Plasma Application To Thermal Processing For Hybrid Functionally Materials

Akira Kobayashi(Joining & Welding Res. Inst. Osaka University)

1. Introduction

In order to apply Nano-science & technology to Material Science, the material processing should be developed towards more precise and controllable smart stage. Regarding an applicable heat source, plasma is one of the most superior heat sources, because of high temperature, high energy density, easy controllable, etc. Therefore more precious 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 Al_2O_3 and ZrO_2 [4]. The characteristics of these ceramic coatings by the gas tunnel type plasma spraying were superior to that by the conventional plasma jet.

The ceramic coatings produced by the plasma spraying are effective as thermal barrier coatings (TBC) for high temperature protection of metallic structures because of having high temperature resistance. For example, the zirconia (ZrO_2) coating is used as TBC in hot sections of gas turbine engines and/or diesel engine and in high temperature parts of detonation furnace. It allows the high temperature operation and results to increasing the efficiency of the engine and the durability of the critical components.

While the large porosity and the high melting point is advantage of ZrO_2 coating, the porosity has disadvantage for the adoption under the critical conditions such as high temperature and high corrosion environment. The resistance for thermal shock and high temperature corrosion are important properties in the high performance TBC. 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.

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 [6-10]. The Vickers hardness of the zirconia (ZrO_2) coating was increased with decreasing spraying distance, and a higher Vickers hardness could be obtained at a shorter spraying distance. At L=30[mm], when P=33[kW], the Vickers hardness of ZrO_2 coating was about Hv=1200 [11]. This corresponds to the hardness of sintered ZrO_2. Usually, the Vickers hardness of this sprayed coating became 20~30[%] higher than that of conventional plasma spraying.

ZrO_2 coating formed has a high hardness layer at the surface side, which shows the graded functionality of hardness [11-12]. 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 very important problem as well as the coating quality.

Another application of gas tunnel type plasma is surface modification of titanium. As the results, TiN films of 10[㎛] thickness were formed in a very short time of several seconds.

In this paper, the performance of high hardness ZrO_2 composite coating was investigated and the merit as TBC (thermal barrier coating) was clarified. 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. Moreover the adhesive characteristics of such high hardness zirconia-alumina (ZrO_2-Al_2O_3) composite coatings were investigated as well as its mechanical properties. Especially, the influence on the thickness of the zirconia composite coating was discussed.

Finally, regarding other application of high-energy plasma to thermal processing, the development of new type of smart plasma system was also discussed. One is the surface modification of metals by gas tunnel type plasma, and the other is the thick nitride coatings by the gas tunnel type plasma reactive spraying.

2. Gas Tunnel Type Plasma System

The schematic of gas tunnel type plasma torch developed by the author is shown in Fig. 2. 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 constricts and stabilizes the plasma jet.

The comparison of the shape of plasma jet is shown in Fig. 1. The gas tunnel type plasma jet is longer and more stable than the conventional ones. Table 1 shows the feature of gas tunnel type plasma jet as compared to the conventional ones. The gas tunnel type plasma system has high energy density and also high efficiency. [1-3]

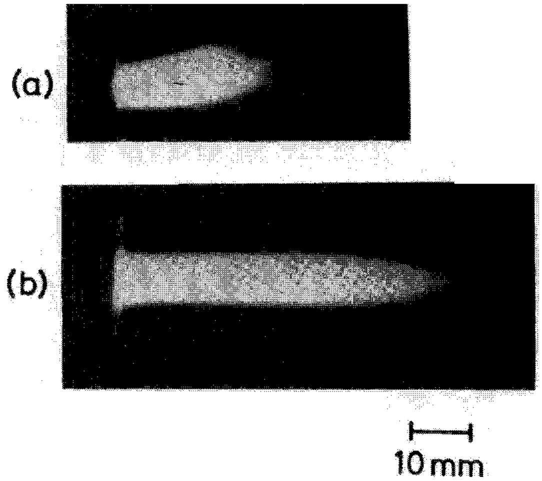


Fig. 1. Comparison of the shape of plasma jet (500[A])
(a) conventional, (b) gas tunnel

