# Study of TiN Thick Coatings Produced by Gas Tunnel Type Plasma Reactive Spraying

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## Abstract

*The titanium nitride (TiN) sprayed coatings of 100 −200μm thickness can be obtained in short times of 10s and produced by means of gas tunnel type plasma reactive spraying. In this paper, in order to study on the properties of TiN sprayed coatings, the cross-section of the TiN coating was observed by optical microscope and the structure of TiN coating was discussed. Vickers hardness of TiN coatings was measured when the spraying distance was L=60mm and L=70mm respectively. The relation between the spraying conditions L and Vickers hardness Hv of TiN coating was clarified. The adhesive strength of the TiN coating and wear weight of the coating were also measured and discussed. The structure of the TiN sprayed coating was investigated by X-ray diffraction (XRD) under various spraying conditions.*

**KEYWORDS:** (Gas tunnel type plasma reactive spraying) (Vickers hardness) (Adhesive strength) (Titanium nitride coating) (Wear resistance) (X-ray diffraction)

## 1. Introduction

Titanium nitride (TiN) coatings have been widely used in many application fields due to the practical properties such as high hardness, good corrosion resistance, heat resistance and excellent wear resistance etc. [1, 2]. In general, they can be deposited by physical vapor deposition (PVD) evaporation, sputtering, ion plating, and chemical vapor deposition (CVD). In addition, the TiN coating can be also deposited by gas tunnel type plasma reactive spraying which was developed by A. Kobayashi [3]. The gas tunnel type plasma jet [4, 5], being a new type of the plasma sources, has the characteristics of high temperature and high energy density. Therefore, a high quality ceramic coating can be obtained by the gas tunnel type plasma spraying such as $ZrO_2$ coatings, $Al_2O_3$ coatings, and, the mixture coatings of $ZrO_2$ and $Al_2O_3$, etc. [6]. These are all a series of very high hardness coatings [7-12]. The high quality coatings produced by the gas tunnel type plasma spraying methods is much denser and harder than those by the common methods. Moreover, a thick TiN coating of more than 100μm can be formed by means of a new plasma spraying technique which is called "gas tunnel type plasma reactive spraying." Titanium powders are injected to be sprayed with a nitrogen plasma jet.

The various performances of the TiN coatings obtained by this method were superior to those by the conventional TiN formation methods. As a typical example of a titanium nitride film, a TiN coating of 100-200μm thickness for which the Vickers hardness was *Hv*: 1300-1800 [13], could be obtained in a short time of less than 10 seconds.

In this paper, the TiN coatings were formed on the traverse substrate by gas tunnel type plasma reactive spraying in a short time of about 8s. Titanium nitride (TiN) coatings were carried out by changing the traverse numbers and the spraying distance. The cross-section of the TiN coatings was observed by optical microscope and the structure of the TiN coatings was discussed. Vickers Hardness of the TiN sprayed coatings was measured when the spraying distances were $L$=60,70mm respectively. The adhesive strength of the TiN coatings was tested by tension tester and the wear weight of the coating was also measured. The crystal form of TiN sprayed coating was examined using X-ray diffraction (XRD) and the TiN intensity ratio in the sprayed coating was calculated by using the formula of the TiN intensity ratio and the calculated value was compared under various traverse numbers at the spraying distance of $L$=70mm.

## 2. Experimental method

**Fig.1** shows a block diagram of the gas tunnel type reactive spraying torch for the formation of titanium nitride (TiN) coating in this experiment. As details of the gas tunnel type plasma jet were described by A. Kobayashi in previous papers [4], only a brief description of the spraying procedure for TiN coatings is given here.

The experimental conditions for the formation of the TiN coatings are shown in **Table 1.** The chemical composition of the sprayed titanium powder is in shown **Table 2.** Here, the titanium powder was the type of T-459. The substrate was stainless steel which was sand-blasted beforehand. A substrate was located at a certain position

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on the rotating sample holder [12]. The substrate was traversed in the horizontal direction to the axis at a speed of *v*. Titanium powder was supplied into the gas tunnel plasma jet from sideways in the vertical direction of plasma flow and was reactively sprayed onto the traversed substrate for the spraying time of *t*. During the plasma spraying, titanium particles were nitrized by the excited nitrogen in the plasma flow, then deposited onto the surface of the substrate. A TiN thick coating was generated on the stainless substrate of size 50×50×2.5mm. The sprayed titanium powder was Ti: 99.7% with a diameter of 10-40 μm.

