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

Akira OHMORI*, Satoru HIRANO and Kazuo KAMADA*****

Abstract

The formation of a TiN-Ti composite coating by thermal spraying of Ti powder with laser processing of the subsequent coating in a low pressure N_2 atmosphere was examined. A thermal spraying system of a low pressure plasma jet for thermal spraying combined with a CO_2 laser was used. Firstly, the coating was plasma-sprayed onto a mild steel substrate using a N_2 plasma jet and Ti powder in a controlled low pressure N_2 atomosphere. The coating was then irradiated with a CO_2 laser beam in a N_2 atomsphere with the coating heated by 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 Ti coating on Vickers hardness of the coatings was examined. It was evident that coating hardness was increased with an increase in TiN content in the coating and a TiN-Ti composite coating of a hardness of over 1200Hv can be obtained with the assistance of laser-irradiation processing.

KEY WORDS: (TiN coating) (Ti powder) (N_2plasma spraying) (Low pressure plasma spraying)

1. Introduction

LOW PRESSURE PLASMA SPRAYING (LPPS) has been increasingly accepted as an effective coating process to form a non-contaminated dense coating[1,2]. Most important advantage of LPPS is that a chemically pure metallic coating with little contamination can be formed because the coating is usually sprayed under a controlled inert gas atmosphere in the exclusion of air including reactive gas species such as oxygen and nitrogen[2,3].

On the other hand, the reaction between the spray material and spray atmosphere could be utilized to produce a composite coating of metal and ceramic which is formed through the reaction of metal powder with atmosphere. It would be difficult to directly spray the ceramic constituent. Therefore, so-called reaction spraying has recently received much attention and has been attempted to synthesize TiN coating through reaction of Ti powder with N_2 atmosphere[4,5], TiC-Fe composite through spraying of ferrotitanium, 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 Ti powder was sprayed under N_2 atmosphere with N_2 plasma jet, TiN can be formed in the coating[5]. Moreover, with the assistance of laser irradiation on the sprayed Ti-TiN composite coating, it was found that the content of TiN in the coating can be further increased. In the present report, the effect of spraying parameters on the formation of TiN during spraying of titanium under 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.

2. Materials and Experimental Procedure

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

The formation of TiN coating was performed by firstly plasma spraying Ti powder onto the substrate (First-step) and then re-melt processing the subsequent coating (Second-step) as shown in **Fig. 2**. Before spraying, the chamber was evacuated to lower than 1 Torr (1.3×10^2Pa)

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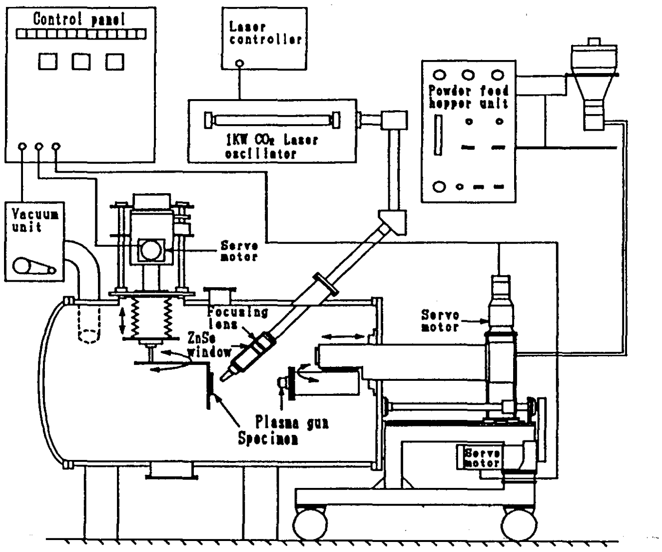

