverses.

In this case, Ar gas flow rate was Q=180 l/min, the power input was P=25 kW and the spraying distance was L=40 mm. The powder feed rate was w=25 g/min. The measurement was carried out at each distance from the coating surface in the thickness direction. The left side vertical axis represents the coating surface. The traverse speed of the substrate was v = 25 cm/min for 1 pass (1 time traverse), or 50 cm/min. for 2 passes, respectively. The coating thickness was approximately 140 μm, which was proportional to the spraying time.

The distribution of Vickers hardness of zirconia composite coatings for a single traverse consists of one

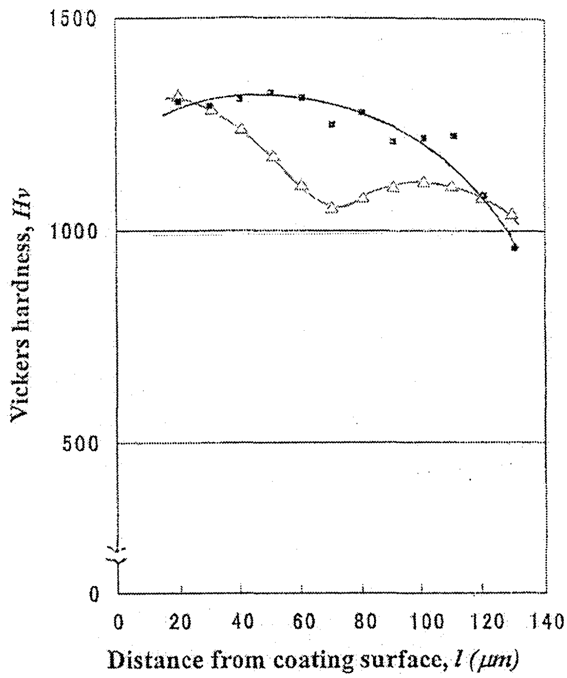

Fig.2 Distribution of Vickers hardness in cross sections of zirconia composite coating sprayed at L=40mm, P=25kW.
Data plots: 1 time traverse, Δ: 2 times traverse.

parabolic curve as shown in Fig.2. The maximum Vickers hardness in the coating was Hv = 1300 at the distance from the coating surface of l=40 μm. The distribution of Vickers hardness of zirconia composite coating for a double traverse consists of two parabolic curves as shown in the same figure. From this distribution, it is found that the Vickers hardness of the coating surface layer (corresponds to the second pass) at the surface side of coating is higher, and the maximum value of this high hardness layer was about Hv = 1300 at the distance from the coating surface of l = 20 μm.

In this case, the hardness difference between the surface side and the substrate side was large. Then the graded functionality of hardness became significant in the thickness direction. The hardness near the substrate was lower value, at Hv=1000, than that near the coating surface, (Hv=1300).

Thus, the maximum hardness 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. The part near the substrate did not change so much, but the Vickers hardness near the coating surface became much higher than that of a less traversed coating. Therefore the graded functionality can be enhanced by an increase in the traverse number, and this leads to the development of a high functionally TBC.

Figure 3 shows the dependence of Vickers hardness of zirconia composite coatings formed by the gas tunnel

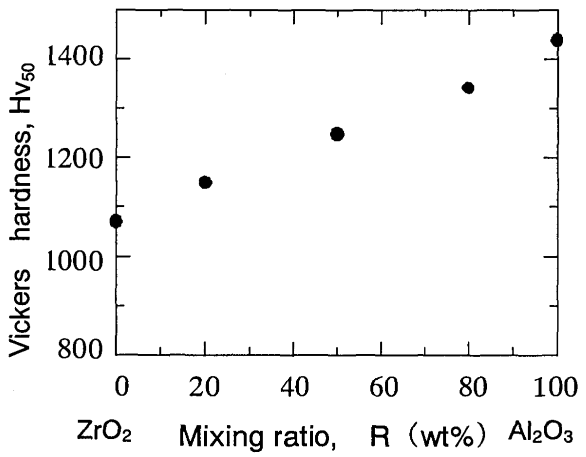

Fig.3 Dependence of Vickers hardness of zirconia composite coating on the alumina mixing rate. Double traverse at L=40mm when P=25kW.