For this study, we selected the sprayed TiN coatings for the traverse numbers of 10, 20, 30 with the spraying distance of *L*=60 mm and *L*=70 mm, respectively.
First, the surface of the specimens of the TiN coatings was observed by the naked eye. Then, the cross-section of the TiN coatings was observed by an optical microscope to make an analysis of the inner structure of the coatings. Vickers Hardness (*H*v) was measured at the non-pore region on a cross-section of the TiN coating in order to compare the hardness value for the various spraying conditions. The Vickers hardness was measured for the conditions: loading weight, 100g; holding time, 30s and more than 5 measuring points. The Vickers Hardness of the cross-section of the TiN coating was measured at each distance from the coating surface side to the substance side in the thickness direction.

In the conventional case, the sprayed Ti particles were deposited as a thin film of 10 μm or less on the substrate by the other plasma methods.

The adhesive strength between the coating and the substrate was measured using by the tension tester shown in **Fig.2**. The tested piece for adhesive strength was approximately 10×10mm square and it was attached to each holder for the coating surface side and the opposite side of the coating by polymer type glue. The load for the tester was changed over a range of 0−200kg. Units of kgf/cm² were used for the adhesive strength of the TiN coatings. Moreover, the X-ray diffraction (XRD) using the CuK*α* radiation in the angle range of 30° and 70° at 1.00Å was used for the analysis of the structure of the TiN sprayed coating before and after being snapped by the tension tester.

## 3. Results and Discussion

### 3.1 Observation of the surface of the coatings and comparison of the coating thicknesses

The surface color of the sprayed coatings was observed. The surface color of the coatings appeared a white-gray after spraying, which indicates that it was

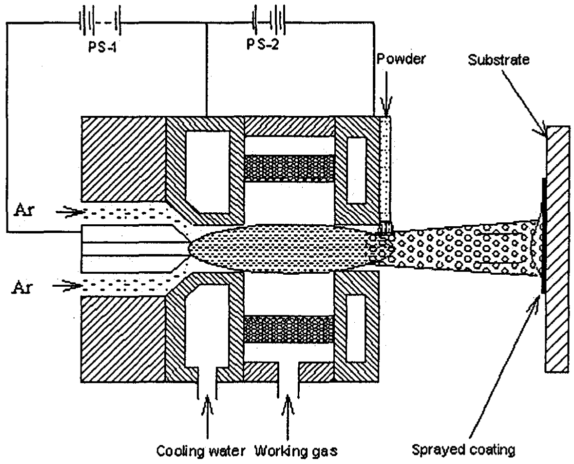



**Fig.1** Block diagram of gas tunnel type plasma reactive spraying torch for the TiN coatings. Diameter of gas diverter nozzle, 20mm, *L*: spraying distance.

**Table 1** Experimental conditions

| | |
|---|---|
| Powder: | Ti-459 |
| Traverse number N: (pass) | 10, 20, 30 |
| Power input P: (kW) | 25,27 |
| Working gas flow rate Q:(Ar, $N_2$) (l /min) | 180 |
| Spraying distance L: (mm) | 60, 70 |
| Traverse speed v: (mm/s) | 60-200 |
| Gas diverter nozzle diameter D: (mm) | 20 |
| Spraying time t: (s) | 8-8.5 |
| Environmental gas flow rate:($N_2$) (l /min) | 100 |

