Characteristics of TiN Coatings by Gas Tunnel Type Plasma Reactive Spraying*†

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TiN coating and film that have excellent properties, have been already used in the various field of industry. But TiN film has problems in the formation process: i.e., low deposition rate and poor thickness of the film. In order to solve these problems and to obtain much thicker Titanium nitride (TiN) coating speedy, TiN coatings were formed by means of a reactive spraying by using the gas tunnel type plasma jet. In this study, the fundamental characteristics of this method were investigated by measuring the properties of the titanium nitride (TiN) coatings formed on the traverse stainless steel substrate. Consequently, TiN coatings of 150㎜ thickness were obtained at P=25kW, t=5s, and the characteristics were discussed.

Introduction

Titanium nitride (TiN) has good corrosion resistance, heat resistance, and wear resistance property [1]. TiN films have been already used in the various field of industry. But, many of the methods usually used to produce TiN film have problems in the formation process: i.e., low deposition rate and poor thickness of the film [2]. Therefore the high cost of TiN material prevents the further application in the industry.

Then in order to solve these problems, the gas tunnel type plasma jet was applied to the surface nitridation of titanium. As a typical example of titanium nitride (TiN) films, the film for which the thickness was 10 μm and the Vickers hardness on the surface of the TiN film was Hv = 2000, was obtained in a short time of t =10 s at P = 29 kW, L = 90 mm [3,4]. This investigation pursued the possibility of the speedy formation of a high functionally thick TiN film.

By the way, the gas tunnel type plasma jet [5-7], whose electrical potential gradient is 40V/cm, has high temperature and high energy density. Also it has high thermal density of 80%. Those are superior to the properties of other conventional type plasma jets [8]. Therefore this plasma has a great advantage of various applications to thermal processing. For example, regarding thermal spraying with ceramics, high quality coatings, which are much denser and harder than that of the conventional one were obtained by the gas tunnel type plasma spraying [9,10]. Especially, the alumina coatings produced had a Vickers hardness of Hv =1200-1600 [11].

Following the above studies, in order to obtain much thicker coating speedy, the gas tunnel-type plasma reactive spraying was developed as a new method by the author. A thick TiN coating of more than 100 μm was formed with this plasma reactive spraying [12].

In this study, TiN coatings were formed on the traverse substrate by means of this gas tunnel type plasma reactive spraying in a short time of about ten seconds. And, the fundamental characteristics of this method were investigated by measuring TiN thickness and Vickers hardness as the mechanical property of the titanium nitride (TiN) coatings.

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Also, the structure of an obtained TiN coating was investigated by X-ray diffraction, and the degree of nitride formation (TiN ratio) on the surface was examined. From the results, the effect of spraying conditions on the properties of TiN coatings was discussed.

Experimental

Figure 1 shows a block diagram of the gas tunnel type plasma reactive spraying torch for producing the TiN coatings. The gas tunnel type plasma jet torch was described in detail in previous studies [1-3]. The torch whose diameter of gas divertor nozzle was 20 mm was used in this study.

Reactive spraying of titanium materials was carried out under atmospheric pressure in the spraying chamber (600 mm diameter). For the experiment, nitrogen (N_2) was used as working gas of gas tunnel type plasma jet. The torch was located at the center of the sidewall of the cylindrical chamber. The Ti powder was fed into the gas tunnel plasma jet at exit of gas divertor nozzle, instead of from center hole of cathode nozzle in the case of plasma spraying of ceramics.

A substrate was located at a certain position; the distance between the torch and the substrate is the spraying distance: *L* Then Ti powder was supplied into the plasma flame and was reactive-sprayed on a substrate for the spraying time: *t.* Ti was nitrided and a TiN coating was formed by traverse of the substrate at speed of *v*.

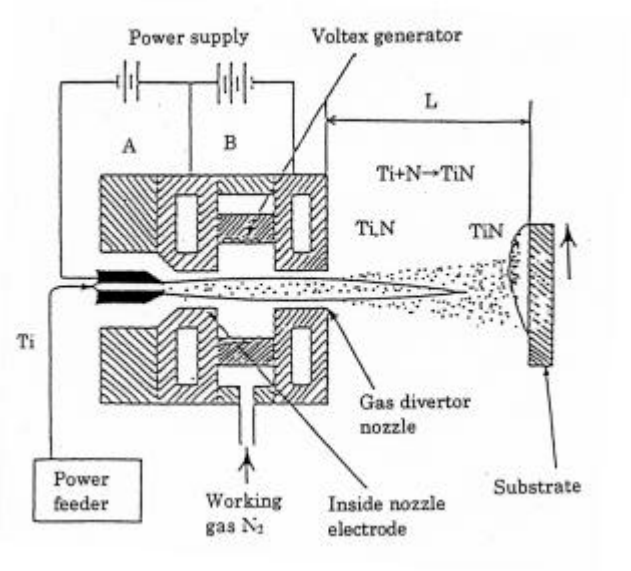

Fig. 1 Gas tunnel type plasma reactive spraying torch for the TiN coatings.