Fig. 1 Schematic diagram of laser-combined low pressure plasma spray system

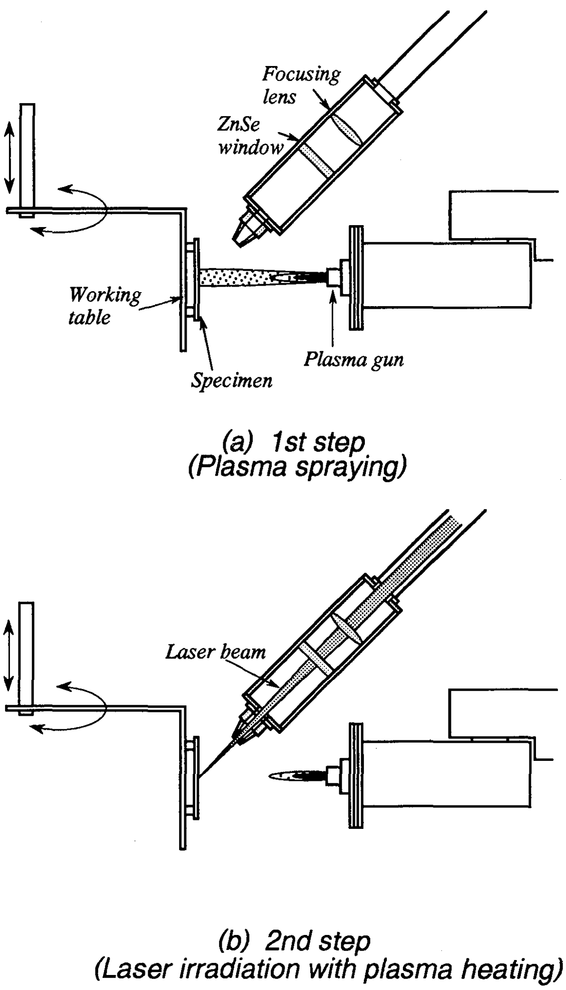

Fig. 2 Schematic diagram of plasma spraying and laser irradiating procedures

and then charged with N_2 gas to a desirable pressure (atmospheric pressure). The formation of TiN in the Ti coating was investigated under different spray conditions including atmospheric pressure of N_2 gas, plasma power, flow rates of plasma operating gases of N_2 and H_2, and also different laser irradiation conditons including laser power, traverse speed of laser beam relative to the coating. **Table 1** shows typical plasma spray conditions. The change of a particular spray parameter was performed so that all the other parameters were fixed at the values as shown in Table 1. **Table 2** shows typical laser irradiation conditons. a particular parameter was changed in the same way as that for spray parameters.

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

$$\text{Ratio of TiN} = \mathbf{I}_{TiN}/(\mathbf{I}_{Ti} + \mathbf{I}_{TiN}) \quad (1)$$

where the ratio of TiN is an index number which denoted the TiN content in the coating, and $\mathbf{I}_{T_i}$ and $\mathbf{I}_{TiN}$ were the intensity of main peak of Ti(200) and that of TiN(011) in the X-ray diffraction pattern, respectively. X-ray diffraction was carried out using a copper tube operated at 40kV and 20mA. The N content in selected typical as-sprayed coatings was analyzed by an inert gas melting analyzer (Horiba EMGA-2800).

The microstructure of a cross-section of a coating was examined by optical microscopy. Microhardness of a coating (Hv) was used as a indication of coating mechanical property, which was measured under a load of 0.98N.

Table 1 Plasma spray conditions

Spraying distance	340 mm
Arc current	533 A
Arc voltage	75 V
Arc power	40 kW
Primary flow (N2)	60 *l*/min
Secondary flow(H2)	10 *l*/min
Traverse speed	200 mm/s
Pressure(N2)	1.3×10^4 Pa

Table 2 Laser-irradiationg conditons

Laser power	600 W
Defocus(Δf)	0 mm
Traverse speed	300 mm/s
Pressure(N2)	1.3×10^4 Pa

