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Spraying TiN by a Combined Laser and Low-Pressure Plasma Spray System

A. Ohmori, S. Hirano, and K. Kamada

The formation of a TiN-Ti composite coating by thermal spraying of titanium powder with laser processing of the subsequent coating in a low-pressure N_2 atmosphere was examined. A low-pressure plasma spray system was used in combination with a CO_2 laser. First, the coating was plasma sprayed onto a mild steel substrate using a N_2 plasma jet and titanium powder in a controlled low-pressure N_2 atmosphere. The coating was then irradiated with a CO_2 laser beam in a N_2 atmosphere, and the coating was heated with a N_2 plasma jet. The amount of TiN formed in the coating was characterized by X-ray diffraction analysis. The influence of plasma spraying conditions such as plasma power, flow of plasma operating gases, chamber pressure, and laser irradiating conditions on the formation of TiN was investigated. The effect of TiN formation in the titanium coating on Vickers hardness of the coatings was examined. It was evident that coating hardness increased with an increase in TiN content in the coating and that a TiN-Ti composite coating with a hardness of more than 1200 HV can be obtained with the use of laser irradiation processing.

1. Introduction

LOW-PRESSURE plasma spraying (LPPS) has been increasingly accepted as an effective process for depositing noncontaminated dense coatings.[1,2] The most important advantage of LPPS is that a chemically pure metallic coating with little contamination can be formed when the coating is sprayed under a controlled inert gas atmosphere that excludes air and contains reactive gas species such as oxygen and nitrogen.[2,3]

On the other hand, a composite coating of metal and ceramic can be formed through the reaction of metal powder with an intentionally reactive atmosphere. Because some ceramic constituents are difficult to spray directly, reactive spraying has recently received much attention and has been used to synthesize TiN coatings through reaction of titanium powder with a N_2 atmosphere,[4,5] TiC-Fe composite through spraying of ferrotitanium with iron and graphite,[6] and also $TiBaO_3$ through reaction between spray materials such as TiO_2 and $BaCO_3$.[7]

A previous report showed that when titanium powder was sprayed under N_2 atmosphere with a N_2 plasma jet, TiN can be formed in the coating.[5] Moreover, with the assistance of laser irradiation of the sprayed Ti-TiN composite coating, the TiN content of the coating increased. In the present article, the effect of spraying parameters on the formation of TiN during spraying of titanium under a N_2 atmosphere was investigated to understand the factors influencing the formation of TiN and to examine the effect of TiN formation on the hardness of the TiN-Ti composite coating.

Keywords: composite coating, laser processing, low pressure plasma spray, processing, TiN-Ti coating, wear coatings

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2. Materials and Experimental Procedure

The powder used in this experiment was commercially pure titanium (Showa-Denko M-20) of 10 to 44 μm particle size. The substrate used was SS41 mild steel plate. Figure 1 illustrates the laser hybrid low-pressure plasma spraying apparatus. A plasma spray gun (METCO 9MB, 80 kW) was horizontally installed inside a chamber equipped with an exhaust system. A CO_2 laser (Mitsubishi 10C, 1 kW) was inserted into the chamber in the direction shown in Fig. 1.

The formation of the TiN coating was performed by first plasma spraying titanium powder onto the substrate and then remelting the deposited coating, as shown in Fig. 2. Before spraying, the chamber was evacuated to lower than 1 torr (1.3×10^2 Pa) and then charged with N_2 gas to a desirable ambient chamber pressure. The formation of TiN in the titanium coating was investigated by varying the following operating conditions; plasma spray parameters such as chamber pressure of N_2 gas, plasma power, flow rates of plasma operating gases (N_2 and H_2), and laser parameters such as laser power and traverse speed of laser beam relative to the coating. Table 1 lists the typical plasma spray conditions. The spray parameters were varied individually so that all the other parameters were fixed at the values as shown in Table 1. Table 2 gives the typical laser irradiation conditions. These were also varied individually.

The content of TiN formed in the titanium coating was semiquantitatively estimated by X-ray diffraction analysis according to the following equation:

Table 1 Plasma spray conditions

Spraying distance	340 mm
Arc current	533 A
Arc voltage	75 V
Arc power	40 kW
Primary flow (N_2)	60 L/min
Secondary flow (H_2)	10 L/min
Traverse speed	200 mm/s
Pressure (N_2)	1.3×10^4 Pa

$$\text{TiN ratio} = I_{TiN}/(I_{Ti} + I_{TiN}) \quad [1]$$

where the TiN ratio is an index number, which denotes the TiN content in the coating, and I_{Ti} and I_{TiN} represent the main peak of Ti(200) and TiN(011) in the X-ray diffraction pattern. X-ray diffraction analysis was carried out using a copper tube operated at 40 kV and 20 mA. The nitrogen contents in selected typical as-sprayed coatings were analyzed by an inert gas melting analyzer (Horiba EMGA-2800).

The microstructure of each coating cross section was examined by optical microscopy. Vickers microhardness (HV), used as an indication of coating mechanical strength, was measured under a load of 0.98 N (100 gf).