Table 1 Experimental conditions

Power input:	*P* ~ 25 kW
Working gas (N_2, Ar) flow rate:	*Q* ~ 200 l/min
Environmental gas(N_2) flow rate:	*Qen* =50-300 l/min
Spraying distance:	*L* = 60 mm
Powder feed rate:	*w* = 30 g/min
Traverse speed:	*v* = 60 –1400 cm/min
Traverse number:	*N* = 1 – 40
Spraying time:	*t* = 2 - 11 s

The experimental conditions for the surface nitriding of Ti are shown in **Table 1**. The working gas, N_2 of industrial use with small amount of argon (Ar), was kept at a constant flow rate, *Q*, of 170-180 l/min. And the flow rate *Qen*, of an environmental N_2 gas, surrounding the substrate, was varied between 50-300 l/min. The power input to plasma torch, *P* was 20-30 kW. In this experiment, the spraying distance was kept at *L* = 60 mm.

Ti powder used was Ti: 99.9% and a diameter of 10-40μm. Stainless steel plate: commercially used type of SUS304 was used as a substrate in this study. The size of the substrate was 25 mm x 50 mm large and 5 mm thick. The surface substrate for the spraying time: *t.* Ti was nitrided and a TiN coating was formed by traverse of the substrate at speed of *v*.

The obtained titanium nitride (TiN) coatings were observed with an optical microscope. The thickness of the TiN coatings was also measured with a micrometer. The structure of the TiN coating was investigated on the surface using the X-ray diffraction method. The source of X-ray was CuKa. The peak intensities of Ti, TiN were measured from the obtained diffraction patterns and the composition of the surface was determined.

The Vickers hardness *Hv* was measured on the surface of the TiN coating formed under the various spraying conditions. The hardness test was also done on the cross section of the TiN coating. The conditions for the measurement of the Vickers hardness were: loading weight 5 g, holding time 25 s, number of measuring points more than 10.

Results and Discussion

Characteristic of Titanium Nitride Coating

Figure 2 shows the dependence of thickness of TiN coating on the flow rate of an environmental N2 gas: *Qen*. The experimental conditions were P = 25 kW, L = 60 mm, and t = 4.8 s. The traverse speed was v =100 cm/min and traverse number was 3 times. The working gas flow rate was a constant value of Q = 180 l/min.

This result shows that an increase in the gas flow rate *Qen* causes an increase in TiN coating thickness in case of 100 l/min < *Qen* < 200 l/min. The thickness was 100 μm at *Qen* =100 l/min, and maximum value of 200-250μm at *Qen* =200 l/min. The surface was gold color.

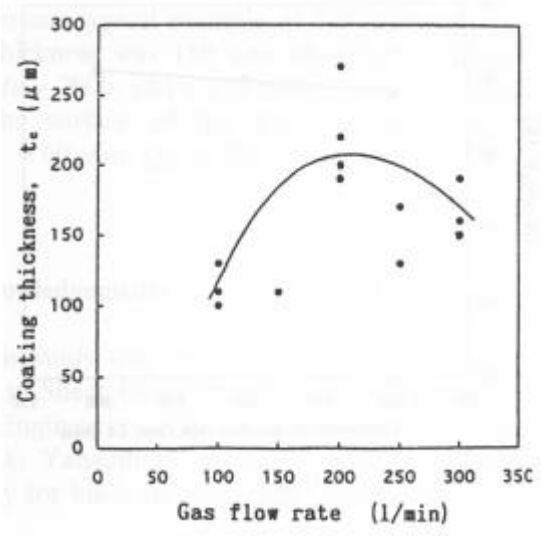

Fig. 2 Dependence of thickness of TiN coating on the flow rate of an environmental N2 gas.