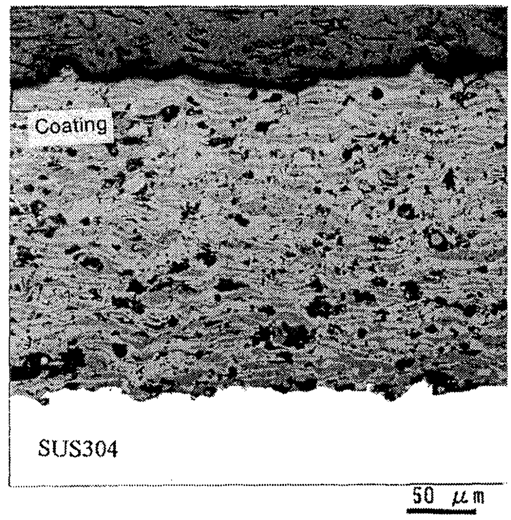

Fig.4 Microphotograph of cross section of ZrO_2-Al_2O_3 composite coating.

type plasma spraying, on the alumina mixing ratio R(wt%).

In this case, the power input was P=25 kW and the spraying distance was L=40 mm, when a double traverse was used. The coating thickness was approximately 200 μm

The Vickers hardness in the cross section of the zirconia composite coating increased with an increase in the almina-mixing ratio. The coating hardness changed from Hv=1070 for the zirconia coating to Hv_{50}=1250 for a 50% alumina/zirconia composite coating. This is a consequence of the high hardness of alumina particles. The Vickers hardness of an alumina coating was Hv_{50}= 1440. The hardness distribution in the composite coating has a remarkably graded functionality in the case of large alumina mixing ratios.

3.2 The influence of plasma thermal process on the coating

For an increase in the number of the traverses, the surface temperature of the coating during spraying becomes higher. Therefore it would be expected that coating density would be increased when the traverse number increases.

Figure 4 shows the microphotograph of a zirconia and alumina coating produced by the gas tunnel spraying on the fixed substrate for 3s, under the condition of P = 25 kW, L = 40 mm, w=22 g/min. The coating thickness was 250μm, and it consisted of 2 different layers, white and gray layers were deposited alternatively. The analysis by EPMA revealed that white is zirconia and gray is alumina.

The white zirconia layer was a flat layer of uniform thickness, and embedded parallel to the alumina matrix of low melting temperature. The black parts in the coating are pores, and are distributed through the whole coating. The surface side has fewer pores compared to the coating near the substrate. The structure is denser towards the surface of the coating. The graded functionality of the structure is well shown in this micrograph.

Figure 5 shows the distribution of Vickers hardness: Hv_{50} in the zirconia/alumina composite coating shown in Fig.4. Here, the left side axis is the surface of the coating, and the thickness of the coating was about 250μm. The distribution in this composite coating has a highest value in the coating at the surface side: $Hv_{50}>1200$, and decreases linearly towards the substrate side. This shows good graded functionality. This means that the structure at the surface of the coating was denser as a result of the thermal process of the high energy plasma. For comparison, the distribution of a single traverse is shown in the same figure. It is a parabolic curve and the maximum hardness appears at the middle of the coating thickness: l ~100 μm.

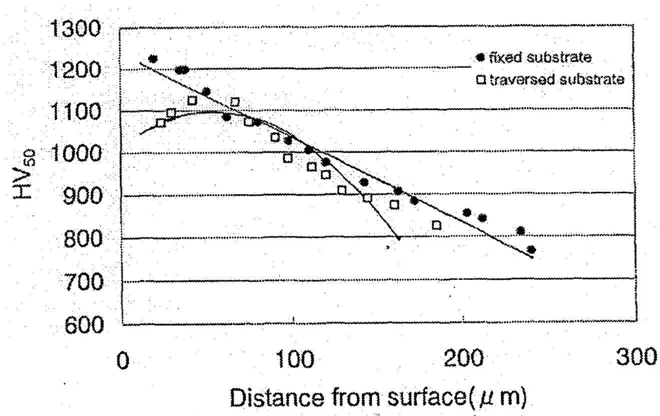

Fig.5 Distribution of Vickers hardness in cross sections of zirconia composite coatings sprayed at L=40mm, P=25kW. Data plots: Fixed. Curve line: 1 time traverse.

