Surface Nitridation of Titanium Metal by Means of a Gas Tunnel Type Plasma Jet

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The surface nitridation of titanium was carried out at a low pressure in nitrogen atmosphere using a gas tunnel type plasma jet. The titanium nitride (TiN) film, 10 μm thick and 2000 HV, could be formed in 10 s. The structure of the TiN film was investigated by XRD. The Vickers hardness on the surface of the film was measured. The effects of deposition conditions on the properties of TiN films (TiN thickness,Vickers hardness, etc.) were investigated, and the advantage of this deposition method was identified from those results.

Keywords
gas tunnel type plasma jet, plasma coatings, surface modification, titanium, titanium nitride coatings

1. Introduction

PROPERTIES of the gas tunnel type plasma jet (Ref 1-3) were proved to be superior to the properties of other conventional type plasma jets (Ref 4). As to the formation of high-performance materials, high-quality coatings were obtained by the gas tunnel type plasma spraying method (Ref 5, 6); for example, one of the alumina coatings produced had a Vickers hardness, HV, of 1200 to 1600 (Ref 7).

Many studies on the surface modification of metals were carried out, and many kinds of high-performance coatings were formed by physical vapor deposition (PVD), chemical vapor deposition (CVD), and other methods (Ref 8). Titanium nitride (TiN) has good corrosion resistance, thermal stability, and wear resistance (Ref 9). Many of the common methods used to produce TiN film have problems in the formation process; i.e., low deposition rate and poor thickness of the film (Ref 10).

To solve these problems, the gas tunnel type plasma jet, which is a high-energy and high-temperature type, was applied to the surface nitridation of titanium. This experiment also investigated the possibility of the speedy formation of a high functionally thick TiN film.

The structure of an obtained TiN film was investigated by x-ray diffraction (XRD), and the degree of nitride formation on the surface was examined. The Vickers hardness of the TiN film is also examined as a mechanical property of the film. From the results, the effect of deposition conditions (deposition distance, power input, etc.) on the properties of TiN films is discussed.

2. Experimental Results

Figure 1 shows a block diagram of the gas tunnel type plasma jet experimental apparatus used for the surface modification. The mechanism and properties of the gas tunnel type plasma torch were described in previous papers (Ref 2-4). The torch was located at the center of the side wall of the cylindrical chamber (600 mm diam). Surface nitriding of titanium was carried out under vacuum of about 50 hPa. A substrate of titanium was located at a certain position apart from the plasma torch; the distance between the torch and the substrate is the irradiation distance, L. Then the gas tunnel plasma jet was irradiated on a surface of the substrate for a certain time; i.e., irradiation time, t.

Table 1 shows the experimental conditions for the surface nitriding of titanium. The experiment was carried out at a low pressure using the gas tunnel type plasma jet with nitrogen as working gas. The working gas flow rate, Q, was kept at a constant value of 180 L/min, and the flow rate of an environmental nitrogen gas, Q_{en}, surrounding the substrate, was varied. The power input to plasma torch, P, was 20 to 30 kW. A TiN film was formed by changing the irradiation time, t. In this experiment, two values of deposition distance were used: 90 and 100 mm L.

Table 1 Experimental conditions

Power input, P	20 to 29 kW
Working gas (N_2) flow rate, Q	180 L/min
Environmental gas (N_2) flow rate, Q_{en}	50 to 200 L/min
Pressure, p	50 hPa
Irradiation distance, L	90 and 110 mm
Irradiation time, t	4 to 26 s

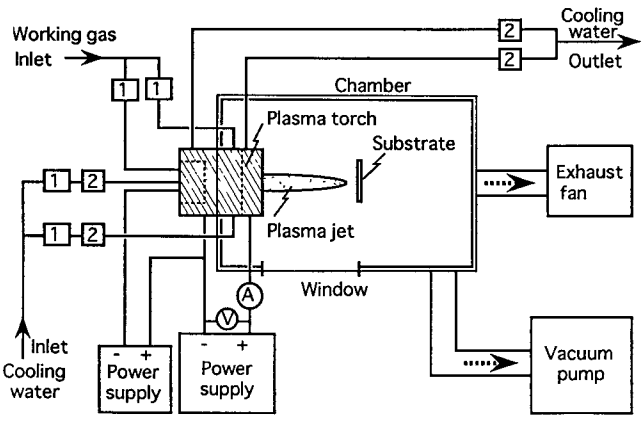

Fig. 1 Block diagram of the experimental apparatus for a surface modification, which is composed of the gas tunnel type plasma torch, power supplies, a cooling water unit, a gas supply unit, gas exhausting units, etc. The vacuum cylindrical chamber is 600 mm diam; 1, regulator with flowmeter, 2, thermometer

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A commercially used type of pure titanium metal (99.9 wt% Ti) was used as a substrate in this study. Each substrate was 20 by 60 mm long and 3 mm thick. The surface was wire-brushed and cleaned by acetone before nitriding.

The obtained titanium nitride (TiN) films were observed with an optical microscope. The structure of the TiN film was investigated using XRD. The source of x-ray was copper Kα. The peak intensities of Ti and TiN were measured from the obtained diffraction patterns, and the composition of the surface was determined.

One of the mechanical properties of the TiN film, the Vickers hardness HV, was measured on the surface of the TiN film formed under the various irradiated conditions. The penetration direction was perpendicular to the surface of the metallographic sample. The hardness test was also done on the cross section of the TiN film. The conditions for the measurement of the Vickers hardness were 5 g loading weight, 25 s holding time, and greater than 10 measuring points.