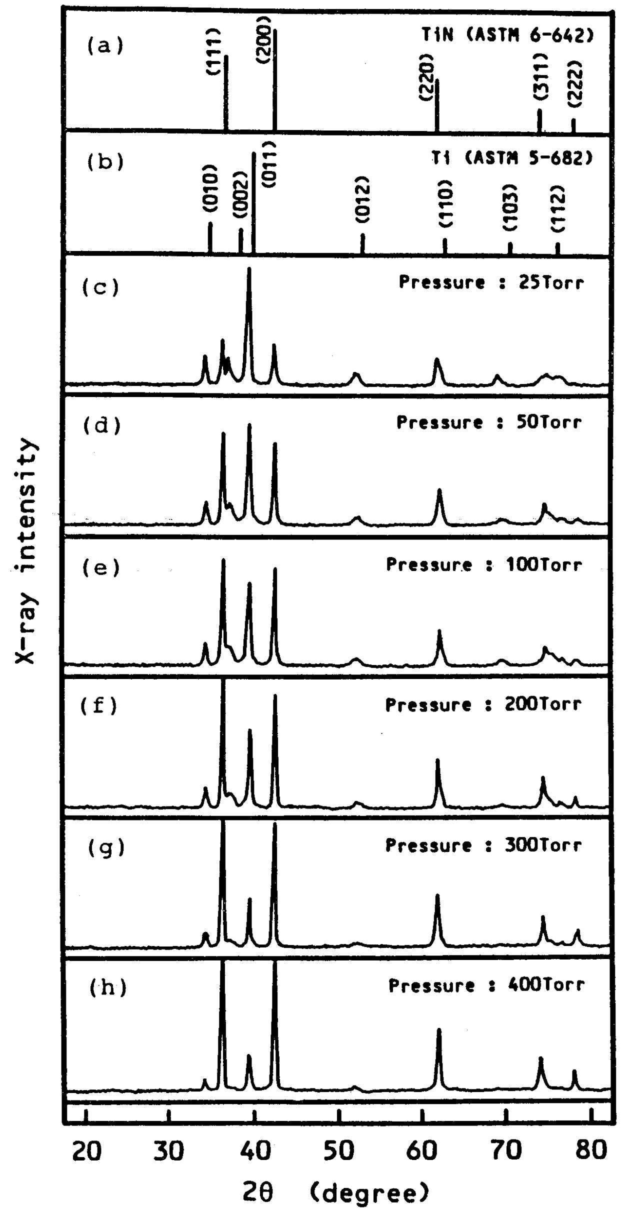

Fig. 3 X-ray diffraction patterns of Ti coatings sprayed under different N_2 atomospheric pressure

3. Results and Discussion

Previous results have shown that TiN can be formed in the coating when Ti powder was sprayed in a N_2 atomosphere by a N_2 plasma jet[5]. This is due to the reaction of Ti with N_2 in the atmosphere during spraying. **Figure 3** illustrates X-ray diffraction patterns of Ti coatings sprayed under different chamber(N_2) pressures. It is evident that TiN was formed in the sprayed coating. As a indication of the phase content formed in the sprayed coating, the ratio of TiN was estimated following Eq. 1. Thereafter, the effect of pressure of N_2 atmosphere on the ratio of TiN is shown in **Fig. 4**. Clearly, the formation of TiN in the coating was

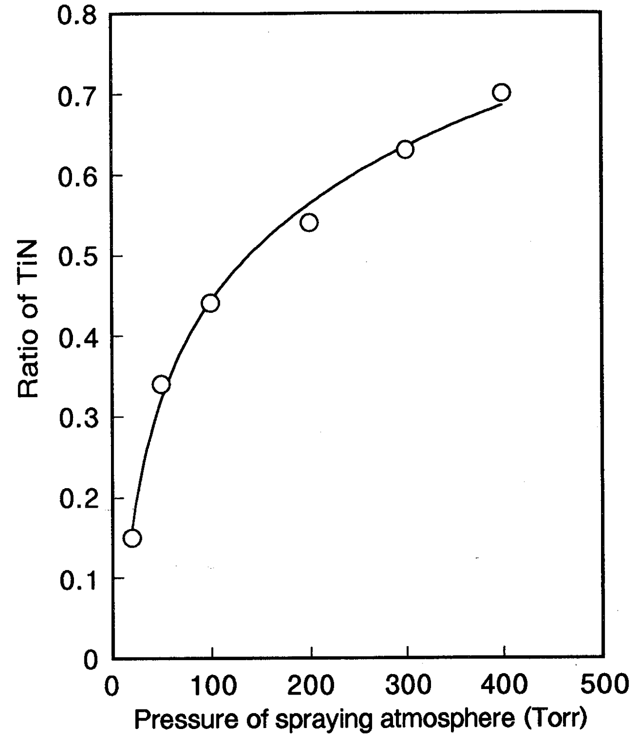

Fig. 4 Effect of N_2 atomospheric pressure on the ratio of TiN in sprayed Ti coatings

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

Sample	Ratio of TiN	N content (wt%)
A	0.16	5.5
B	0.35	7.2
C	0.70	10.9

increased by the increase in pressure of N_2 atmosphere. Measurement of N_2 content in selected typical coatings, as shown in **Table 3**, showed that increases in the ratio of TiN from the X-ray diffraction pattern of a coating corresponded to the increase of N content in the coating. This suggests that the ratio of TiN can present qualitatively the formation of TiN in the coating. However, it should be indicated that the ratio of TiN evidently overestimated the content of TiN in the coating according to the results in Table 3 and does not account of N dissolved in Ti coating.