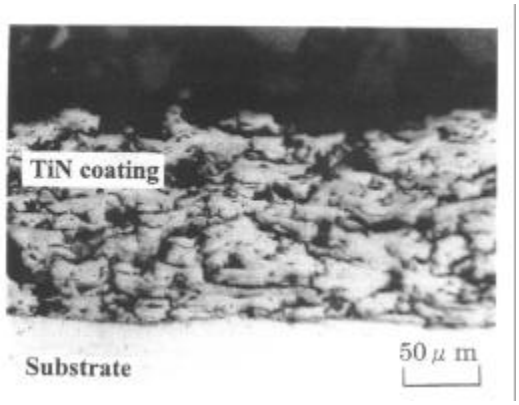

Fig. 3 Photomicrograph of the cross section of the same TiN coating.

However, when the *Qen* was further increased (from 200 l/min to 300 l/min), the TiN thickness became smaller. This reason is thought that the increase in the *Qen* caused the decrease of substrate temperature as described below.

Figure 3 shows a typical photomicrograph of the cross section of the above TiN coating at *Qen* =200 l/min obtained by an optical microscope. The spraying condition was the same as Fig. 2. In this case, the thickness was more than 150 μm, and the surface color was almost gold color.

Many pores existed in this TiN coating as the normal plasma sprayed ceramic coating. But, the density of this TiN coating was much higher than the case of 100 l/min, also the adhesion between coating and substrate was in a good condition. The maximum value of Vickers hardness of this coating on the cross section was near Hv = 2000.

The dependence of Vickers hardness on the cross section of TiN coating on *Qen* is shown in **Fig. 4**. These TiN coatings are the same ones as shown in Fig. 2. The deviation among the measured values at each *Qen* was very large, 50-70%. The reason is that these were formed by the spray method and had some pores somewhere. But Vickers hardness of TiN coating increased as the *Qen* increased.

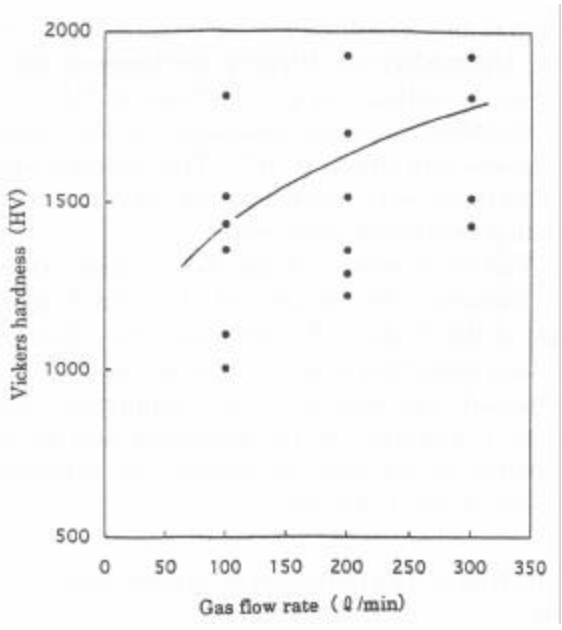

Fig. 4 Dependence of Vickers hardness on the cross section of TiN coating on *Qen*.

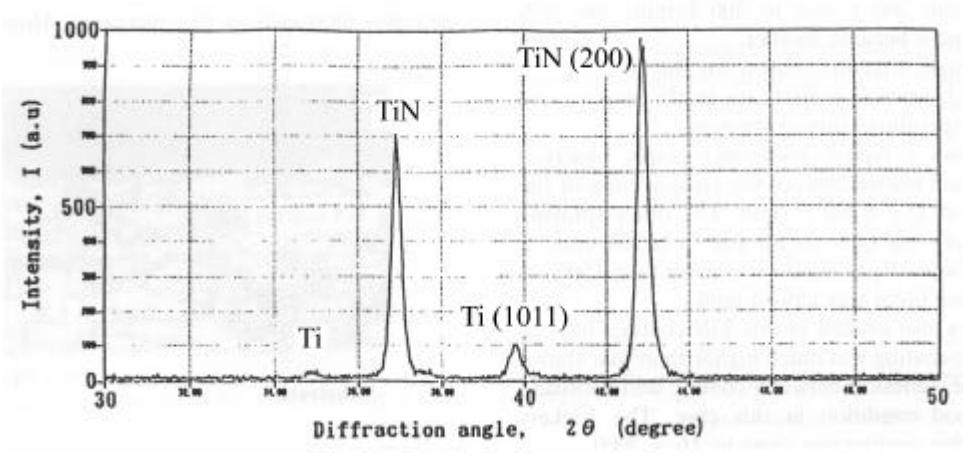

Fig. 5 X-ray diffraction on the surface of the TiN coating. XRD spectrum.