3. Results and Discussion

3.1 *Surface Nitridation of Titanium Metal*

Figure 2 is a micrograph of the cross section of a titanium nitride (TiN) film produced on the surface of titanium by the gas tunnel type plasma jet method. For understanding, this is observed by an optical microscope. TiN film was formed in the surface layer of the Ti substrate. In this case, the film was about 10 μm thick. An acicular structure existed under this TiN film as shown in Fig. 2.

To determine the structure of the obtained TiN film, an XRD analysis was carried out on the surface of the same sample. Figure 3(a) shows the spectrum from the exposed surface. Figure 3(b) is the same surface prior to exposure. These two XRD patterns show the difference between these materials. For the as received Ti substrate, there are only peaks of hexagonal close-packed Ti, but for the substrate after plasma irradiation, a few sharp TiN peaks appeared. The Ti peak intensity decreased, and the peaks became much smaller than the corresponding peaks from the original substrate.

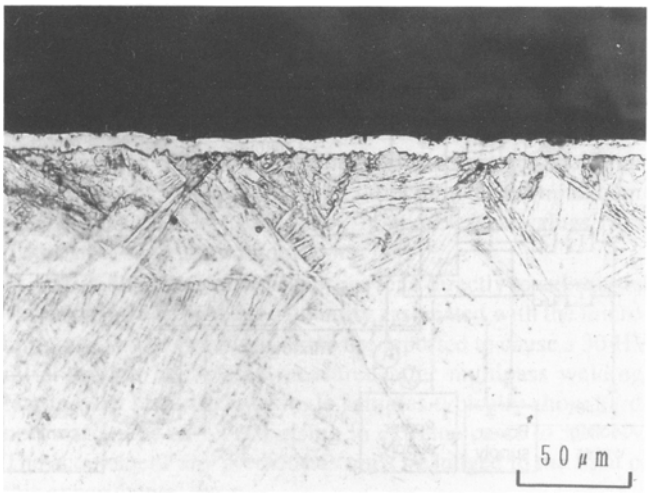

Fig. 2 Micrograph of the cross section of a titanium metal after surface nitriding. The TiN film produced was about 10 μm thick for the conditions: P = 29 kW, Q = 180 L/min, L = 90 mm, t = 10 s.

Figure 4 shows the distribution of Vickers hardness in the thickness direction on the cross section of TiN film and the substrate shown in Fig. 3(a). In the region less than 10 μm from the surface, the Vickers hardness is greater than 800 HV; i.e., the surface was very hard. This hard layer corresponds to TiN film, which is shown in Fig. 2.

Furthermore, the layer that is 40 μm thick has a Vickers hardness of greater than 250 HV. The substrate was hardened due to the solid solution of nitrogen in titanium. This region corresponds to the region where the acicular structure appeared in the substrate as shown in Fig. 2.

Figure 5 shows the distributions of chemical compositions—Ti, N, and O—in the same plasma irradiated substrate, which was obtained by electron probe microanalysis (EPMA). The standards were pure Ti for Ti, Si_3N_4 for N, and Al_2O_3 for O. From this result, the surface layer less than 10 μm from the surface indicated that the mass fraction for a composition of N is

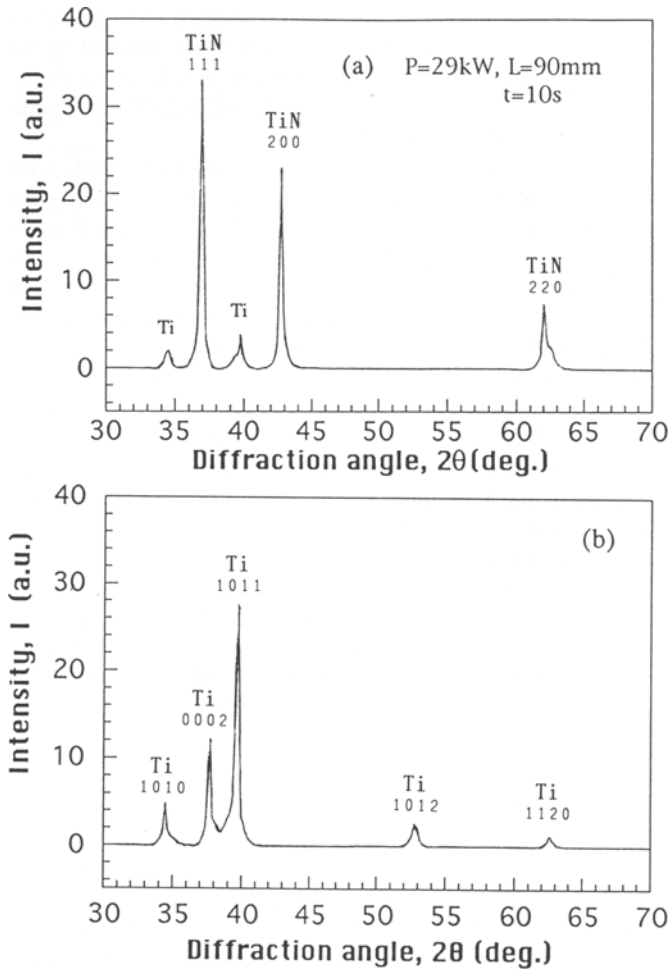

Fig. 3 XRD patterns of the surface of the Ti substrate: (a) plasma irradiated substrate shown in Fig. 2, (b) as received Ti substrate. In (a) after plasma irradiation, sharp TiN peaks appeared.

greater than 40%. The coating should be nominally 23% N (for stoichiometric TiN). The abnormally high values for nitrogen in the coating may be due to inadequate corrections in the EPMA analyses. In the region 10 to 40 μm from the surface, the mass fraction of N is still at the high value of 25%. This shows the solid solution of nitrogen in titanium.