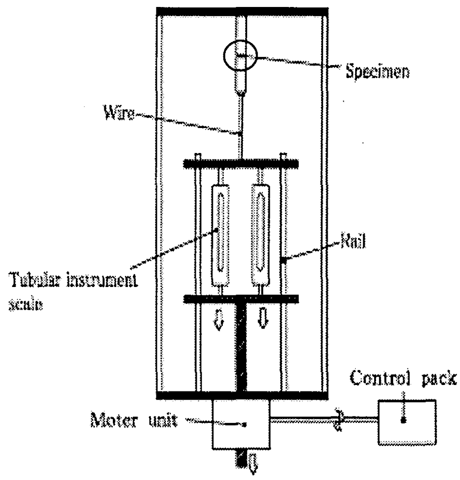
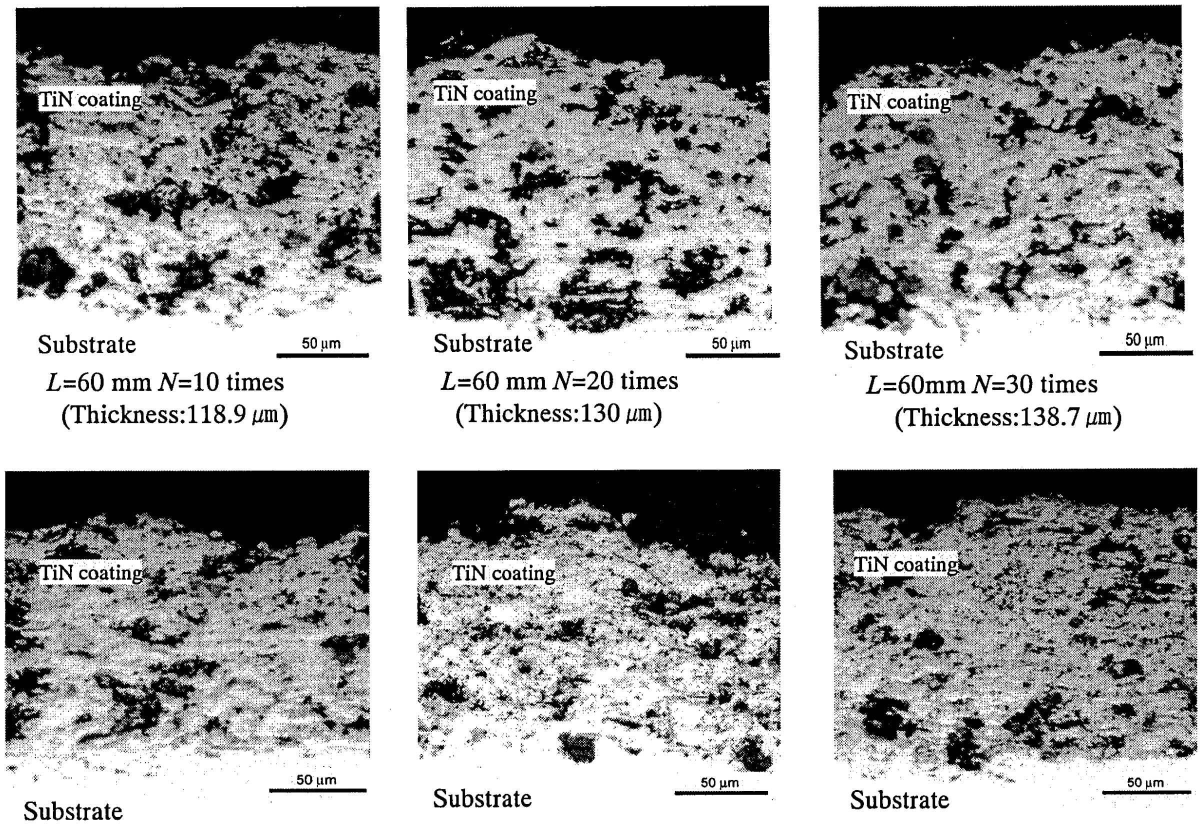



**Fig.2** Schematic diagram of tension tester, the tested range, 0~200 kg.

**Table 2** Chemical composition of titanium powder (*wt %*).

| Chemical component | Ti | Fe | Si | N | O |
|---|---|---|---|---|---|
| Ratio of composition | 99.7 | 0.03 | 0.01 | 0.02 | 0.24 |




$L$=60 mm $N$=10 times (Thickness:118.9 $\mu$m)

$L$=60 mm $N$=20 times (Thickness:130 $\mu$m)

$L$=60mm $N$=30 times (Thickness:138.7 $\mu$m)

$L$=70 mm $N$=10 times (Thickness:118 $\mu$m)

$L$=70 mm $N$=20 times (Thickness:126 $\mu$m)

$L$=70 mm N=30 times (Thickness:133.5 $\mu$m)

**Fig.3** Photomicrograph of cross-section of TiN coatings at the different traverse numbers and the spraying distance; for the other conditions: $P$=25kW, $v$=62, 127, 193mm/s, t=8s; the range of the thickness value of the coatings: 100-140 $\mu$m.

covered by titanium powder in the surface of the coatings. When the white-gray was erased, a gold color appeared at the center of the plasma spraying axis which indicated a large TiN content. The coating surface color was compared at the different traverse numbers when the spraying distances were $L$=60mm and $L$=70 mm, respectively.

The compared results showed that the surface color of the coatings became dark golden as the traverse number was increased at the same traverse speed of $v$=193 mm/s and spraying time of about $t$=8.1s. The reason was thought to be that the titanium sprayed onto the substrate was superheated by the plasma when the traverse number was increased.

### 3.2 Analysis of the cross-section for the TiN coating

**Fig.3** shows the six photomicrographs of the cross-sections for the TiN coatings which were observed by an optical microscope.