3.3 Effect of a high speed traverse on the coating quality, the schematic of the composite coating and the thermal property

Regarding the effect of traverse number, the uniformity of pores is increased and the deviation of hardness distribution is improved. As a result, high speed and high number of traverses will improve the grade functionality of coating hardness. This shows the possibility of producing high performance TBCs by the high speed traverse processing.

Figure 6 is the cross section of a composite coating produced by high speed traverse at P = 25 kW, L = 40 mm. Traverse was repeated 30 times. This speed,: 1000cm/min, was 10 times higher than the normal speed traverse as in Fig.2. The thickness was about 150 μ m. In this case the distribution of Vickers hardness was linear in the thickness direction. The maximum hardness was near to Hv = 1300 at a distance from the coating surface of l=40 μm.

This microphotograph shows that zirconia ZrO_2 and alumina Al_2O_3 are deposited alternately in the same way as in Fig.4, and that small pores are distributed irregularly. However, some large pores existed near the substrate, although porosity was decreased and became finer. For this reason there was a suppression of the deviation of the hardness distribution.

The microstructure of the ZrO_2 composite coating shows a dense ceramic matrix composite coating with thin ZrO_2 particles embedded inside a dense Al_2O_3 matrix. The ZrO_2 is in the form of flat stripes. This anisotropic composite coating combined with the large difference in thermal conductivity between ZrO_2 and Al_2O_3 will alter the thermal behavior of the coating. The coating structure might suppress the pores as compared with the ZrO_2 coating described in the previous paper.

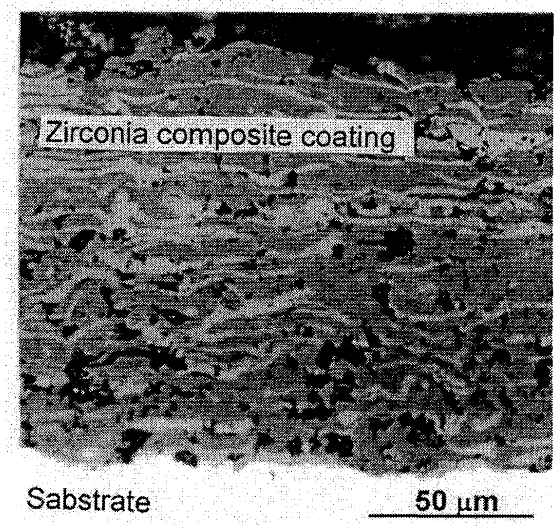

Fig.6 Microphotograph of cross section of zirconia composite coating. The traverse number was 30. Sprayed at L=40mm when P=25 kW.

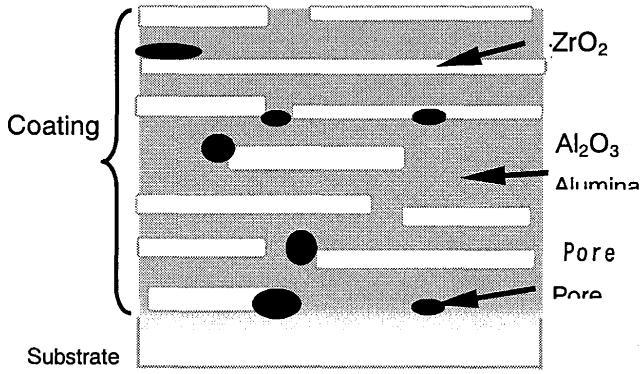

Fig.7 Schematic of zirconia composite coating.