3.2 *Formation Characteristic of Titanium Nitride Film*

This section describes the properties of the TiN formation under the various conditions.

3.2.1 Effect of Environmental Gas

Figure 6 shows the XRD results on the surface of the TiN film with changing Q_{en}; i.e., the flow rate of an environmental N_2 gas surrounding the substrate. Experimental conditions were 29 kW power input P, 90 mm irradiation distance L, and 8 s irradiation time t. These XRD patterns show that an increase in the gas flow rate Q_{en} causes an increase in intensity of TiN peaks in the case of 50 L/min < Q_{en} < 100 L/min. However, when the gas flow rate is further increased from 100 to 200 L/min, the TiN peaks become smaller.

An intensity ratio of TiN, R, is defined according to the following equation in order to assume the thickness of the TiN layer.

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

Here, $I_{Ti(1011)}$ and $I_{TiN(200)}$, respectively, indicate the peak intensity of the (1011) plane of the Ti phase and that of the (200) plane of the TiN phase. The peaks used are indicated in Fig. 6(a).

Figure 7 shows the relation between the environmental gas flow rate and the TiN ratio obtained from the XRD patterns of Fig. 6 using Eq 1. The TiN ratio was maximum: 78% R at 100 L/min Q_{en}. Therefore, it shows that the film thickness was also maximum at 100 L/min Q_{en}. Too little or too high a flow rate of environmental gas will suppress the deposition rate of TiN film.

Figure 8 shows the Vickers hardness on the surface of the TiN films shown in Fig. 6. The dependence of the Vickers hardness on the environmental gas flow rate corresponds to that of the TiN ratio shown in Fig. 7. There is an optimum value for the environmental gas flow rate, Q_{en}, of 100 L/min, for which the observed value of the Vickers hardness is maximum, 1750 HV. The experiment described below was carried out with this optimal value of Q_{en}.

3.2.2 Effect of Plasma Irradiation Time

Figure 9 shows the relation between the thickness of TiN and plasma irradiation time, t (deposition time). The experimental conditions are 29 kW power input P and 100 L/min environmental gas flow rate Q_{en}, for 90 and 110 mm irradiation distance L.

For each irradiation distance, the thickness of TiN increased with increasing deposition time. In particular, with 90 mm L, the rate increase of the TiN thickness was the largest in the interval; i.e., t = 6 to 8 s. At t = 10 s, the TiN thickness reached 10 μm; R = 90%.

With L = 110 mm, it took more time to get the same TiN thickness. In this case, the deposition time to reach 10 μm was 18 s. For longer irradiation time, the titanium substrate surface would dissolve.

Figure 10 shows the relation between the Vickers hardness on the surface of the TiN film and the deposition time. The experimental conditions are the same as those in Fig. 9. For L = 90 mm, the Vickers hardness increased sharply at deposition time greater than 6 s and reached 2000 HV at 10 s. These results show that the nitriding of titanium was greatly enhanced at the deposition time of 8 s. The surface of the titanium material changed its color and became a gold color. For long irradiation

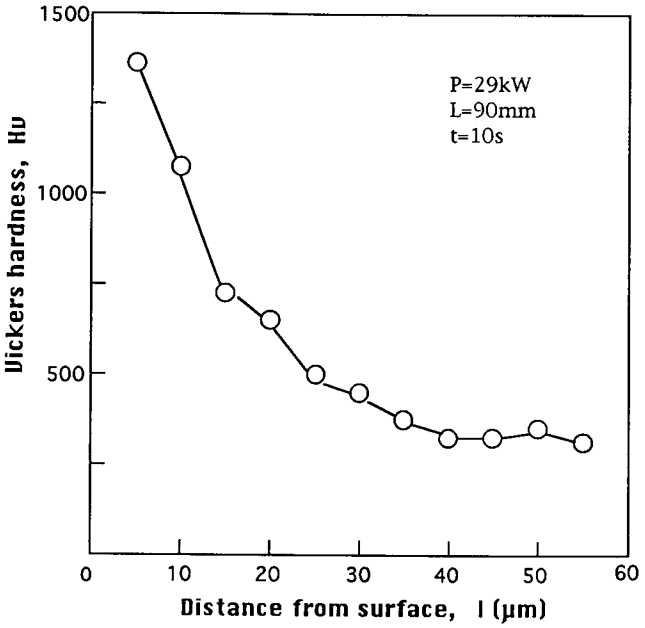

Fig. 4 Distribution of the Vickers hardness in the thickness direction of the cross section of the plasma irradiated substrate shown in Fig. 3(a)