The density of the coating became a little higher as the traverse number was increased and the thickness value of the coating was marked below each photo in which the whole range was between 100 and 140 µm. There were a few pores on the cross-section of the coatings as shown in **Fig.3**.The density of the coating became a little higher as the traverse number was increased at the same spraying distance. In general, the properties of the coatings might be better when the sprayed coating became dense; however it was well known that the size of the TiN crystalloid in the coating was much larger than that of Ti crystalloid. Therefore, there was the possibility that Ti powder which had not transformed to TiN existed in the coating. In this case, despite the structure of the formation becoming denser, the mechanical properties might become worse.

The coating thickness was increased as the spraying distance decreased at the same traverse number and spraying time. The coating thickness was also increased as the traverse number was rising at the traverse speed of $v$=193mm/s; the spraying time of around $t$=8s; the spraying distance of $L$=60,70mm respectively.

### 3.3 Characteristics of Vickers hardness in the cross section of TiN coatings

The Vickers hardness *H*v, was measured on a cross-section of the TiN coatings. The distribution of Vickers hardness (*Hv*) from the surface side to the substrate side of the coating show that the Vickers hardness value of the TiN coatings hardly changed between the surface side and inner side of the coatings. However, the hardness value near to the surface side of the coatings seemed to be lower than those of other parts. Then, the average value in the cross section was adopted as the coating hardness. The conditions of the coatings sprayed for the test were as follows: the power input $P$=25kW, traverse number $N$=10, 20, 30; spraying distance $L$=60, 70mm at the spaying time of about $t$=8s.

**Fig.4** shows the dependence of Vickers hardness (*H*v) of the coating on the traverse number at the different spraying distance of $L$=60, 70mm. These results show that the Vickers hardness of the coatings was in the range of *H*v=1100-1300, the highest when the traverse number was $N$=10 and $L$=60mm. among the different traverse numbers. The Vickers hardness decreased with an increase in the traverse number. It also decreased when the spraying distance was increased to $L$=70mm.

One reason for this result was thought to be that the internal stress of the coating was decreased in the case of the large traverse numbers. This would mean that the residual stress was increased and caused the low Vickers Hardness of the coating.

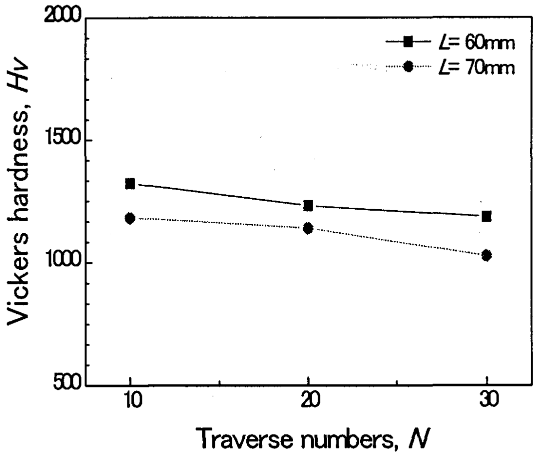



**Fig.4** Dependence of Vickers hardness of the TiN coatings on the traverse number for different spraying distance: $L$=60mm,70mm.

### 3.4 Relationship between adhesive strength and coating thickness

**Fig.5** shows the relationship of adhesive strength and the coating thickness at traverse number $N$=20 at the spraying distance of $L$=70mm under the condition of $P$=25kW, spraying time $t$=8.2s;

It appeared that the value of the adhesive strength decreased as the coating thickness was increased in the case of the same traverse number. In this case, the highest adhesive strength was approximately 145kgf/cm$^2$ at the coating thickness of 100$\mu$m or so.

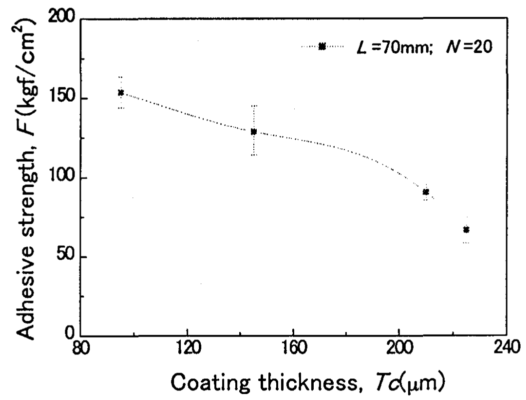



**Fig.5** Relationship of the adhesive strength and coating thickness between coating and substrate at traverse number, $N$=20. The spraying conditions: spraying distance $L$=70mm, power input $P$=25kW.