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

	Gas tunnel type plasma jet	*conventional ones*
Temperature	15,000[K]	10,000[K]
Energy density	105[W/㎠]	104[W/㎠]
Heat efficiency	80[%]	50[%]

One example of application of the gas tunnel type plasma is the thermal spraying. Fig. 2 shows the gas tunnel type plasma spraying torch. The behavior of the gas tunnel type plasma spraying is shown in Fig. 3. This is the case of the Deposition of Al_2O_3 powder. 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 [4,6-9].

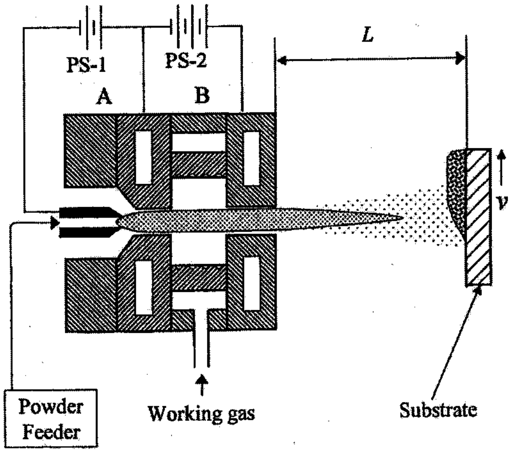


Fig. 2. Schematic of the gas tunnel type plasma spraying torch

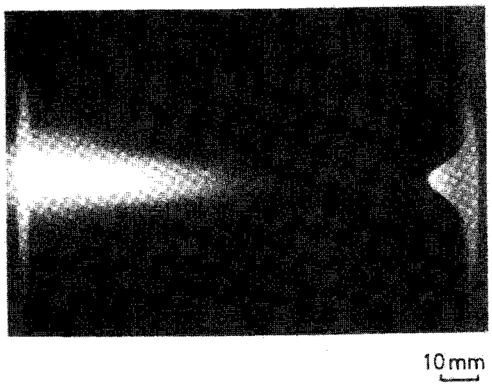


Fig. 3. Behavior gas tunnel type plasma spraying in. the case of deposition of Al_2O_3 powder. Spraying distance: 10[cm]

3. Gas Tunnel Type Plasma Spraying

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].

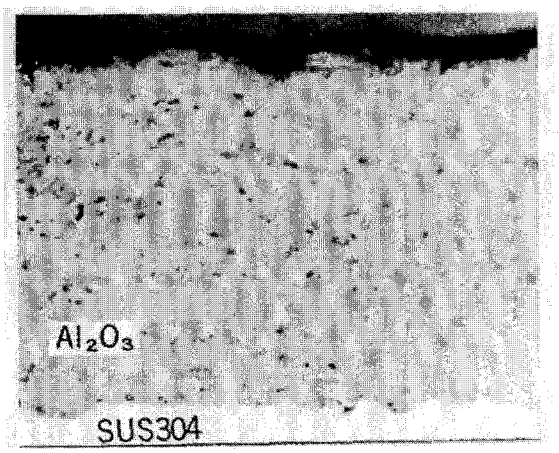
This plasma system has many possibilities for the industrial applications to the various thermal processing, such as plasma spraying, surface modification. The typical applications are:

1) Plasma spraying of ceramics (Al_2O_3 and ZrO_2 etc.)
2) Surface modification of Ti materials (Nitridation)
3) Other Applications such as nano-science, functional materials processing technology
4) Application to environmental problems, others.