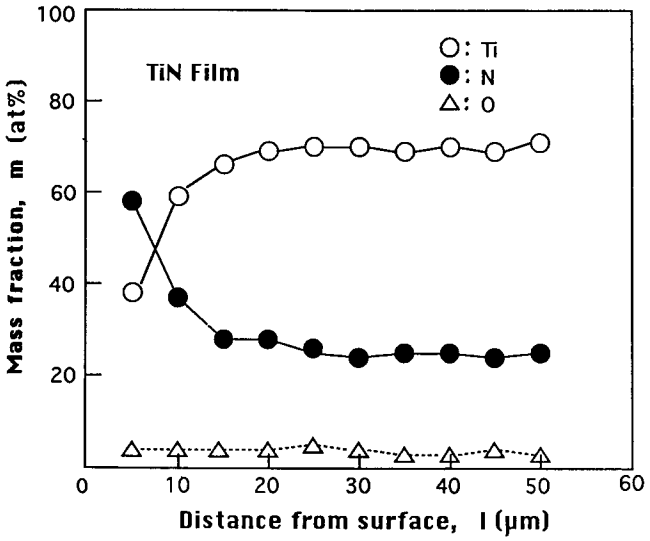

Fig. 5 Distributions of the chemical compositions (Ti, N, O) in the thickness direction of the same material as in Fig. 4. This result was obtained by EPMA: JEOL; JXA-8600S/M-type.

distance, L, 110 mm, the time at which the Vickers hardness, HV, reached 2000 was longer.

3.2.3 Effect of Plasma Power Input

This section describes the effect of the plasma power input on the TiN thickness and Vickers hardness for L = 90 mm and t = 8 s. The working gas flow rate was constant, Q = 180 L/min. The environmental gas flow rate, Q_{en}, was 100 L/min.

Figure 11 shows the relation between the TiN thickness and the power input. The TiN thickness increased with increasing torch input. Especially at power inputs between 26 and 29 kW, the increase rate of the TiN thickness was very large, and at P = 29 kW, TiN thickness, t_c, reached 10 μm. At greater power input, the titanium substrate surface would dissolve due to the thermal energy of the plasma.

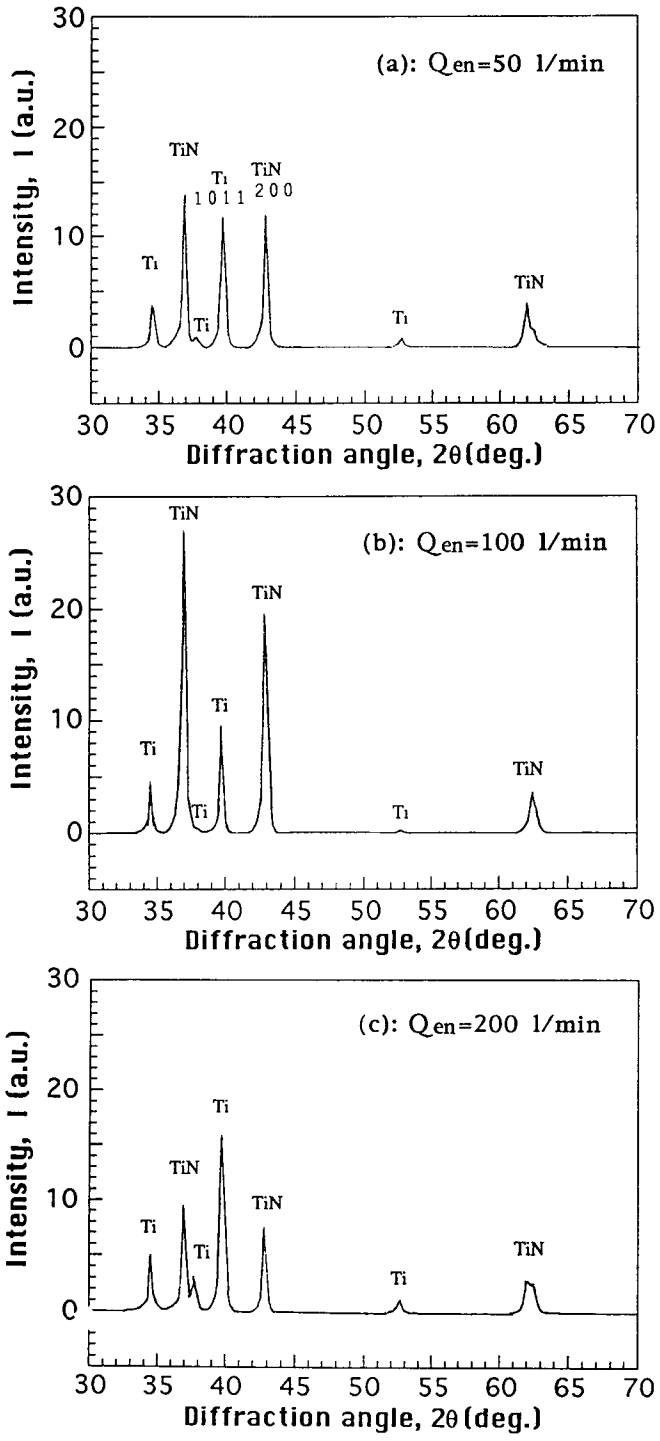

Fig. 6 XRD patterns on the surface of the TiN film for different flow rates of environmental N_2 gas under the conditions: P = 29 kW, L = 90 mm, and t = 8 s