Table 2 Laser irradiating conditions

Laser power...	200 to ~600 W
Defocus (Δf)...	0 mm
Traverse speed...	300 mm/s
Pressure (N_2)...	1.3×10^4 Pa

3. Results and Discussion

Previous results have shown that TiN can be formed in coatings when titanium powder was sprayed in a N_2 atmosphere by a N_2 plasma jet.[5] This is due to the reaction of titanium with N_2 in the atmosphere during spraying. Figure 3 illustrates X-ray diffraction patterns of titanium coatings sprayed under different chamber (N_2) pressures. It is evident that TiN was formed in the sprayed coating. The TiN ratio was estimated from Eq 1 as an indication of the phase content formed in the sprayed coating. The effect of N_2 pressure on the TiN ratio is shown in Fig. 4. Clearly, the formation of TiN in the coating was increased by increasing the pressure of the N_2 atmosphere. Measurement of N_2 content in selected typical coatings, as given in Table 3, showed that increases in the TiN ratio from the X-ray diffraction pattern of a coating corresponded to an increase in the nitrogen content of the coating. This suggests that the TiN ratio can present qualitatively the formation of TiN in a coating. However, it should be noted that the TiN ratio results in Table 3 do not take into account nitrogen dissolved in the titanium phase in the coating.

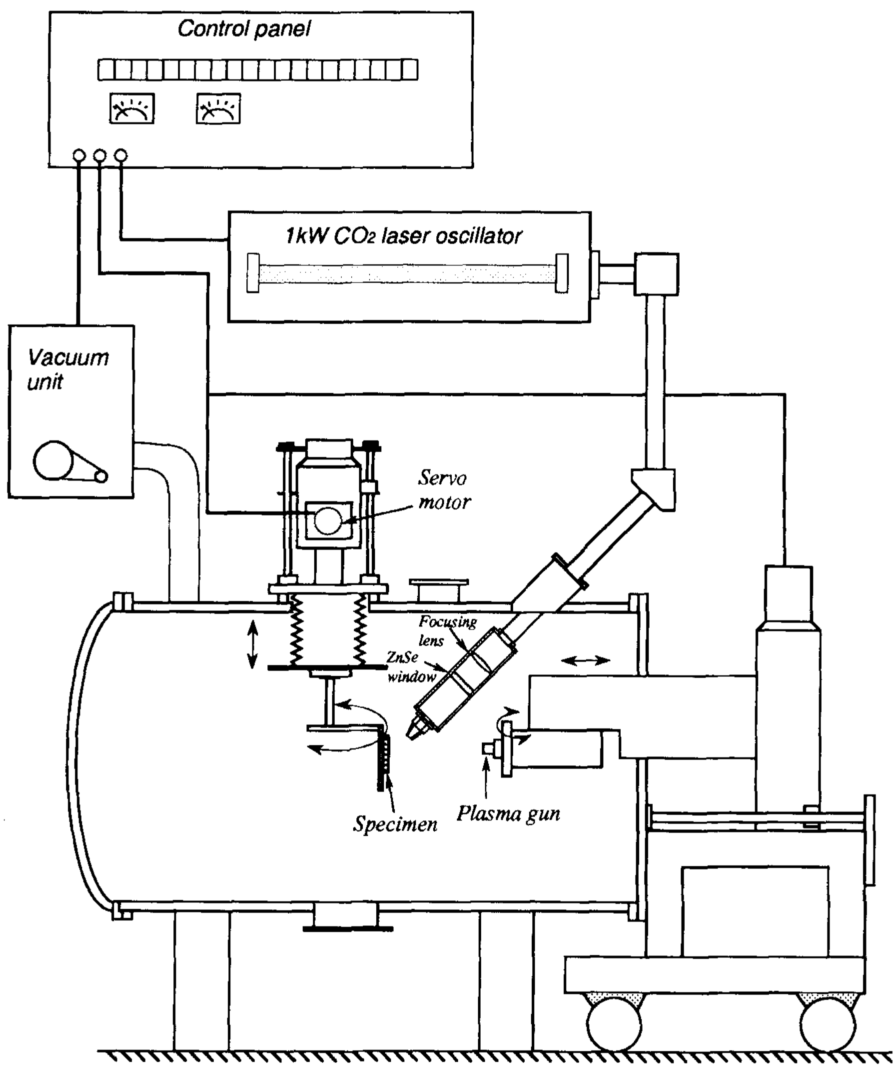

Fig. 1 Schematic of laser-combined low-pressure plasma spray system.

Figure 5 shows the effect of plasma power on the TiN ratio. Evidently, the TiN ratio tended to increase with an increase in plasma power. On the other hand, one might expect that a reactive species such as N at high temperatures would increase with an increase in N_2 plasma gas flow. The TiN ratio actually decreased, as shown in Fig. 6. Figure 7 illustrates the effect of H_2 plasma gas flow on the TiN ratio of the coating. The effects of N_2 pressure in the chamber and N_2 plasma gas flow on the TiN ratio suggested that TiN forms downstream in the plasma jet at relatively low temperatures. This is consistent with the fact that formation of TiN is only thermodynamically stable below about 3400 K.[8]

Decreasing chamber pressure results in spreading of the plasma jet. The increase in plasma jet volume at a medium high temperature is not suitable for the formation of TiN. Increasing plasma gas flow consistently leads to spreading of the plasma jet in the high-temperature region. This may explain the decrease in the TiN ratio with an increase in both N_2 and H_2 gas flow, although reactive species will decrease with an increase in H_2 gas flow. Accordingly, a plasma jet with a long low-temperature region is most suitable for the direct formation of TiN in a sprayed coating. To promote the formation of TiN during thermal spraying in a titanium coating, the partial pressure of N_2 gas should be increased by raising the chamber pressure of N_2, not by raising the N_2 plasma gas flow.