Figure 5 shows the effect of plasma power on the ratio of TiN. Evidently, the ratio of TiN tended to increase with an increase of plasma power. On the other hand, although it may be considered that the reactive species such as N at high temperature are increased with an increase of N_2 gas flow in plasma gases, the ratio of TiN was decreased as shown in **Fig 6**. **Figure 7** illustrated the effect of H_2 gas flow in plasma on the ratio of TiN in the coating. According to the effect of N_2 pressure in the chamber and N_2 flow in plasma gases on the ratio of TiN, it may be suggested

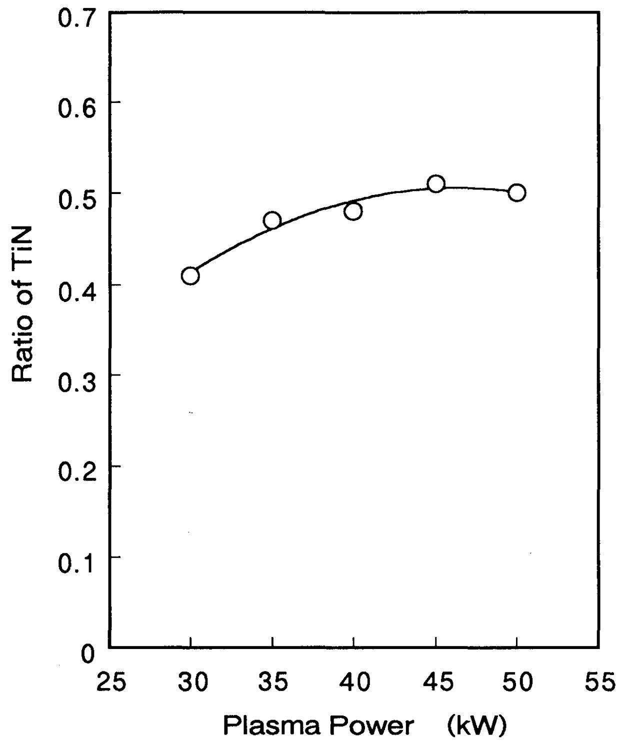

Fig. 5 Effect of plasma power on the ratio of TiN in sprayed Ti coatings

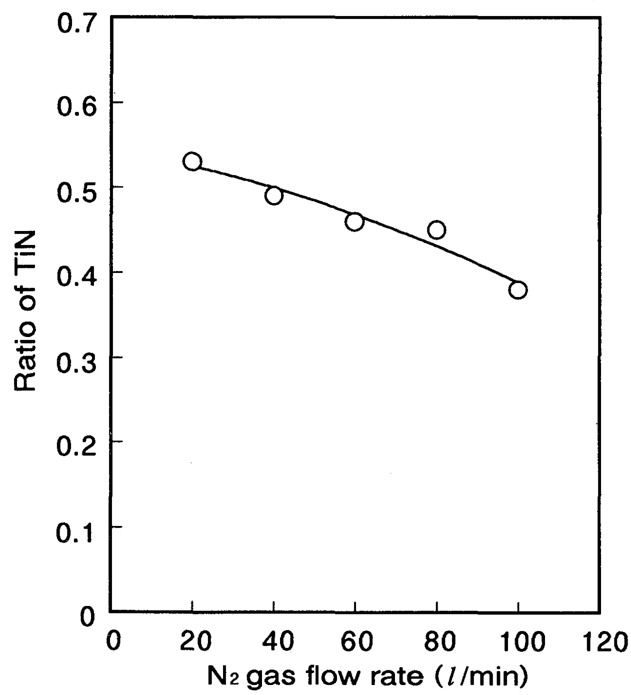

Fig. 6 Effect of N_2 flow in plasma on the ratio of TiN in sprayed Ti coatings

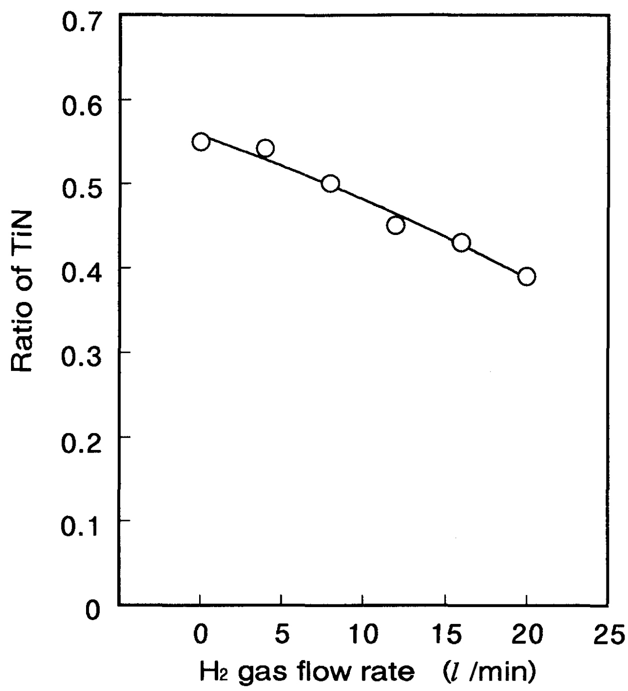

Fig. 7 Effect of H_2 flow in plasma on the ratio of TiN in sprayed Ti coatings

that TiN is forms down stream in the plasma jet at relative low temperature. This is consistent with the fact that formation of TiN is only thermodynamically under a temperature below about 3400K[8].

The decrease of the pressure results in the spreading of plasma jet and subsequently the increase of volume of plasma jet at a medium high temperature which is not suitable for the formation of TiN. Increasing flow of plasma operating gases consistently leads to spreading of the plasma jet at the high temperature range. This may explain the decrease in the TiN ratio with the increase in both N_2 and H_2 gas flow; although reactive species will be decreased with an increase in H_2 gas flow. Accordingly, it can be considered that a plasma jet with a long low temperature range is suitable for the direct formation of TiN in a sprayed coating. In order to promote the formation of TiN during thermal spraying in a Ti coating, the partial pressure of N_2 gas shoud be increased through chamber pressure of N_2 rather than N_2 gas flow in the plasma gases.

The investigation of the effects of spray parameters on the coating hardness showed that the microhardness of a coating tended to increase with the content of TiN formed in the sprayed coating. **Figure 8** illustrates the effect of plasma power on the Vickers hardness of sprayed coatings. For those coatings in which the ratio of TiN was lower than 0.55, a plot of Vickers hardness against the ratio of TiN, as shown in **Fig. 9**, confirms the positive effect of the formation of TiN on the hardness of coatings. However, it