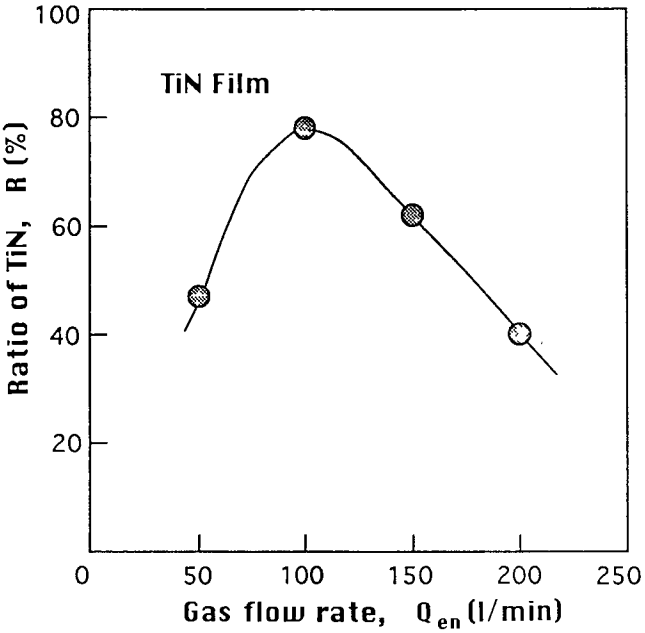

Fig. 7 Relation between the environmental gas flow rate and the TiN ratio obtained from XRD patterns of Fig. 6

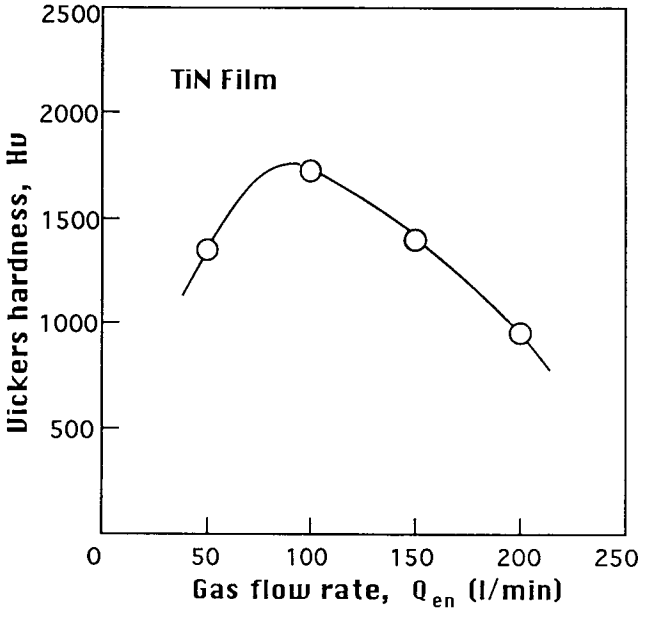

Fig. 8 Vickers hardness on the surface of the TiN film versus the environmental gas flow rate. Conditions are the same as in Fig. 6.