In the case of 300 l/min, the average of the Vickers hardness was more than *Hv* = 1750: Vickers hardness obtained is lower than its expected value of *Hv* = 2000. The reason is due to the low hardness of Ti remained no reactive phase. But, the maximum value obtained was about *Hv* = 2000 on a certain part of the coating.

Analysis of TiN coating

Figure 5 shows the result of X-ray diffraction on the surface of the TiN coating in the case of *Qen* =200 l /min. The spraying conditions were the same as in Fig.2. The conditions were: *P* = 25 kW, *L* = 60 mm, and *t* = 4.8 s. The measurement was carried out at the diffraction angle between 30-50 degree.

Observing these X-ray diffraction pattern, a few strong and sharp TiN peaks appeared, while the Ti peaks' intensity was very small. Also we could not find out the TiO_2 peaks in this pattern.

The X-ray diffraction patterns in the case of changing *Qen* showed that an increase in the *Qen* caused an increase in intensity of TiN peaks in case of 100 l/min < *Qen* < 200 l/min. However, when the gas flow rate was further increased (from 200 l/min to 300 l/min), the TiN peaks became a little smaller than that of the maximum value.

Thus the peaks in the pattern at *Qen* = 200 l/min were almost TiN, while Ti peak was small. Therefore, composition of TiN in the coating may be nearly 100%, almost complete TiN coating was formed at *Qen* = 200 l/min.

Now, the intensity ratio of TiN (TiN ratio: *R*) is introduced as the following equation [3].

$$R = I_{TiN(200)} / (I_{Ti(1011)} + I_{TiN(200)}) \times 100\ (\%) \qquad (1)$$

Here, $I_{Ti(1011)}$, $I_{TiN(200)}$ respectively indicate the peak intensity of the (1011) plane of Ti phase and that of the (200) plane of TiN phase. The peaks used are indicated in Fig.5.

The relation between the *Qen* and TiN ratio obtained from the X-ray diffraction patterns of Fig.5 by using the equation (1) was shown in **Fig.6**.

The TiN ratio was increased as increase in *Qen*, and was maximum: *R* = 92 % at *Qen* = 300 l/min in this case. This corresponds to the result that the Vickers

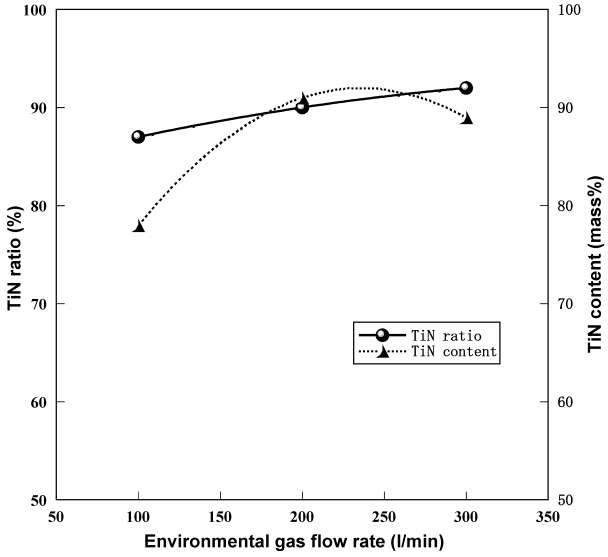

Fig. 6 Dependence of the TiN ratio of TiN coating on *Qen*.

hardness was increased with the increase in *Qen*. But in any cases, the TiN ratio was a high value of about 90%.

Figure 6 also shows the results of X-ray Luminescence Analysis. In this case, the ratio of TIN/(TiN+TiO_2) was used. As is shown in this figure, the value of TiN content (mass%) was a similar value of about 90%. The dependence on *Qen* corresponds to that of the TiN coating thickness shown in Fig.2. There was also an optimum value of TiN content for the environmental gas flow rate. At the *Qen* =200 l/min, for which the measured value of TiO_2 content was minimum, TiN content was a maximum value of about 92%.

Effect of temperature of substrate

The temperature of substrate will be most important key for the effective formation of TiN. Then the effect of the temperature on the coating process was considered by measuring the substrate temperature.

Figure 7 shows the dependence of substrate temperature of back surface on the environmental gas flow rate, *Qen*. The main experimental conditions were: P = 25 kW, L = 60 mm.