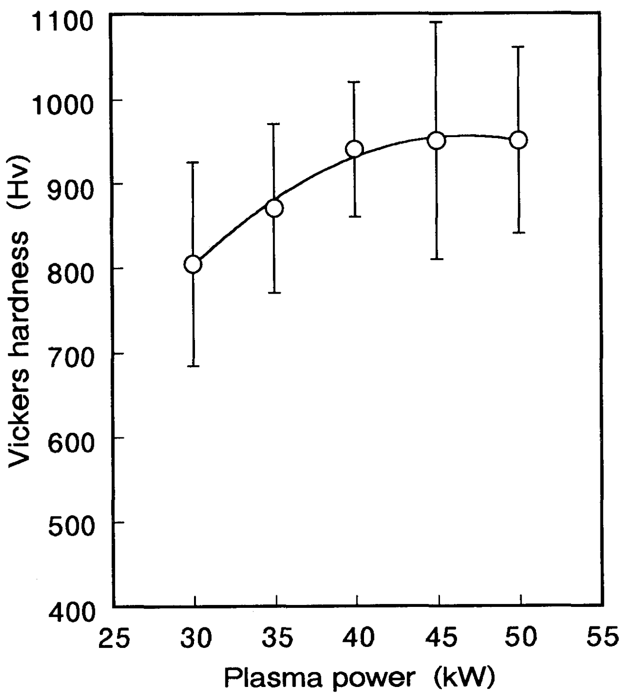

Fig. 8 Effect of plasma power on coating hardness

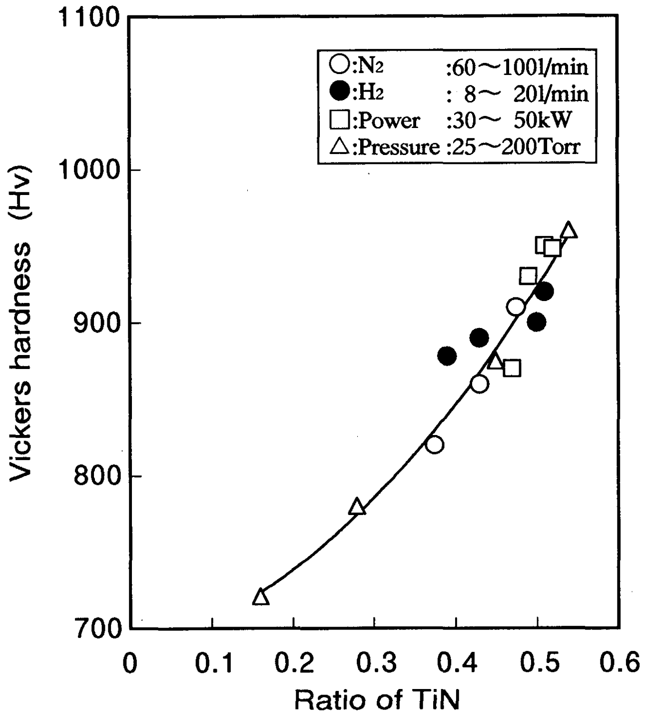

Fig. 9 Relationship between coating hardness and the ratio of TiN in the coatings

was also found that for the as-sprayed coatiangs with a further high ratio of TiN over 0.55, the measurement of Vickers hardness induced the occurrence of cracking of coating along the interface between flattened particles in the coating and subsequently yielded a low coating hardness. 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 of coating cohesion.

For an as-sprayed coating which has a lamellar structure with a low cohesion, remelting processing with high energy desity sources such as laser beam may be an effective alternative method for improvement. **Figure 10** shows an X-ray diffraction pattern of a laser-remelted Ti-TiN coating sprayed under conditions shown in Table 1. The ratio of TiN was 0.45. Compared to an as-sprayed coating shown in Fig. 3(e), it can be recognized that further nitriding of coating after laser-irradiation took place.

The investigation of the effect of the laser-irradiation parameter on the further nitriding of the coating with the ratio of TiN of 0.45 showed that the increase of laser power and the decrease of traverse speed of laser beam had a positive effect on the formation TiN during laser-irradiation. Such a laser-irradiation induced nitriding is probably the reaction of molten Ti with dissolved nitrogen in the coating. **Figure 11** illustrates the microstructure of a TiN-Ti composite coating in both as-sprayed and laser-irradiated conditions. It is evident that the laser-irradiated coating presented a homogeneous structure compared with the lamellar structure of the as-sprayed coating. Compari-

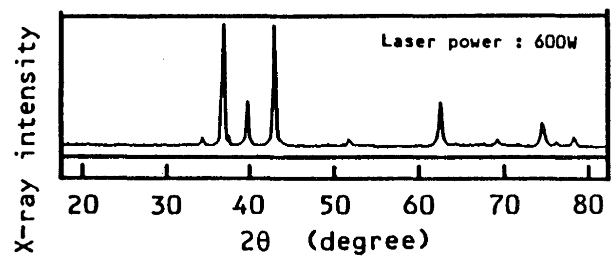

Fig. 10 X-ray diffraction pattern of a laser-irrădiated Ti-TiN coating

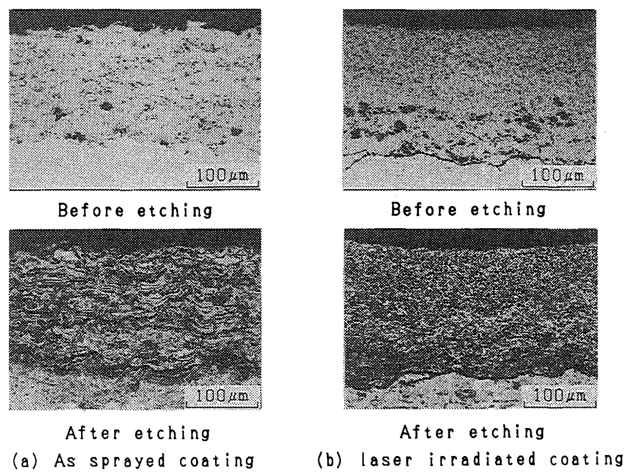

Fig. 11 Comparison of the microstructure between as-sprayed and laser-irradiated coatings