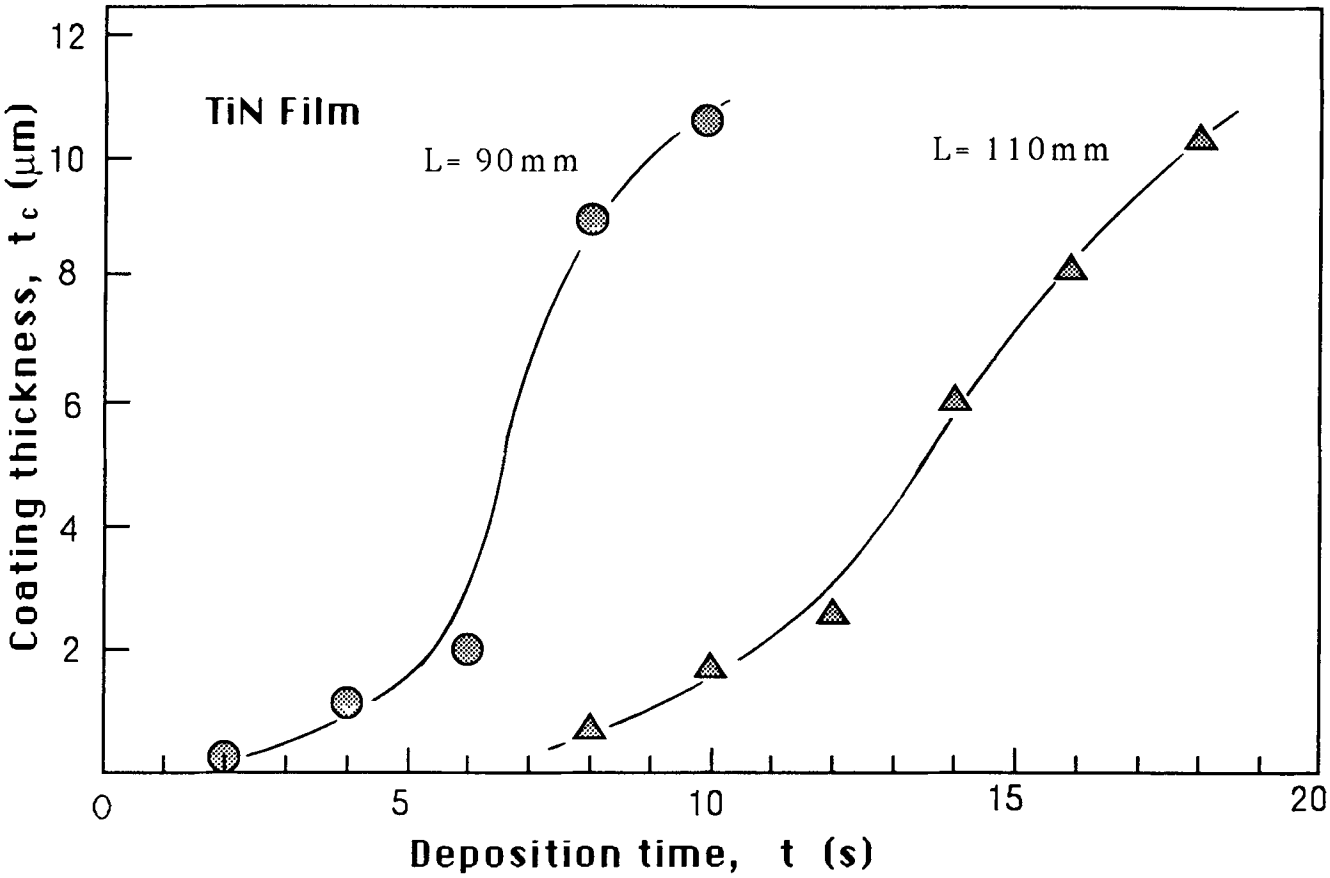

Fig. 9 Dependence of the TiN thickness on the deposition time: P = 29 kW, Q_{en} = 100 L/min

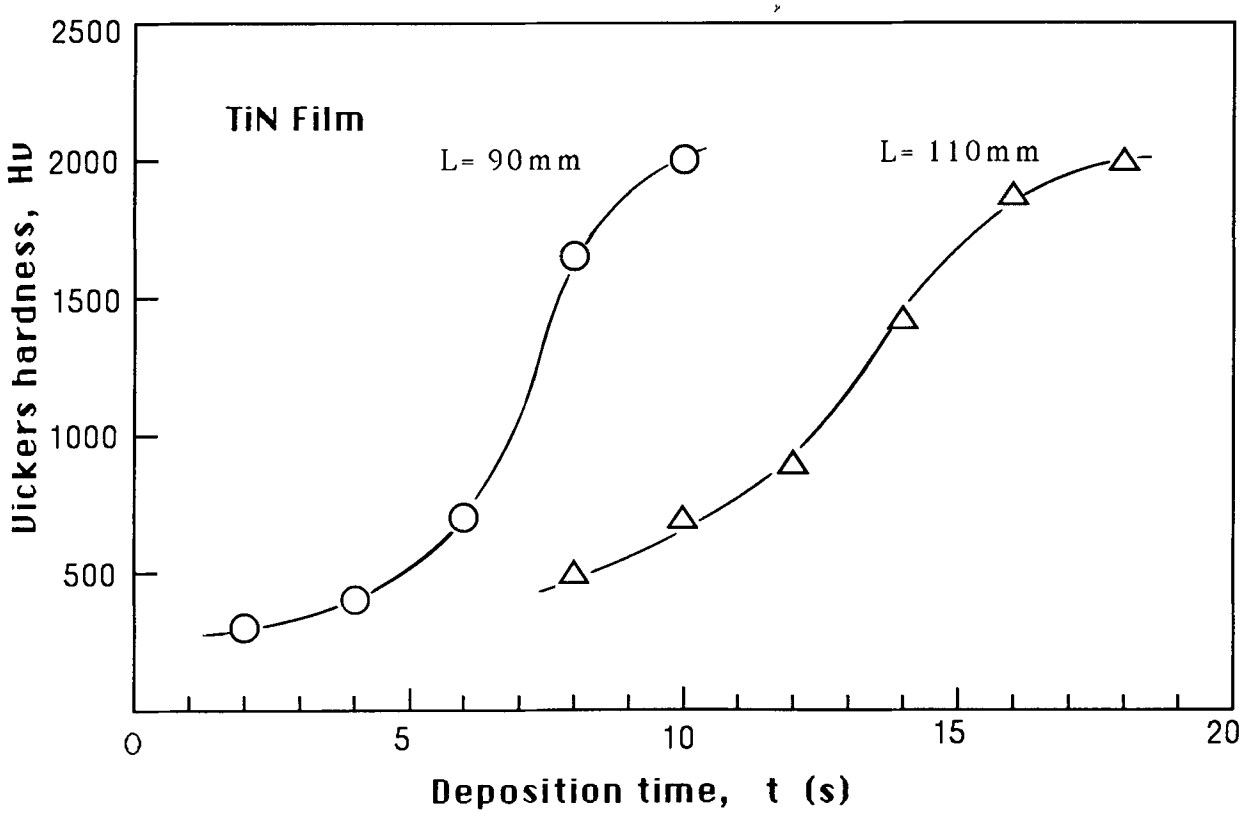

Fig. 10 Relation between the Vickers hardness on the surface of the TiN film and the deposition time for the same conditions as in Fig. 9

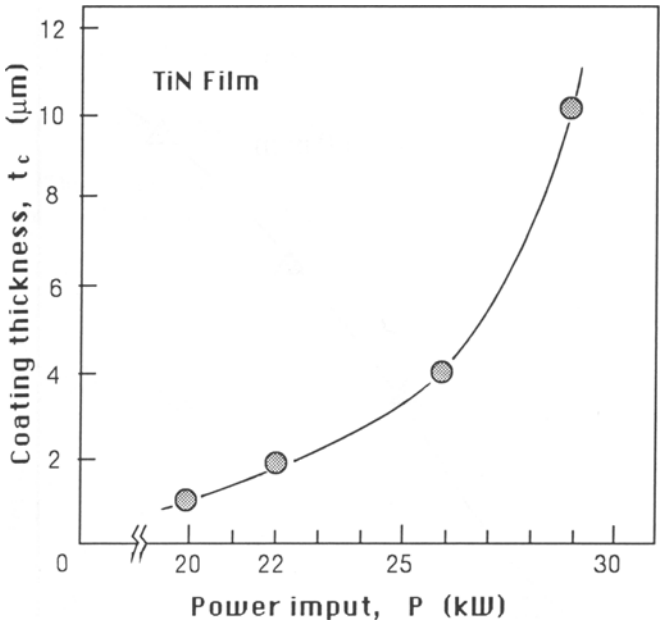

Fig. 11 Relation between TiN thickness and power input for Q = 180 L/min, Q_{en} = 100 L/min, L = 90 mm, and t = 8 s