### 3.5 Relationship between wear resistance and traverse number

**Fig.6** shows the relation of wear weight loss of the sprayed coating and the traverse number when the traverse number was 10, 20, 34, 40 respectively at the spraying distance $L$=70mm. The wear weight loss of the stainless steel is also indicated in this figure. It appeared that the wear weight became larger as the traverse number increased.

These results show that wear resistance of the sprayed coating was much stronger than that of stainless steel. It can be estimated that the wear resistance value of the sprayed coating at the traverse number of $N$=10 was around 30 times that of the stainless steel.

### 3.6 Comparison of TiN intensity raito in TiN sprayed coatings

**Fig.7** shows the comparison of TiN intensity ratio at traverse numbers $N$ of 15, 20, 34 respectively under the condition of spraying distance $L$ of 70mm. First, the calculation formula of TiN intensity ratio was given by the following equation (1):

$$\text{TiN intensity ratio} = \frac{I_{TiN\,(200)}}{I_{TiN\,(200)} + I_{Ti\,((002)}} \quad (1)$$

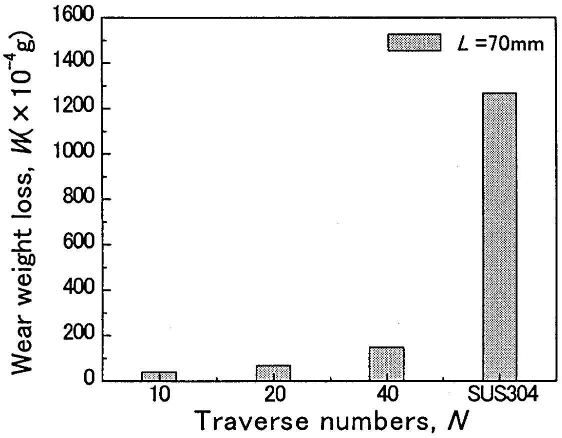



**Fig.6** Relationship of the wear resistance and traverse number as well as stainless steel at the condition of the spraying distance $L$=70mm, traverse speed $v$=62, 127, 193mm /s; spray time $t$=8.2s; power input $P$=25kW.

where $I_{TiN\ (200)}$ , $I_{Ti(002)}$ were the intensity value of TiN(200), TiN(002) shown in the pattern of X-ray dif fraction. It can be seen from **Fig.8** that the TiN intensity ratio decreased with an increase of traverse numbers either before or after being snapped. This can be explained if the mixture of Ti and $N_2$ was deposited sufficiently at the condition of less traverse numbers within the nearly same spraying time when the other spraying conditions were approximately the same.

## 4. Conclusions

The following results were obtained in this study:

(1) It was found that it was possible to produce TiN coatings of more than 100$\mu$m thickness by gas tunnel type plasma reactive spraying. In this study, the thickness value reached approximate 140$\mu$m.

(2) The TiN coating structure was similar under various spraying conditions. The coating was thicker when the traverse number was large at the same spraying distance.

(3) The Vickers hardness of the coatings was $H$v=1100-1450, and it became lower as the traverse number was larger.

(4) In the case of the same spraying distance, the value of the adhesive strength was highest of 145kgf/cm$^2$ at the coating thickness of around 100$\mu$m. The adhesive strength became weaker as the coating became thicker.

(5) As the traverse number increased, the wear resistance of the sprayed coating became weaker. However, the wear resistance of the coating was still much stronger than that of the stainless steel.

(6) TiN intensity ratio decreased slightly with the in crease of traverse numbers. That is, in the same spraying time, the properties of TiN sprayed coating

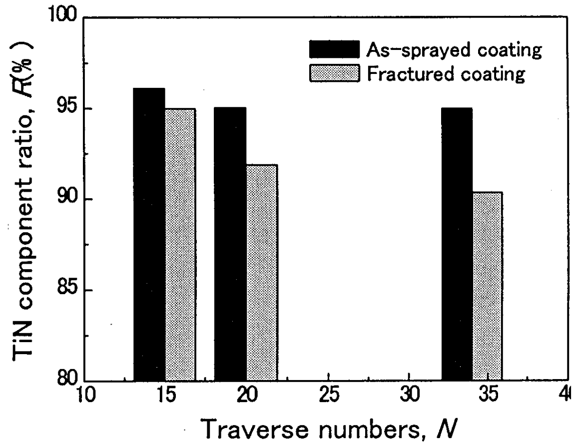



**Fig.7** Comparison of TiN intensity ratio at traverse numbers N of 15, 20, 34 respectively under the condition of spraying distance $L$ of 70mm.

at less traverse numbers should be better than that at more traverse numbers when the other spraying conditions were almost the same.

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