Table 3 Ratio of TiN and N content in selected TiN-Ti coatings

Sample	Ratio of TiN	N, wt%
A...	0.16	5.5
B...	0.35	7.2
C...	0.70	10.9

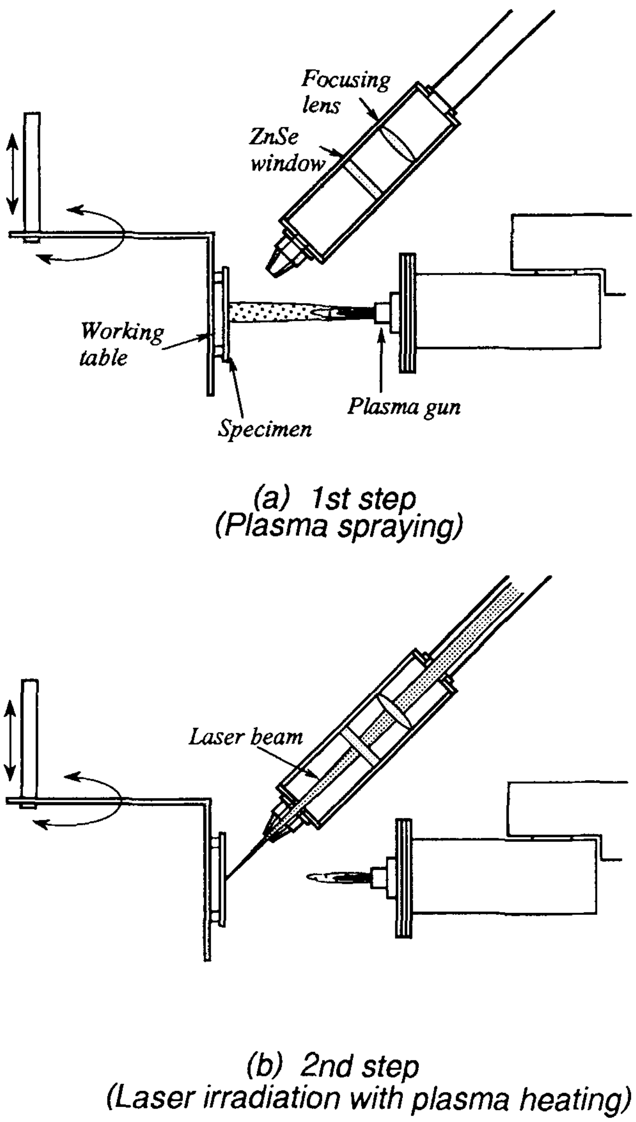

Fig. 2 Schematic of plasma spraying and laser irradiating procedures.

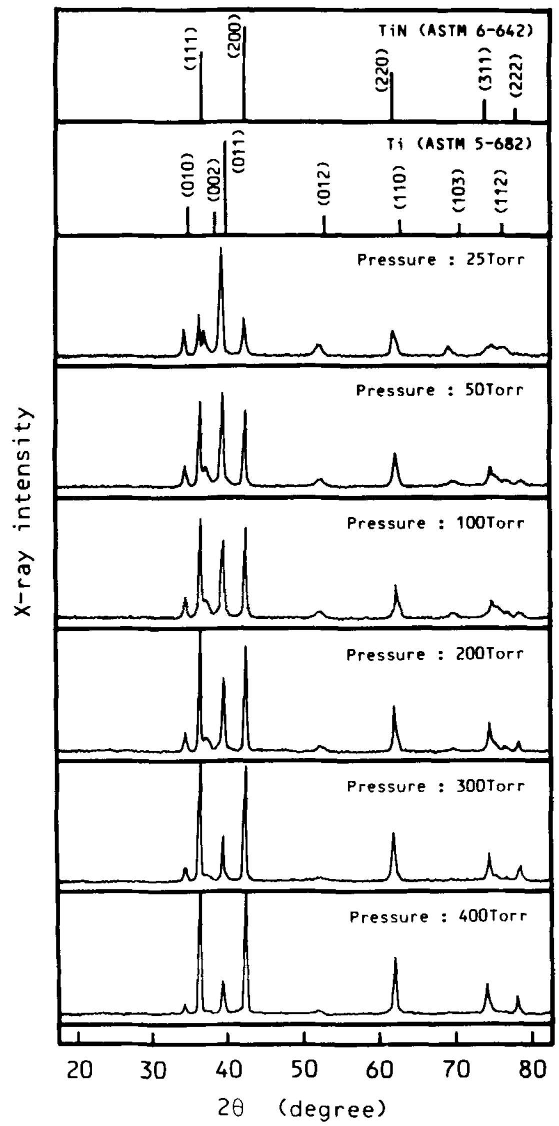

Fig. 3 X-ray diffraction patterns of titanium coatings sprayed under different N_2 atmospheric pressures.

