Reaction Spray by Laser-Plasma Jet

— Synthesis of TiN Coatings —

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Abstract

The synthesis of TiN coating has been investigated with using the laser-plasma spraying, Ti sprayed coating was formed by N_2 plasma jet, and it was irradiated with CO_2 laser beam in a low pressure nitrogen atmosphere. Main results obtained was summarized as follows: Ti sprayed coating can be more nitrized with irradiation of CO_2 laser in N_2 atmosphere, and the nitridation degree of the Ti sprayed coating was increased with the increasing of the laser output and number of the laser irradiation times. The hardness of the TiN coating obtaied was about 1300 HV.

KEY WORDS : (Plasma Spraying) (Laser Irradiation) (N_2 Low Pressure Atmosphere) (Ti Powder) (TiN Coating)

1. Introduction

Low pressure plasma-spray (LPPS) has been widely utilized in the filed of spraying techniques, this process apply a low pressure gas atmosphere that can be changed to some gas needed.[1-2] In-using the reaction between the spraying powder and gas atmosphere, it becomes possible to obtain ceramic sprayed coatings of oxides and nitrides and also to from the cermet sprayed coatings by using metal powder.

Especially in applying the laser beam to treat the surface of the sprayed coating, there are considered to be various advantages: removing of porosity and oxides in the sprayed coating; improving of the bonding strength between base metal and sprayed coating; improving the surface appearance and the roughness of coating.[3-8]

Considering these observations, this investigation was carried out to obtain Ti nitrized compound sprayed coating, Ti powder was sprayed on SS 41 steel plate by using (N_2) plasma spraying in low pressure nitrogen gas atmosphere. The obtained coating was irradiated by laser beam in a low pressure nitrogen gas atmosphere and then this coating is evaluated by X-ray diffraction.

The result of the X-ray diffraction indicated that the amount of TiN produced in sprayed coating was largely depended upon the irradiation conditions of laser beam and the gas charged atmospheric condition.

2. Meterials used

SS41 steel plates (C: 0.06 wt%) size 60x100x2 mmt and 60x60x3 mmt, are used as a base metal and they were sandblasted as the pre-treatment. Ti powder (H-20) made by SHOWADENKO was used as a spray powder which was dried at 100°C for about 60 minutes in a special furnace to eliminate poor powder flow due to humidity. **Table 1** shows the chemical composition of this Ti powder and **Table 2** shows the grain size distribution of the powder.

3. Experimental procedure

Figure 1 shows the schematic diagram of apparatus with the low pressure gas laser-plasma sprayed system used in this experiment. The plasma spray gun used is METCO TYPE-9MB with a specification of Max 80 kW. The powder feeding system is designed to supply it to the top of the spray gun.

The setting of plasma spraying condition (selection of primary gas and secondary gas, adjusting of gas flow,

Table 1 Chemical composition of Ti powder

Chemlcel composltion of Ti powder (wt%)							
Ti	Fe	Si	O	Cl	H	N	C
Bal	0.011	0.010	0.330	0.016	0.012	0.015	0.006

Table 2 Grain size distribution of Ti powder

Graln size distrlbutlon of Ti powder							
(μm)	+40	40−30	30−20	20−15	15−10	10−8	−8
(wt%)	2.0	2.0	28.0	33.0	30.0	4.0	1.0

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current, voltage and output power) and the control of plasma are designed to be carried out by IBM computer in accordance with ATCS (Advanced Thermal Coating System). The laser exciter used in this experiment is MITSUBISHI ELECTRIC. This laser is specified to give a parallel beam with diameter of 13 mm in single-mode and of 16 mm in multi-mode. The condensing lens used is made of ZnSe and the lens focal length is 330.2mm (13 inch). In order to protect the lens and supply reaction gas, 20l/min N_2 gas or Ar gas is supplied to the laser nozzle.

The charged N_2 gas or Ar gas pressure of the chamber can be adjusted to be any pressure between 1 - 760 Torr (1.3×10^{2} - 1.0×10^5 Pa). The manipulating system of test specimen in the chamber is designed to make it move up and down, rotate and swing.

Figure 2 shows the schematic diagram of various types of compound spray coating processes. **Table 3** shows the applied sprayed conditions and **Table 4** shows the applied conditions of laser beam iradiation. The structure was analyzed with using X-ray diffraction. The hardness of the sprayed coating was measured by micro-Vickers hardness testers.