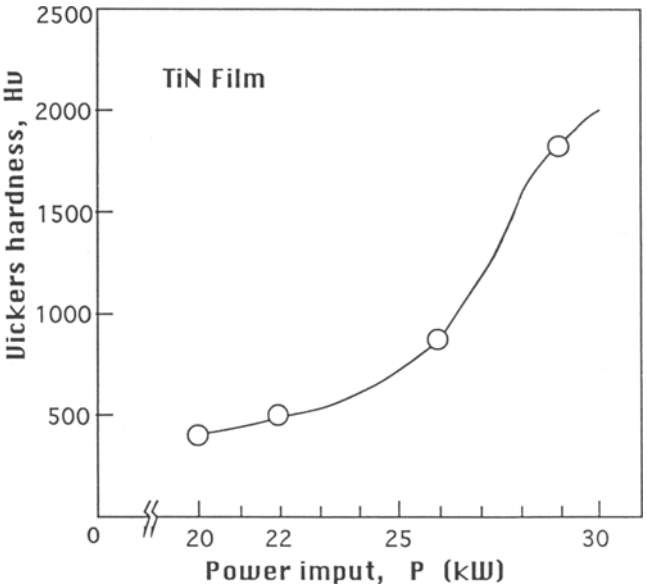

Fig. 12 Vickers hardness on the surface of the TiN film versus the power input for the same conditions shown in Fig. 11

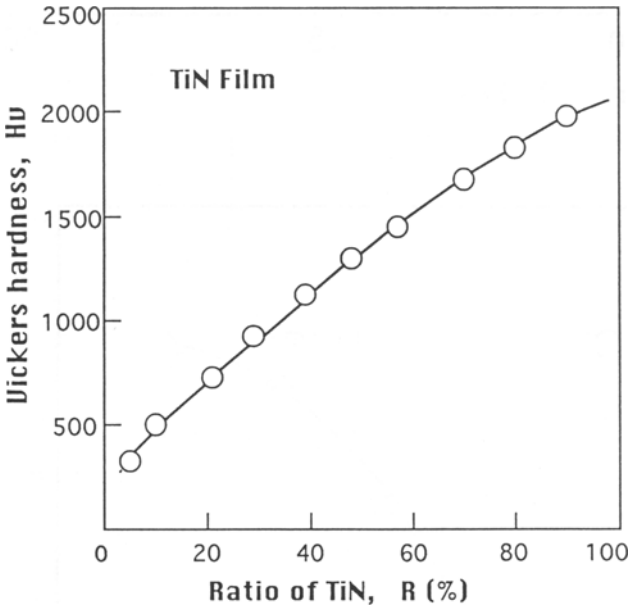

Fig. 13 Relation between the TiN ratio and the Vickers hardness of the TiN film obtained in this study for Q_{en} = 100 L/min

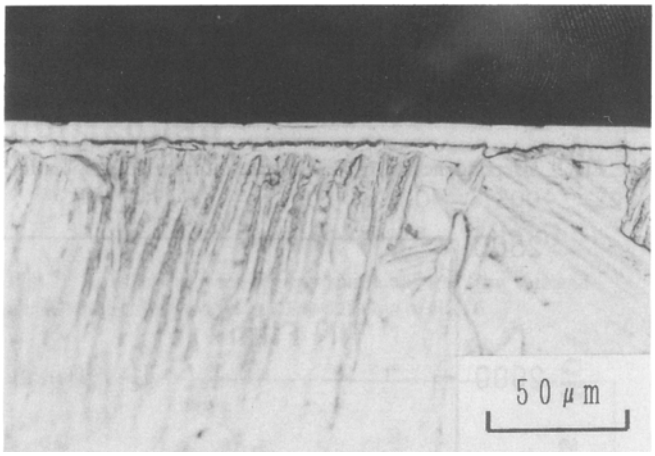

Fig. 14 Micrograph of the cross section of a TiN film. TiN thickness was about 10 μm for P = 29 kW, Q = 180 L/min, L = 90 mm, and t = 8 s

Figure 12 shows the relation between the Vickers hardness of the same TiN film surface as shown in Fig. 11 and the power input. The Vickers hardness also increased sharply for 26 to 29 kW power input, P. At P = 29 kW, the surface hardness reached about 1800 HV.

3.3 *Discussion*

The above results show a set of optimum conditions for the surface nitriding of a titanium metal by plasma irradiation. It requires a certain irradiation time, a large power input, and a certain flow rate of an environmental gas in order to obtain a complete TiN film. The TiN ratio R increased as t and P were increased. In this experiment, the data were obtained within plasma jet parameters that would not lead to melting of the substrate surface.

Figure 13 shows the relation between the TiN ratio and the Vickers hardness obtained under various conditions listed in Table 1, for Q_{en} = 100 L/min. This figure confirms the linear-like relation between the TiN ratio and the Vickers hardness. The Vickers hardness increased linearly with the increase of the TiN ratio. The hardness was about 2000 HV when R was greater than 90%.