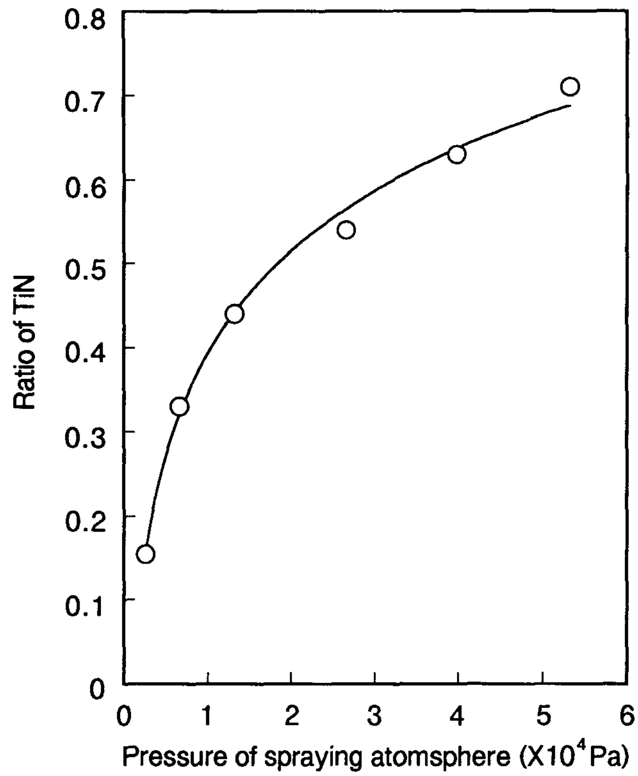

Fig. 4 Effect of N_2 atmospheric pressure on the ratio of TiN in sprayed titanium coatings.

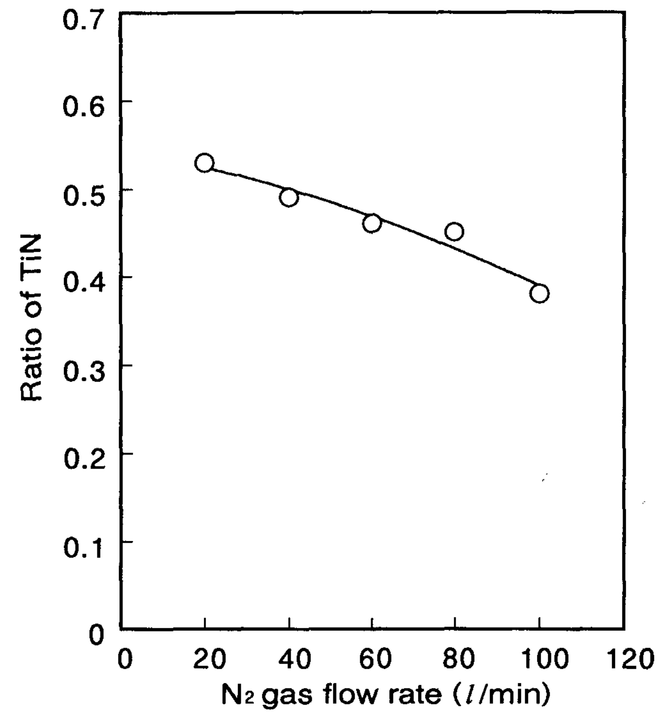

Fig. 6 Effect of N_2 flow in plasma on the ratio of TiN in sprayed titanium coatings.

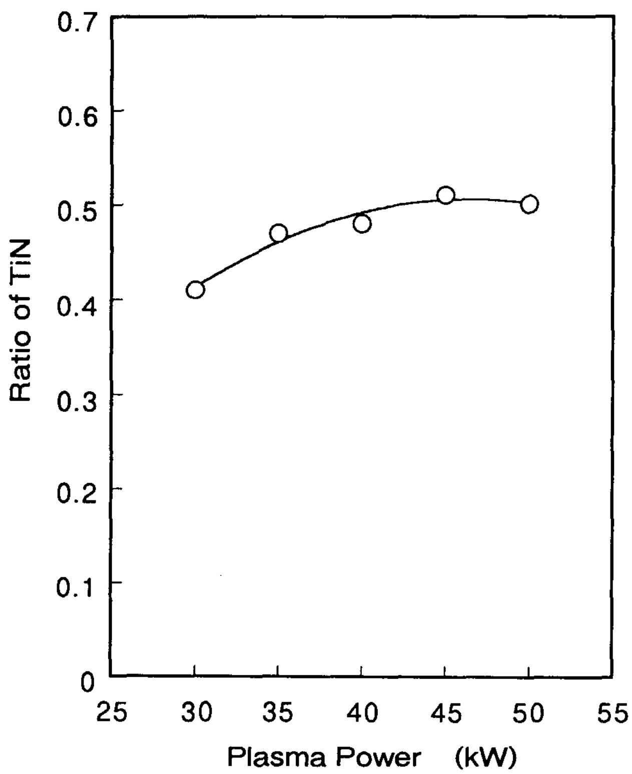

Fig. 5 Effect of plasma power on the ratio of TiN in sprayed titanium coatings (pressure of spray atmosphere, 1.3×10^4 Pa).