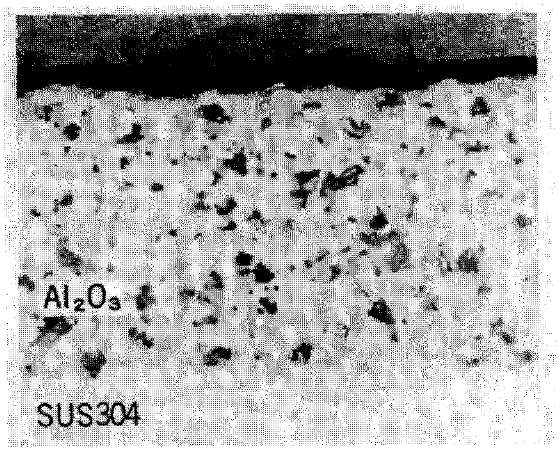
Moreover, the development of new type of smart plasma system is planned in order to apply to thermal processing of materials and the environmental problems and so on.

3.1 Characteristics of Gas Tunnel Type Plasma Spraying

The gas tunnel type plasma spraying can make high quality ceramic coating compared to other plasma spraying method. Fig. 4 is the comparison of the cross section of the Al_2O_3 coating between by gas tunnel type plasma spraying and by the conventional one. The cross section of the coating by gas tunnel type plasma spraying is much denser. Table 2 shows the quality (hardness, porosity, etc.) of the Al_2O_3 coating by gas tunnel type plasma spraying [6-7]. The hardness was like sintered alumina: *Hv*=1,200 and high



(a) Alumina coating by gas tunnel type plasma spraying



(b) Alumina coating by conventional type plasma spraying

Fig. 4. Comparison of the cross section of alumina coating between gas tunnel type plasma spraying (a) and conventional type (b).

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.

Table 2. Comparison between gas tunnel type plasma spraying and conventional type for Al_2O_3 coating(Input=45[kW], Distance = 65~100[mm])

	Gas tunnel type plasma spraying	*Conventional ones*
Vickers hardness	1200	800
Porosity	10[%]	20[%]

Thus it can be easy to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying.

3.2 Experimental Procedure

The gas tunnel type plasma spraying torch used was shown in Fig. 2. 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.

The experimental conditions 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].

Table 3. 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]):	25~1,000
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 1,000[cm/min]. Also the traverse number was changed 1~30 times. The thickness of the coating was 50~250[μm]. Also, high speed traverse of v=1,000[cm/min], 30times.

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 4. 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.

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 50g, 100 g and its load time was 15sec 25s. 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 microstructure of the cross section of zirconia composite coating was observed by an optical microscope.

Table 4. Chemical composition and size of zirconia and alumina powder used. (20~80[%] Al_2O_3 Mixture)

	Composition (wt[%])					Size([㎛])
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 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 10[mm] 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 0~200[kg]. The [kgf/㎠] 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.

4. Results and Discussion

4.1 Effect of Alumina Mixing Ratio on Vickers Hardness of Zirconia Composite Coating

Regarding the Vickers hardness on the cross section of ZrO_2 composite coating produced by the gas tunnel type plasma spraying at the same spraying time, the coating thickness was the same and the maximum Vickers hardness of ZrO_2 composite coating was also same. But the graded functionality became much better with increase in the traverse number.

Fig. 5 shows the dependence of Vickers hardness and porosity of ZrO_2 composite coatings, on the Al_2O_3 mixing ratio R(wt[%]). In this case, the coating thickness was approximately 200[㎛] at P=25[kW], L=40 [mm], when the traverse number was two times.

The Vickers hardness of ZrO_2 composite coating was increased as the increase in the Al_2O_3-mixing ratio. The coating hardness corresponds to the high hardness of Al_2O_3 particles. Namely, the Vickers hardness of Al_2O_3 coating was Hv_{50}=1,440.

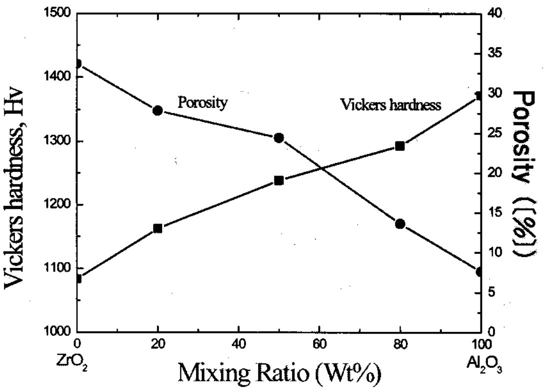


Fig. 5. Dependence of Vickers hardness and porosity of zirconia composite coating on the alumina mixing rate. L=40[mm] when P=25[kW]

The hardness distribution of the ZrO_2 composite 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. This leads to the development of a high functionally TBC.