The Vickers hardness of TiN is generally reported as 2000 to 2200 HV. This corresponds to the Vickers hardness value of the TiN film obtained in this experiment. The hardness of titanium

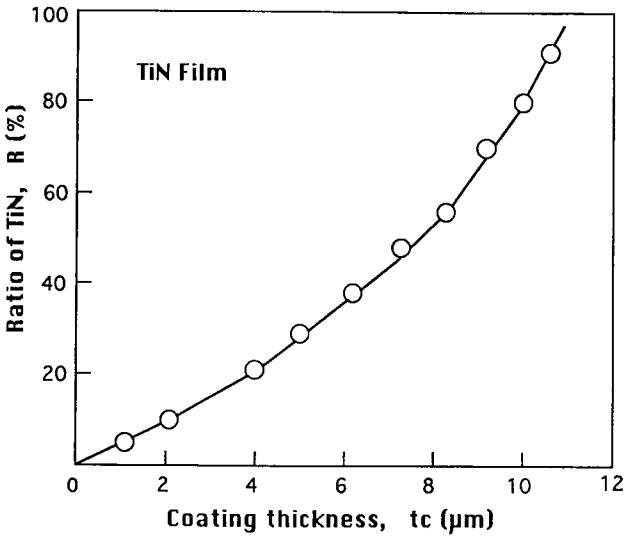

Fig. 15 TiN ratio versus thickness of the TiN film produced under various conditions

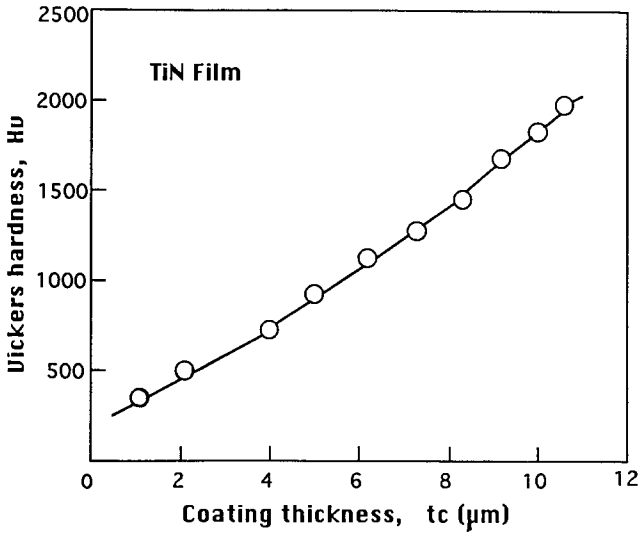

Fig. 16 Effect of the TiN film thickness on the Vickers hardness on the surface of the TiN film

material, which has the original hardness of 200 HV, can be greatly increased by surface nitriding.

The formation of TiN film depends on whether the formation is uniform or not on the surface. It can be estimated from the above results that the uniformity would be achieved only at $R = 100\%$. The uniformity of the TiN film was considered by examining the effects of the thickness of TiN on both the TiN ratio and the Vickers hardness of the TiN.

The TiN film thickness was measured with a microscope. Figure 14 shows a typical micrograph of the cross section of a TiN film. Observation of this cross section proved that the TiN film was formed uniformly on the surface of the Ti metal and that the film thickness was constant at all points on the substrate for a set of deposition conditions where the plasma irradiation was done.

TiN ratio increased when the thickness of the TiN film was increased as shown in Fig. 15. In the XRD method, when the thickness of the film is thinner than a few micrometers, the transparency of the material to x-ray is a problem. Even if the TiN film was formed uniformly on the substrate surface, Ti peaks appeared in the XRD patterns, and the TiN ratio became low. Also, even for uniform thin films, the x-rays penetrate through the film.

The quality of the TiN film might vary with the location on the substrate surface. Therefore, the Vickers hardness was measured over the whole surface. Results revealed a small deviation in the value of the film of the Vickers hardness; i.e., the hardness was almost uniform at each position measured. The above discussion shows that even if the film thickness is small, a complete TiN film can be formed.

The effect of the TiN film thickness on its Vickers hardness is shown in Fig. 16. The Vickers hardness of the TiN surface increased linearly with the film thickness. In the case of a thin TiN film, the measured Vickers hardness is lower than its expected value of 2000 HV, because the Vickers indenter is sensing both the TiN coating and the substrate metal. The effect becomes smaller as the thickness is increased, and the measured value indicates its own value, about 2000, when the thickness was greater than approximately 10 μm.

4. Conclusions

The TiN film was formed by the irradiation of the titanium metal by the gas tunnel type plasma jet. In this study, the formation of the TiN film could be carried out in a short time of about 10 s. The structure of the obtained TiN film was approximately homogeneous over the irradiated surface.

As one typical example of TiN films, the film for which the thickness was 10 μm and the Vickers hardness was 2000 HV was obtained when $P = 29$ kW, $L = 90$ mm, and $t = 10$ s. The TiN ratio was 91% on the surface of the TiN film.

The Vickers hardness of the TiN film increased as the irradiation time increased. TiN formation suddenly increased at a certain irradiation time. The TiN film was formed uniformly on the surface of the substrate.

The measured values of both the Vickers hardness and the TiN ratio were directly related to the TiN film thickness. They both increased as the thickness of the TiN film increased. If the thickness of the TiN film was greater than 10 μm, the Vickers hardness of the surface was greater than 2000 HV.

Acknowledgments

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