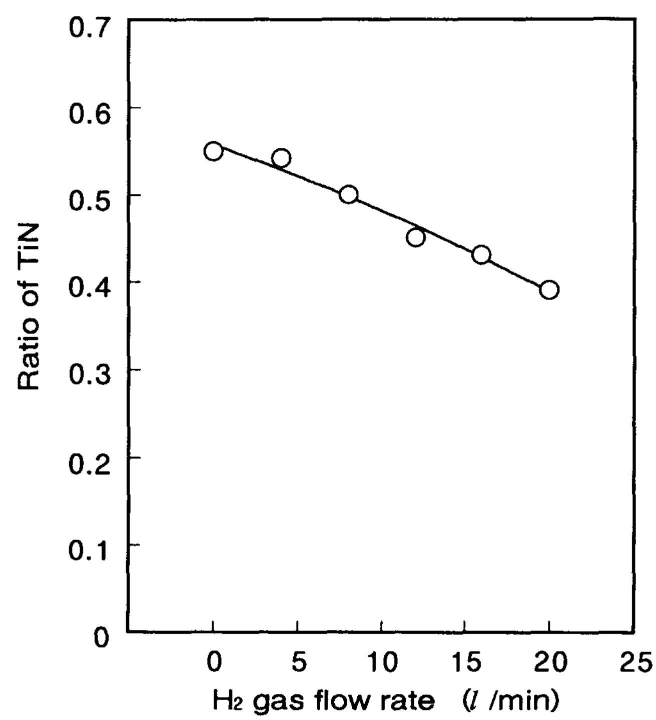

Fig. 7 Effect of H_2 flow in plasma on the ratio of TiN in sprayed titanium coatings.

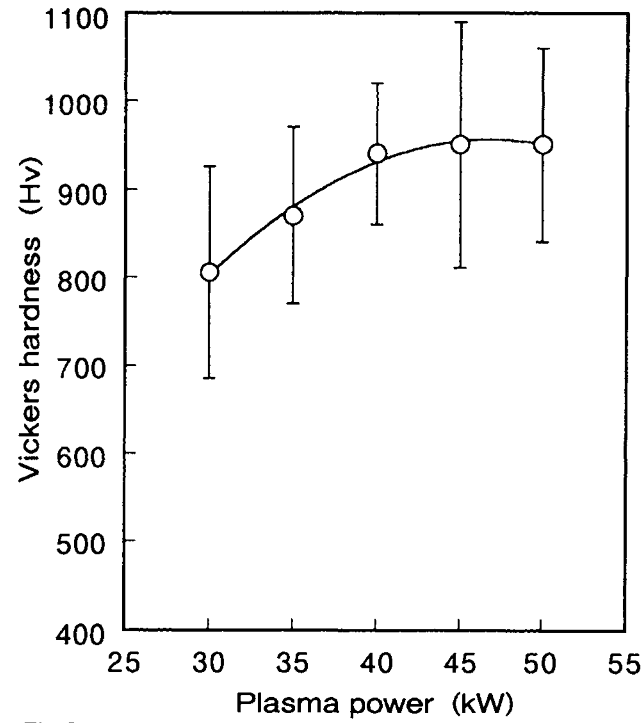

Fig. 8 Effect of plasma power on coating hardness (load, 0.98 N).

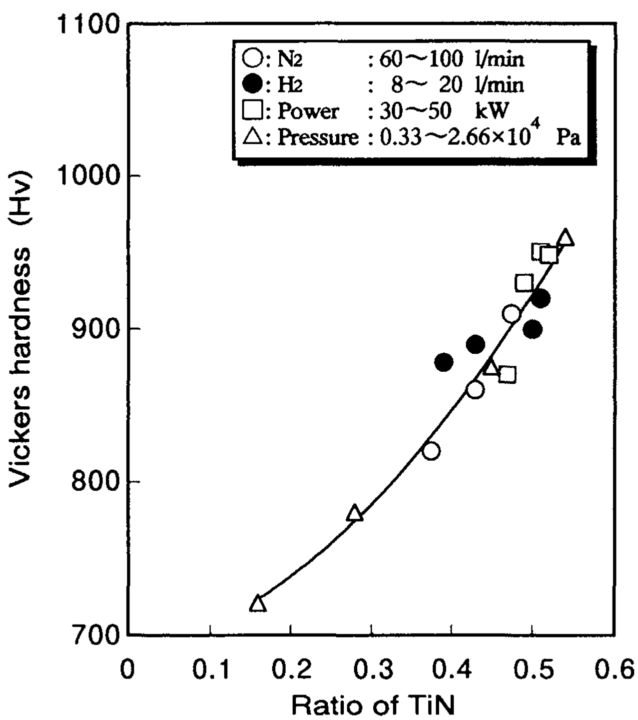

Fig. 9 Relationship between coating hardness and the TiN ratio in coatings.

Investigation of the effects of spray parameters on coating hardness showed that the microhardness of a coating tended to increase with the content of TiN formed in the sprayed coating.