4.2 Effect of High Speed Traverse on Coating Quality

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 [14].

Fig. 6 is the cross section of composite coating produced by high speed traverse at $P = 25$[kW], $L = 40$[mm]. Traverse times was 30 times. This speed: 1,000[cm/min] was 10 times higher than normal speed traverse like Fig. 2. The thickness was about 150[㎛]. It consisted of 2 different layers, white and gray layers were deposited alternatively. The analysis by EPMA revealed that white is zirconia (ZrO_2) and gray is alumina (Al_2O_3).

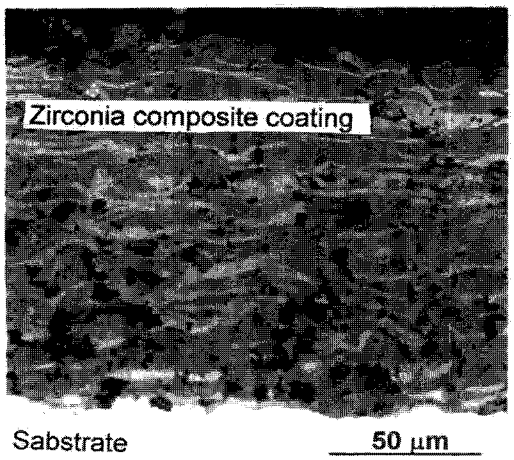


Fig. 6. Microhotograph of cross section of zirconia composite coating. The traverse number was 30 time traverse. Sprayed at L=40[mm] when P=25[kW]

White ZrO_2 layer was a flat sprat of uniform thickness, and embedded parallel in the Al_2O_3 matrix of low melting temperature. The black parts in the coating are pores, and are distributed in 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.

Fig. 7 shows the distribution of Vickers hardness: Hv_{50} of the zirconia/alumina composite coating shown in Fig. 6 (coating thickness: about 150[㎛]). Here, the left side axis is the surface of the coating. 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 distance from the coating surface of l=40[㎛], and decreased linearly like towards the substrate side.

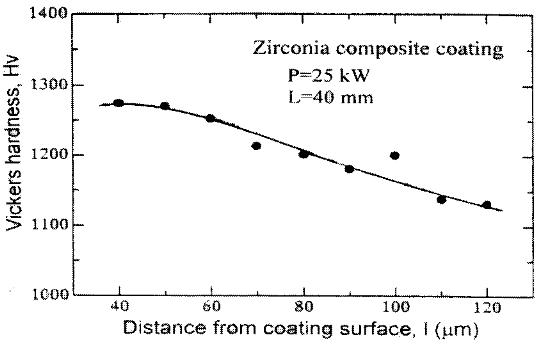


Fig. 7. Surface morphology of the zirconia/ alumina composite coating

Regarding the effect of traverse number, the uniformity of pores was improved and the deviation of hardness distribution was decreased. Therefore, the high speed and high number traverse improved the grade functionality of coating hardness. It shows the possibility of high performance TBC by the high speed traverse processing.

4.3 Influence of Plasma Thermal Process on Coating Quality

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. Fig. 8 shows the SEM photograph of the surface of the zirconia/alumina composite coating. It shows that the surface is formed by the mechanical interlocking at Al_2O_3 and ZrO_2 interface, and it resulted to the higher surface roughness of alumina resulted in higher bond strengths.