Figure 7 shows a schematic of the cross section of the 50/50-wt% ZrO_2/Al_2O_3 composite coating constructed following the above discussion. The area of Al_2O_3 is larger than that of ZrO_2 because the weight density of Al_2O_3 is smaller. The two oxides have vastly different melting points, boiling points, and heat of formations [12]. These properties influence all aspects of the coating process, from melting to solidification. The Al_2O_3 powder of lower melting point will undergo far more melting inside the plasma flame.

Adding Al_2O_3 in the powder enhances the properties of TBC of ZrO_2. By investigating the microstructure of the ZrO_2-Al_2O_3 coatings, they are found to be similar to laminate structures. Therefore, we may be able to extend composite laminate theory [10-11] to model the anisotropic properties of the coating. By using this simple model, the thermo-elastic properties, such as Young's modulus, shear modulus, Poisson's ratio, thermal expansion, and thermal conductivity can be introduced. Each property was calculated in two directions; longitudinal and transverse, where the longitudinal properties being parallel to the coating.

Thermal conductivity is an important property of TBCs. The thermal conductivity of ZrO_2 is rather low and does not change significantly when temperature increases. While the thermal conductivity of Al_2O_3 decreases by a factor of 3.75, when the temperature increases from room temperature to 800℃.

Table 3 Thermal conductivity of predicted.

Property		50%-50% (ZrO_2-Al_2O_3)	
		Room Temp.	800°C
Thermal Conductivity (W/m-K)	L	15.82	4.44
	T	3.52	2.31

The thermal conductivities for 50%-50% ZrO_2-Al_2O_3 composite coatings calculated by the classical laminate theory are shown in **Table 3.** The differences between the longitudinal and transverse values are very significant at room temperature. Thermal conductivity in the longitudinal direction is 4.5 times that in transverse direction. This indicates that heat transfer in the transverse direction may be suppressed relative to the longitudinal direction. When the temperature increases, the difference between the two directions decreases, but still, the transverse thermal conductivity is smaller. By assuming that ZrO_2 is deposited in the composite coating in layers, the lower thermal conductivity in the transverse direction is explained.

For a TBC, a low transverse thermal conductivity is desirable. These results show that the effect of the mixture gives a higher thermal resistance in the transverse direction when heat flux moves perpendicular to the coating surface.

3.4 Effect of coating thickness and alumina mixing ratio on the adhesive strength of zirconia composite coating

The adhesive strength of such high hardness zirconia composite coatings in the case of different coating thickness and in the case of different alumina mixing rate, was investigated as well as their mechanical properties.

Figure 8 shows the results of tensile tests for the zirconia composite coatings formed by the gas tunnel type plasma spraying (P = 25 kW, L = 40 mm). The adhesive strength between coating and substrate was indicated as the value of F (kgf/cm^2) and the horizontal axis shows the thickness of the composite coating tc (μm).

As shown in this figure, the adhesive strength decreased when the thickness increased. In the case of small coating thickness, the adhesive strength was large. For example, the obtained value was more than 150 kgf/cm^2 under the condition of below 50 μ m. But it seems that the influence of the glue may have been large for this measurement. So, more precise measurement will be required at the next stage of this study.

The strength value was F = 50～80 kgf/cm^2 when the thickness was more than 150μm. And the adhesive strength between coating and substrate decreased. Therefore a thick coating was much easier to break than thin coating. These composite coatings were formed by 1 ～3times traverses. The influence on the adherence was improved when the traverse number was large

Figure 9 shows the dependence of adhesive strength between zirconia composite coating and substrate on the alumina-mixing ratio R (wt%). These composite coatings were formed by the gas tunnel type plasma spraying, under the condition of P=25kW, L=40mm, double traverse. In this case the coating thickness was 150～200 μm.

The adhesive strength of zirconia composite coating decreased with an increase in the alumina- mixing ratio. But it increased only a little when the mixing ratio was more than R =80 wt%. The adherence of zirconia composite coating was a minimum when R =50-80%, and the coating would be easy to spall. The value of the adhesive strength was F = 50-60 kgf/cm^2. The alumina coating has strong bonding strength, and the break point was the interface between coating and substrate.