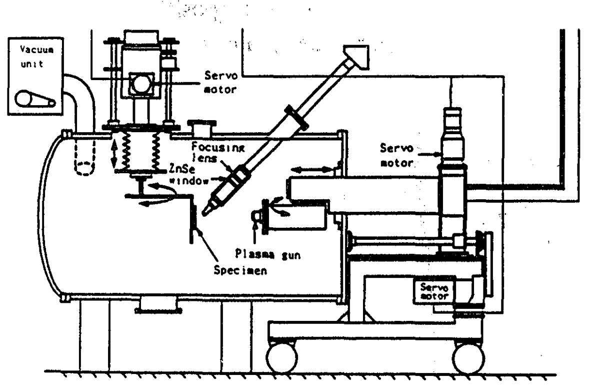


Fig. 1 Schematic diagram of laser-plasma jet spraying apparatus

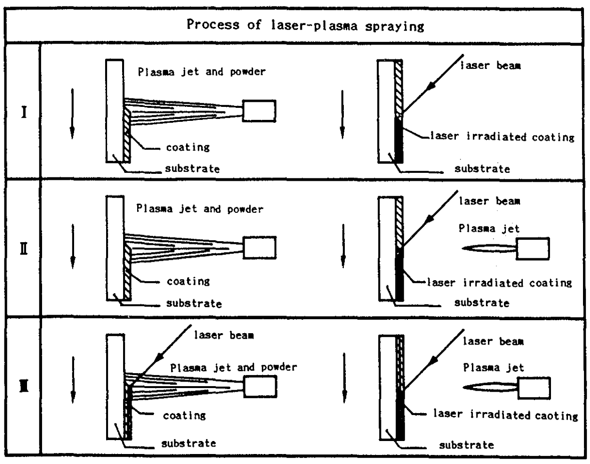


Fig. 2 Processes of laser-plasma jet spraying

4. Experimental results

Figure 3 shows the result of X-ray diffraction patterns of Ti powder dried by heating (100 °C for 60 min.). **Figure 4** shows the result of X-ray diffraction of the plasma (Ar) sprayed coating obtained in an Ar atmosphere. It becomes apparent from these figures that the obtained sprayed coating consists only of Ti without Ti oxides contamination.

Figure 5 shows the result of X-ray diffraction of plasma (N_2) sprayed coating which was formed with using process Type I (a) showed in Fig. 2 and applied condition showed in Table 3. Figure 4 and 5 are compared with each other, and it can be noticed that both sprayed coating structure are constituted mainly of Ti except 2 unknown peak in Fig. 5. In comparing the mean Vickers hardness of the sprayed coating showed in Fig. 4 with that showed in Fig. 5, the latter shows about 630 Hv and the former shows about 300 Hv. This difference can be considered to be due to the effect of the difference of charged gas in the

Table 3 Plasma spraying conditions for laser irradiation

Spraying distance	440[mm]
Arc current	500[A]
Arc voltage	68[V]
Arc power	35[Kw]
Primary flow(N_2)	40[l/min]
secondary flow(H_2)	6[l/min]
Traverse speed	200[mm/s]
Pressure(N_2)	100[Torr]

Table 4 Laser-irradiation conditions

Laser power	500-700	[W]
Defocus	0	[mm]
Traverse speed	17.2	[mm/s]
Pressure (N_2)	100	[Torr]

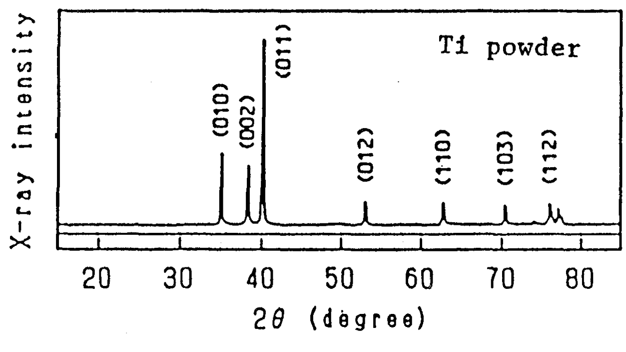
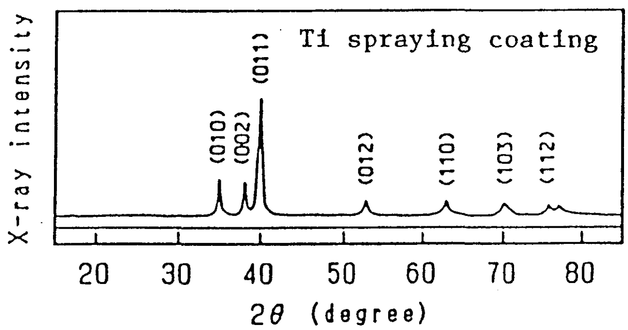


Fig. 3 X-ray diffraction pattern of Ti powder

chamber. It is also considerd that the two unknown peaks observed in Fig. 5 which shows the effect of a large amount of the solid solution of nitrogen producing in the sprayed coating of Ti. **Figure 6** shows the results of X-ray diffarction of the sprayed coating obtained with use of Type III(a) process showed in Fig. 2 that is CO_2 laser-N_2 plasma jet compound spray coating process. It can be recognized from Fig. 6 that the sprayed coating was considerably nitrized. The surface of this sprayed coating looks gold in colour and the hardness attained about 1100 Hv. Another types of compound spray coating was obtained by the process of Type III(a) and (b). The hardness of this sprayed coating is about Hv 1360 if it is irradiated again with laser.