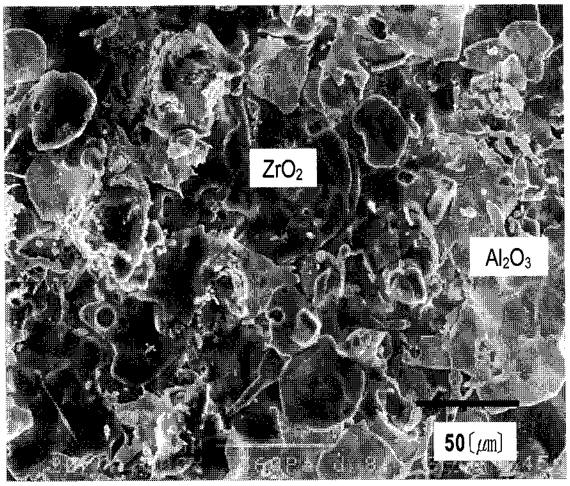


Fig. 8. Surface morphology of the zirconia/ lumina composite coating

Regarding the microphotograph of ZrO_2/ Al_2O_3 coating produced by the gas tunnel spraying on the fixed substrate for 3s spraying time, the coating thickness was about 250[㎛], and white and gray layers were deposited alternatively as shown in Fig. 9.

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. The dense microstructure led to the suppression of the deviation of the hardness distribution. This coating will be useful for high performance TBC.

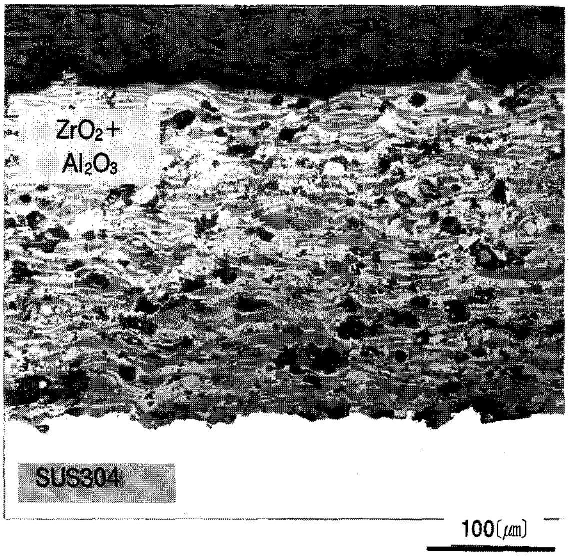


Fig. 9. Typical ZrO_2/Al_2O_3 coating produced by the gas tunnel spraying on the fixed substrate for 3s spraying time

4.4 Adhesive Strength of ZrO_2 Composite Coating

Fig. 10 shows the dependences of adhesive strength of the ZrO_2 composite coatings on the coating thickness. The adhesive strength of the ZrO_2 composite coatings was decreased when the thickness was large. In the case of small coating thickness (100(㎛)), the adhesive strength was large: it was more than 140(kgf/㎠) for the coating thickness below 100(㎛). While, the value was $F = 100 \sim 120$(kgf/㎠) when the thickness was more than 200(㎛). Therefore the thick coating was much easier to break than thin coating, but the adherence was improved when the traverse number was large.

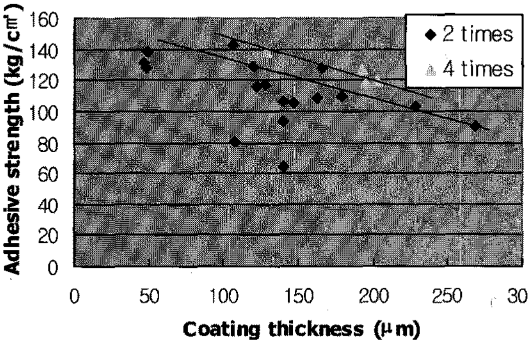


Fig. 10. Adhesive strength of the ZrO_2 composite coatings vs. the coating thickness

5. Other Application of Smart Plazma System

Other application of gas tunnel type plasma is surface modification of metals such as nitridation, carbonization, etc. For example the TiN films were formed in a very short time of 5s by the irradiation of N2 plasma jet as shown in Fig.11. The thickness of TiN film was 10[㎛] and the film is high quality (homogeneous and high density). The Vickers hardness was about 1,700 on the cross section of the film [15].