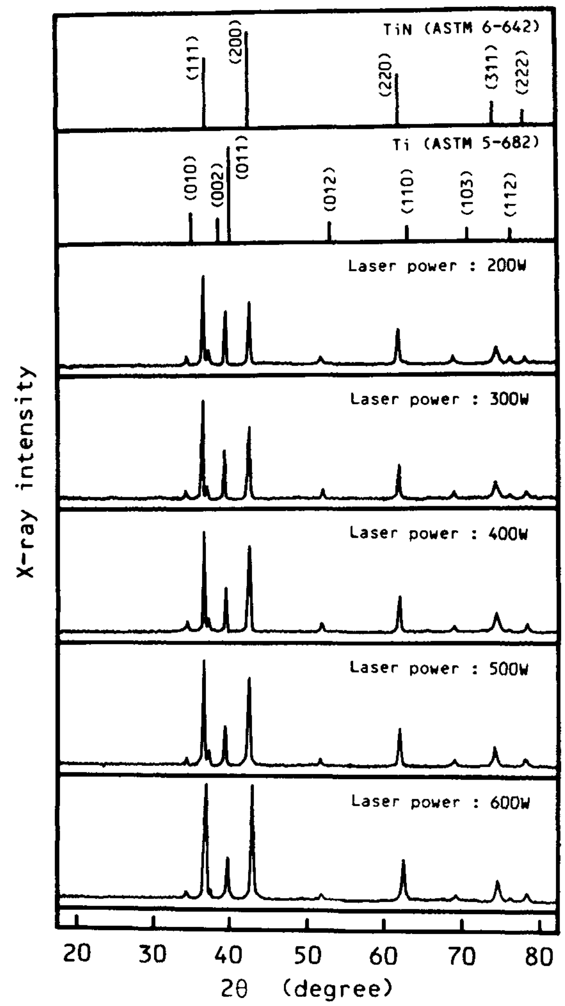

Fig. 10 X-ray diffraction patterns of laser-irradiated Ti-TiN coatings.

Figure 8 illustrates the effect of plasma power on the Vickers hardness of sprayed coatings. For those coatings in which the TiN ratio was lower than 0.55, a plot of Vickers hardness versus the TiN ratio, as shown in Fig. 9, confirms the positive effect of the formation of TiN on the hardness of coatings. However, it was also found that, for the as-sprayed coatings with a high TiN ratio (over 0.55), the Vickers hardness indentation induced cracking of the coating along the interface between flattened particles in the coating, which yielded a low hardness value. This may imply that the hardening of a flattened particle does not indicate the formation of TiN and does not always lead to an increase in coating cohesion.

For an as-sprayed coating that has a lamellar structure with low cohesion, remelting with high-energy density sources such as a laser beam may be an effective method for improvement. Figure 10 shows X-ray diffraction patterns of laser-remelted Ti-TiN coatings sprayed under the conditions shown in Table 1. The TiN ratio was 0.45. Compared to the as-sprayed coating shown in Fig. 3, further nitriding of the coating is observed after laser irradiation. The formation of TiN increased greatly with an increase in laser power. Figure 11 shows the cross sections of la-