The temperature of the substrate decreased linearly with the increase in the *Qen.* The temperature was more than T = 800°C at *Qen* = 100 l/min. On the other hand, it became a lower value of T = 600°C at *Qen* = 100 l/min. This was because the large volume of N_2 gas cooled the substrate temperature down.
As the result, deposition rate was decreased at too much *Qen.* I this way, the coating thickness was maximum value at a certain flow rate: too high a flow rate of environmental gas will suppress the deposition rate of TiN coating. Also it will suppress the quality of TiN coating because of a law temperature condition. In this study, the optimum value for the environmental gas flow rate was *Qen* = 200 l/min, for which we obtain the maximum coating thickness and the best coating quality.

As the above results show that there is a set of optimum conditions for the reactive spraying of a Ti powder; it requires a certain spraying time, a proper power input, and a certain flow rate of an environmental gas in order to obtain a complete TiN coating.

Figure 8 shows the relation between the TiN ratio and the Vickers hardness obtained under various conditions listed in Table 1. The Vickers hardness *Hv* was increased almost linearly with the increase of the TiN ratio in the experimental range. *Hv* became the maximum value of the Vickers hardness was *Hv* = 1750 at R = 92%. The Vickers hardness was predicted to be about *Hv* = 2000 when R was more than 95 %, up to 100%.

Thus, the measured values of the Vickers hardness were directly related to the TiN ratio of the produced coatings.

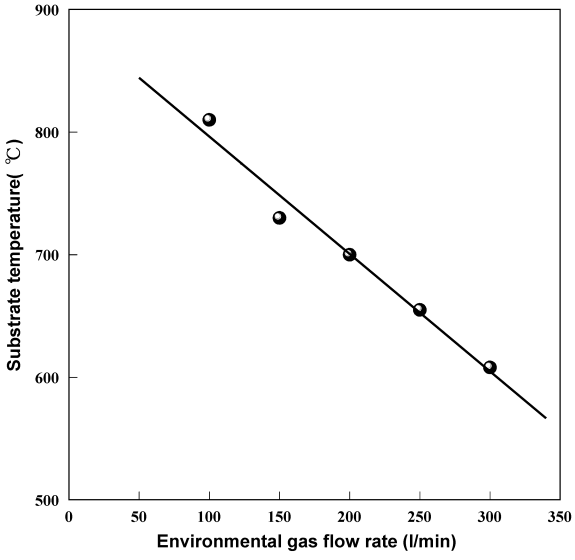

Fig. 7 Dependence of substrate temperature on *Qen*.

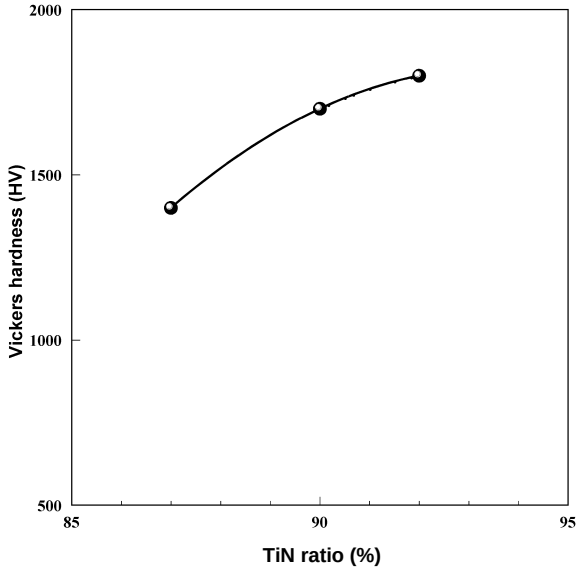

Fig. 8 Relation between the TiN ratio and the Vickers hardness of the TiN coating

CONCLUSION

The TiN coating was formed using the titanium powder by the gas tunnel type plasma reactive spraying, and the following results were obtained.

1) The TiN coating in which the oxidization was much more suppressed could be formed in a short time of about ten seconds. The obtained TiN coating was more than 200 μm in thickness.

2) The structure of the obtained TiN coating was composed of TiN mainly including small ratio of Ti. The TiN coating was formed smoothly on the surface of the coating. The TiN ratio was more than 90 % on the surface of this TiN coating.

3) As one typical example of TiN coatings, the coating thickness was 150 μm and the Vickers hardness was near Hv = 2000, was obtained under the following conditions: P = 25 kW, L = 60 mm, and t = 5 s. The TiN ratio was 91 % on the surface of the TiN coating.

4) The Vickers hardness of the TiN coating increased as the *Qen* was increased. But, the Vickers hardness was saturated at more than *Qen* = 200 l/min. The TiN ratio was also increased as increase in *Qen*.

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