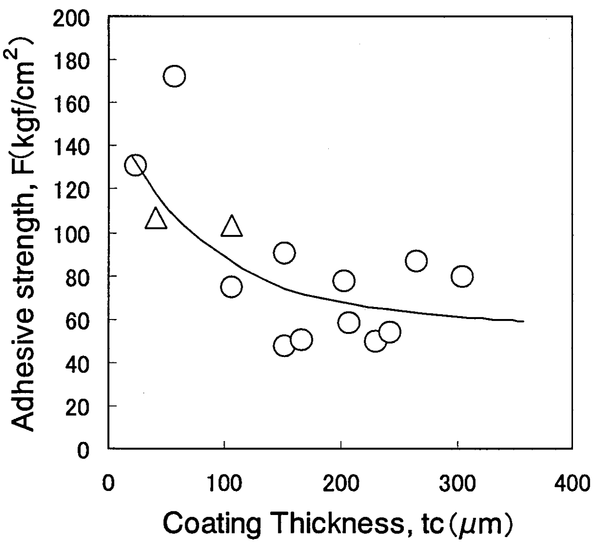

Fig.8 Dependence of the adhesive strength between coating and substrate on the coating thickness of zirconia composite coating sprayed at L=40mm, P=25kW. 1-3 times traverse.

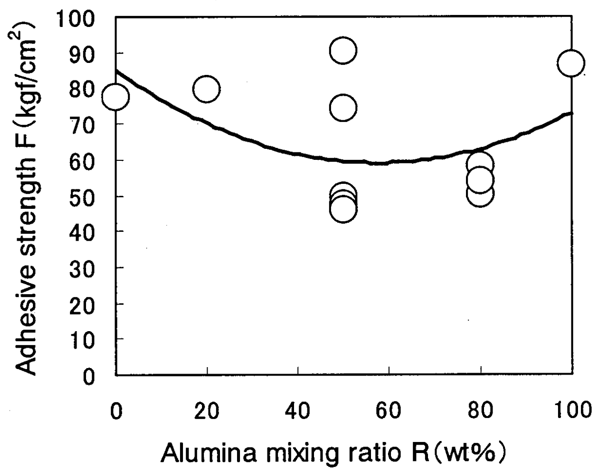

Fig.9 Dependence of adhesive strength between coating and substrate on of zirconia composite coating on the alumina mixing rate. 2 times traverse at L=40mm when P=25kW.

4. Conclusion

The performance of the functionally graded ZrO_2-Al_2O_3 composite coating formed by the gas tunnel type plasma spraying was investigated and its merit as a thermal barrier coating (TBC) was investigated. The results obtained are as follows.

(1) From the distribution of Vickers hardness in the cross sections of those coatings for single and double traverse spraying, the effect of thermal process of high energy plasma was clarified.
(2) With an increase in the alumina mixing ratio, the Vickers hardness of the high hardness layer became large, and changed from Hv=1100 to 1240. The graded functionality of hardness was enhanced by the increase in the alumina mixing ratio
(3) The graded functionality was enhanced by an increase in the traverse number. Also, the hardness distribution became smoother as the number increased. Enhancement of graded functionality should be achieved by controlling the traverse number and the coating thickness.
(4) For ZrO_2-Al_2O_3 thermal barrier composite coatings, a dense ceramic matrix composite coating with zirconia plates embedded inside a dense alumina matrix was formed.
(5) By the calculation using laminate theory, the thermal conductivity of such ZrO_2-Al_2O_3 composite coatings in the thickness direction was shown to be much smaller than that in the longitudinal direction. The combination of the high hardness of Al_2O_3 with the low thermal conductivity of ZrO_2 will contribute to the development of high functionally graded TBC.
(6) The adhesive strength for the zirconia composite coating decreased gradually from $F = 60 \sim 80$ kgf/cm^2 when the thickness was more than 100 μm.
(7) The adhesive strength of zirconia composite coating decreased as the alumina mixing ratio increased. The adherence of zirconia composite coating was a minimum when R =50-80%,

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