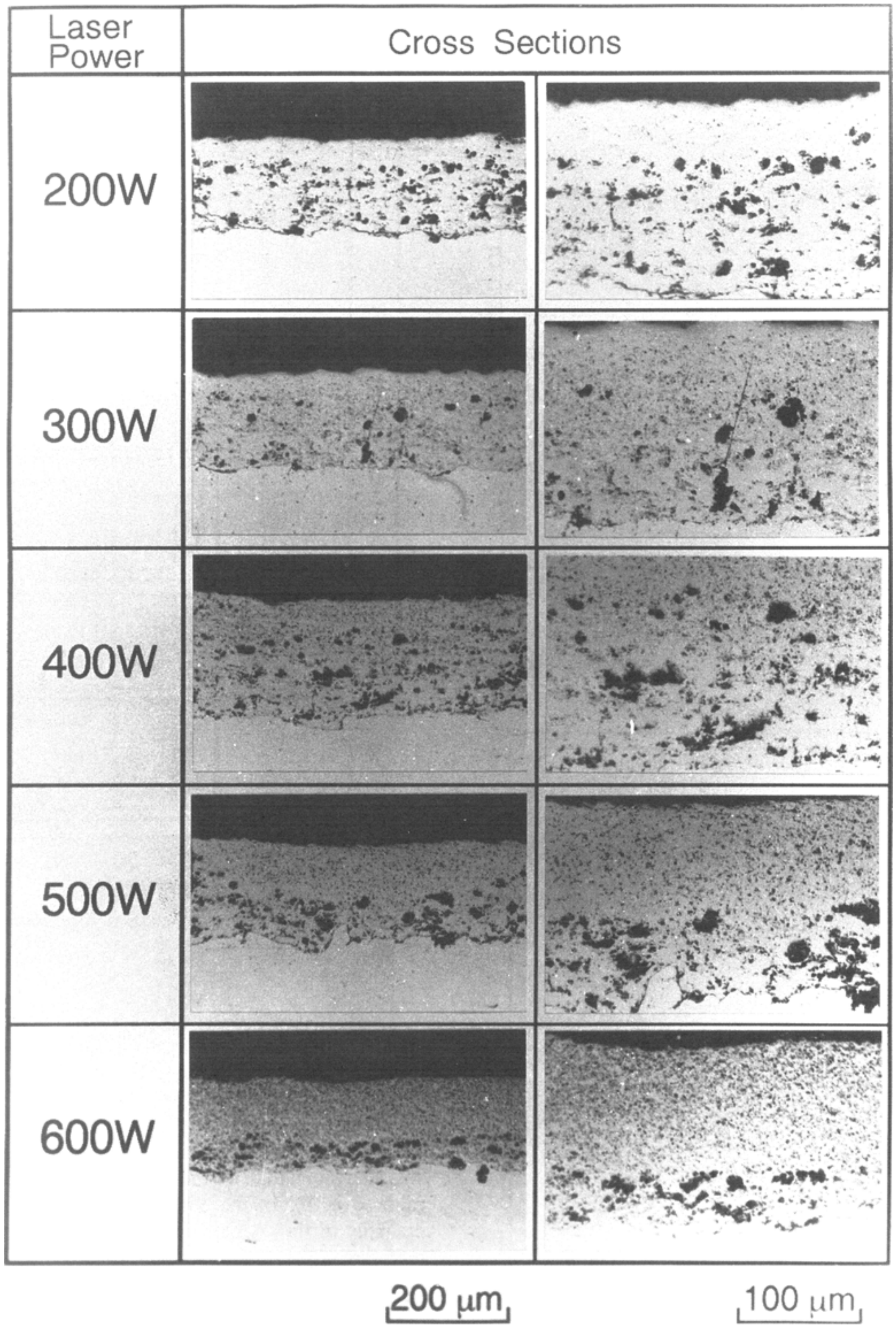

Fig. 11 Cross sections of laser-irradiated TiN-Ti coatings.

ser-remelted coatings. The laser-remelted portion exhibits a dense structure, and the laser-remelted portion increases with an increase in laser power.

For an as-sprayed coating with a TiN ratio of 0.45, the increase in laser power and the decrease in laser beam traverse speed enhanced the formation of TiN during laser irradiation. Such laser irradiation-induced nitriding is probably the reaction of molten titanium with nitrogen dissolved in the coating. Figure 12 shows the microstructure of a TiN-Ti composite coating in both the as-sprayed and laser-irradiated conditions. The laser-

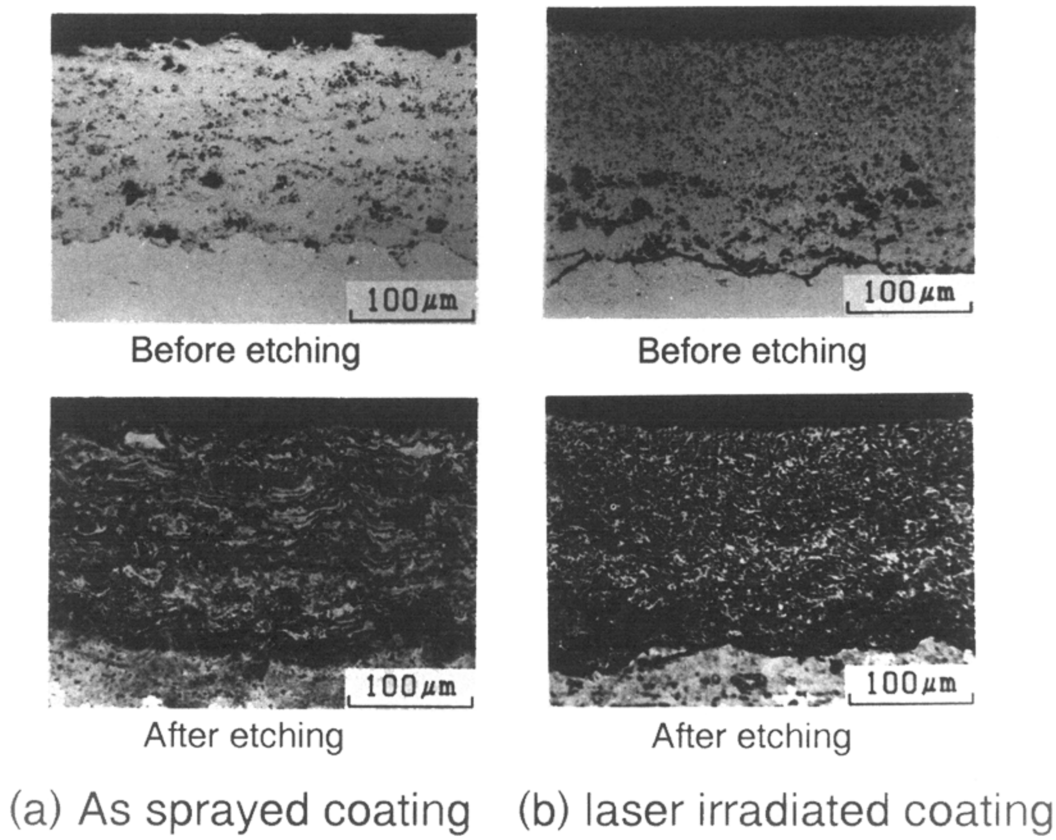

Fig. 12 Comparison of the microstructures of as-sprayed and laser-irradiated coatings.