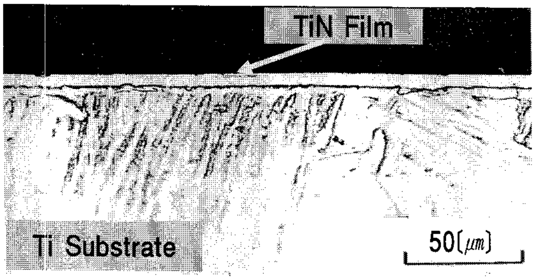


Fig. 11. Microhotograph of cross section of TiN film. Ti substrate irradiated at L=70[mm] when P=20[kW]

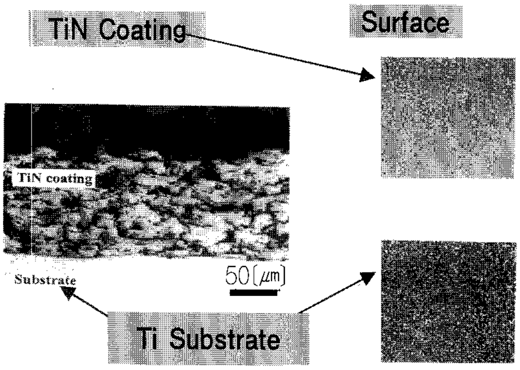


Fig. 12. Cross section of typical TiN coating (P=25[kW], L=60[mm], t=5s) and the surface view of the TiN coating (Hv=2,000) and the substrate

Now, the new type plasma reactive spraying was developed by using the gas tunnel type plasma spraying. The thick TiN coatings were obtained by the gas tunnel type plasma reactive spraying [16]. Fig. 10 shows the cross section of typical TiN coating and the surface view of the coating and the substrate. In this case, the spraying conditions of the gas tunnel type plasma reactive spraying were P=25[kW], L = 60[mm], and t =4.8s. The cooler of the TiN coating is gold color and the Vickers hardness was about Hv=2,000.

For the further wide application of plasma system, the development of new type of smart plasma system: confront electrode type plasma jet has been conducting. The new plasma system has a possibility for producing new materials such as nano-carbon, nano-tube, etc. Here in order to develop smart plasma process, the precise control of plasma factors is a key of the success, which is shown in Table 5.

Table 5. Design of Smart Plasma System for thermal processing

	Control Object
1. Performance of Plasma Jet	
*Power Sources	current, voltage
*Flow rate control system	gas flow rate
2. Control of process materials	substrate, powder
3. Operating system	
*Process precise control of time and spatial distribution	
*Automatic control of thermal process	

6. Conclusions

The following results were obtained during the application of the gas tunnel type plasma system developed.

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.
2) One typical application is plasma spraying of ceramics such as Al_2O_3 and ZrO_2. And the characteristics of these ceramic coatings were superior to the conventional ones
3) The ZrO_2 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).
4) Another application of gas tunnel type plasma is surface modification of metals. TiN films and coatings were formed in a very short time of 5s.

The development of new type of smart plasma system, and application of high-energy plasma to other fields are now undergoing by controlling the operating conditions, etc.

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◇ 저 자 소 개 ◇

Akira Kobayashi, Ph.D.

Professor, JWRI, Osaka University, 11-1 Mohogaoka, Osaka 567-0047, Japan. He was born in July 8, 1948. Academic background: Graduate School of Osaka University (Doctor Degree) in 1976. Discipline and Areas of specialization: Plasma application (plasma spraying /surface modification).

Award : Award for the excellent paper of a year from High Temperature Society of Japan in 1988. Okada Encouraging Prize from Okada Memorial Welding Promotion Society in 1999 Special Prize for the Thermal Spray from High Temperature Society of Japan in 2001

Fax : 81-6-6879-8694

kobayasi@jwri.osaka-u.ac.jp