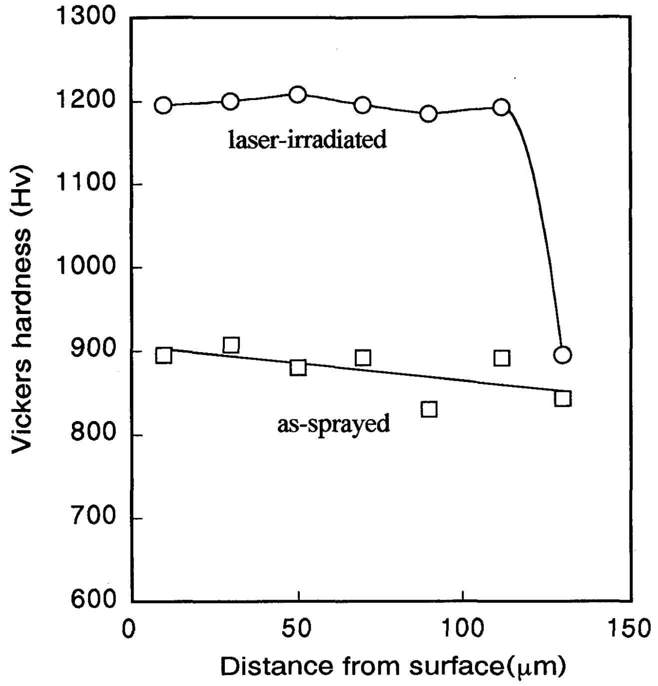

Fig. 12 Illustration of hardness distribution of as-sprayed and laser-irradiated coatings

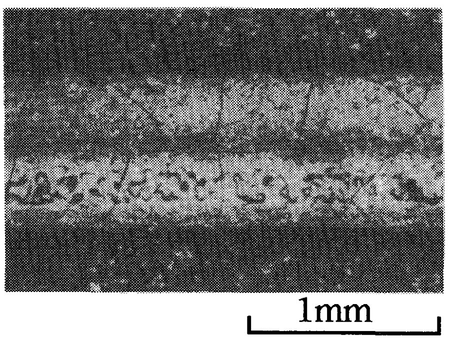

Fig. 13 A typical surface morphology of laser-irradiated TiN-Ti coating

son of the hardness distribution along the coating thickness between as-sprayed and laser-irradiated coatings, as shown in **Fig. 12**, also confirmed the formation of homogeneous TiN-Ti composite coatings after laser-irradiation.

Furthermore, the coating hardness after laser-irradiation reached about 1200Hv compared with about 900Hv of an as-sprayed coating. Therefore, it may be expected that the content of TiN in a TiN-Ti composite coating can be controlled by thermal spraying conditions with laser-assisted irraditation with the aid of further investigation of laser-irradiation to the coatings with a different ratio of TiN in as-sprayed conditions.

The examination of morphology of the surface of laser-irradiated coatings revealed the occurrence of crack in the remelted area, as shown in **Fig. 13**, which is usually observed during laser remelting processing of ceramic coatings[9-10]. This fact also supports the substantial formation TiN in the coating. It is considered that such occurrence of cracks is due to thermal stress from the restrain of thermal contract during rapid cooling of the remelted zone and low ductility of TiN ceramics formed in the coating.

4. Conclusions

The thermal spraying of Ti powder under N_2 atomosphere using N_2 plasma jet resulted in the formation of a TiN-Ti composite coating due to the reaction of Ti with the N_2 atomsphere. The formation of TiN by thermal spraying of Ti powder under controlled N_2 atmosphere was dependent on the thermal spray conditions, in particular, N_2 atmosphere pressure. The increase of N_2 pressure in the chamber showed a positive effect on the formation of TiN and the increase of N_2 gas flow in H_2-N_2 plasma jet showed a negative effect. The formation of TiN in the Ti coating can be increased by laser-irradiation of a sprayed coating. The formation of TiN increased the microhardness of the Ti coating. A further increase in hardness was achieved by laser-irradiation of the coating.

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