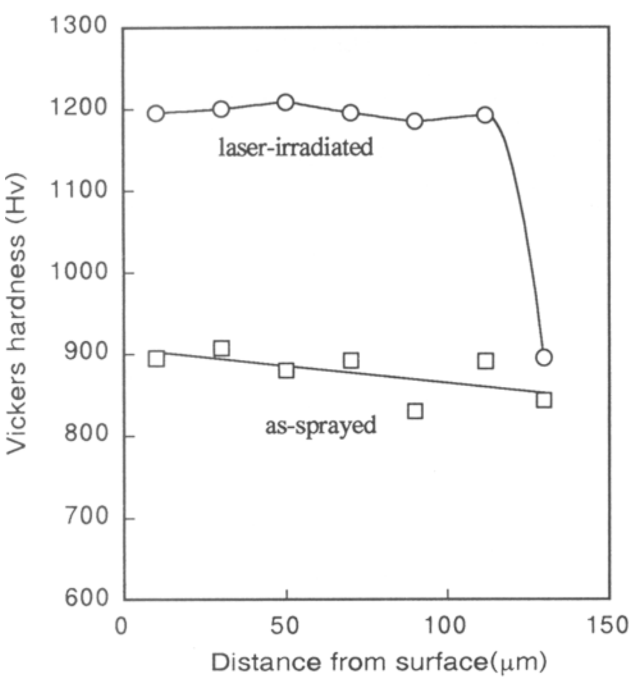

Fig. 13 Hardness distribution of as-sprayed and laser-irradiated coatings.

irradiated coating exhibited a homogeneous structure compared to the lamellar structure of the as-sprayed coating. Comparison of the hardness distribution along the coating thickness between as-sprayed and laser-irradiated coatings, as shown in Fig. 13, also confirmed the homogeneity of TiN-Ti composite coatings due to laser irradiation.

Furthermore, the coating hardness after laser irradiation reached about 1200 HV compared with about 900 HV for an as-sprayed coating. One would therefore expect the content of TiN in a TiN-Ti composite coating to be controllable by adjusting the thermal spraying and laser-assisted irradiation parameters. Further investigation of laser irradiation should be undertaken using coatings with a different TiN ratio in the as-sprayed condition.

Examination of the surface morphology of laser-irradiated coatings revealed cracks in the remelted area, as shown in Fig. 14, which are typically observed after laser remelting of ceramic coatings.[9,10] Cracking is evidence of substantial formation of TiN in the coating. Such cracks result from thermal stress due to the restraint of thermal contraction during rapid cooling of the remelted zone, along with the low ductility of TiN ceramics formed in the coating.

4. Conclusions

The thermal spraying of titanium powder under N_2 atmosphere using a N_2 plasma jet resulted in the formation of a TiN-Ti composite coating due to the reaction of titanium with the N_2 atmosphere. The formation of TiN by thermal spraying of tita-

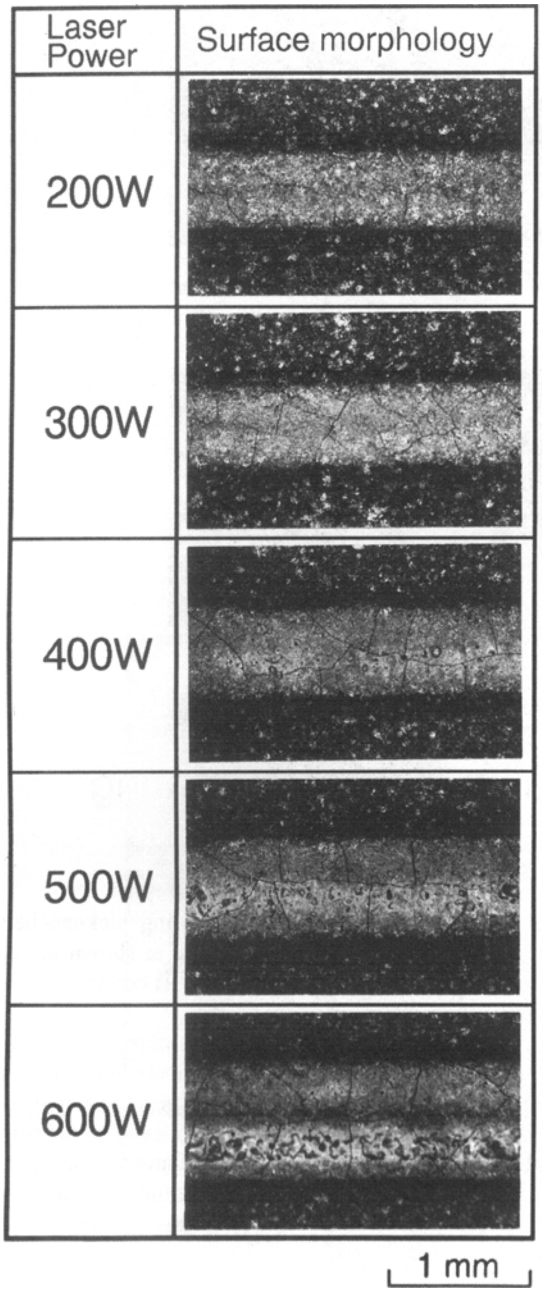

Fig. 14 Typical surface morphology of laser-irradiated TiN-Ti coatings.

nium powder in a controlled N_2 atmosphere was dependent on the thermal spray conditions, in particular, the N_2 atmosphere pressure. Increasing the N_2 pressure in the chamber enhanced the formation of TiN, whereas increasing N_2 gas flow in the H_2-N_2 plasma jet impeded formation. The formation of additional TiN in the titanium coating can be achieved by laser irradiation of the sprayed coating. The formation of TiN during spraying increased the microhardness of the titanium coating. A further increase in hardness was achieved by laser irradiation of the coating.

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