The mean hardness value of these 4 types of sprayed coatings is shown in **Fig. 7.** From Fig. 7 we can recognize that the hardness of the sprayed coating obtained by processes Type III(a) and (b) shows about 6 times as high as that obtained by Ar-plasma sprayed process in an Ar gas atmosphere and about 2 times as high as that obtained by N_2-plasma sprayed in a N_2 gas atmosphere.

Figure 8 shows the section-photo of these sprayed coatings: (a) shows the section-photo of sprayed coating obtained in Ar atmosphere; (b) shows the section-photo of sprayed coating obtained in N_2 atmosphere; (c) shows



Spraying conditions:

Spraying distance	340[mm]
Arc current	530[A]
Arc voltage	75[V]
Arc power	40[Kw]
Primary flow(Ar)	60[l/mm]
Secondary flow (H_2)	10[l/mm]
Traverse speed	200[mm/s]
Pressure in chamber	100[Torr]

Fig. 4 X-ray diffraction pattern of Ti coating sprayed by Ar plasma jet in Ar atmosphere

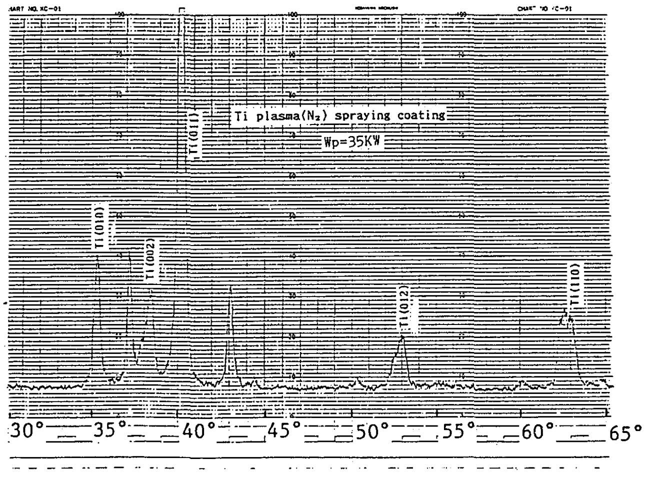


Fig. 5 X-ray diffraction pattern of Ti coating sprayed by N_2 plasma jet in N_2 atmosphere

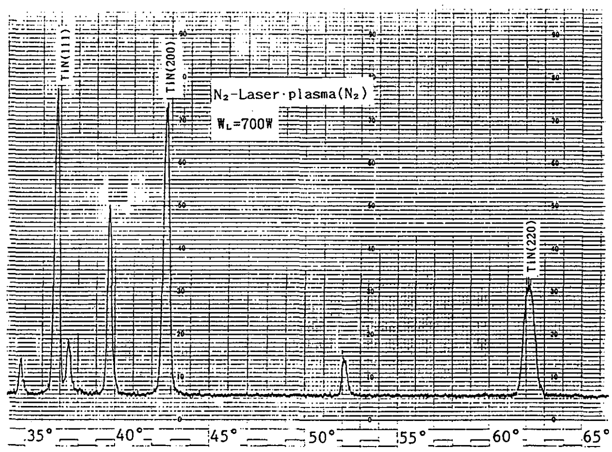


Fig. 6 X-ray diffraction pattern of Ti coating sprayed by Laser-plasma jet in N_2 atmosphere

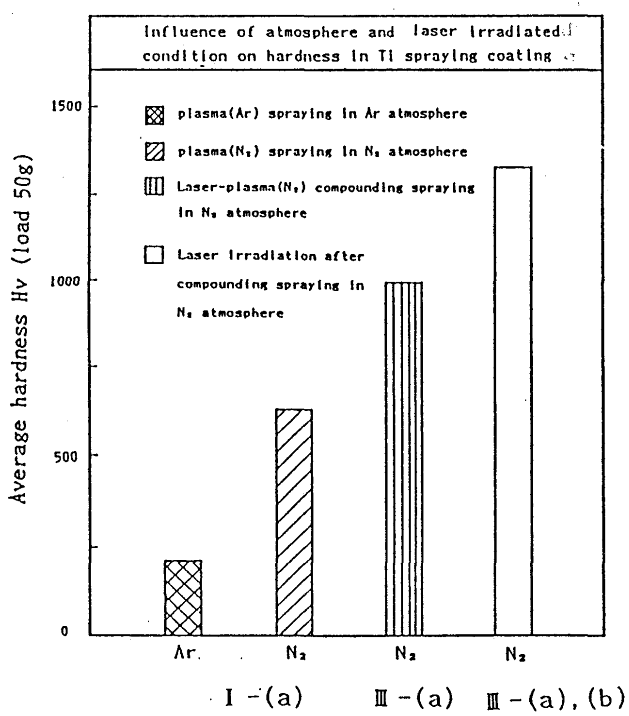


Fig. 7 Influence of atmosphere and laser irradiated condition on hardness of Ti sprayed coating

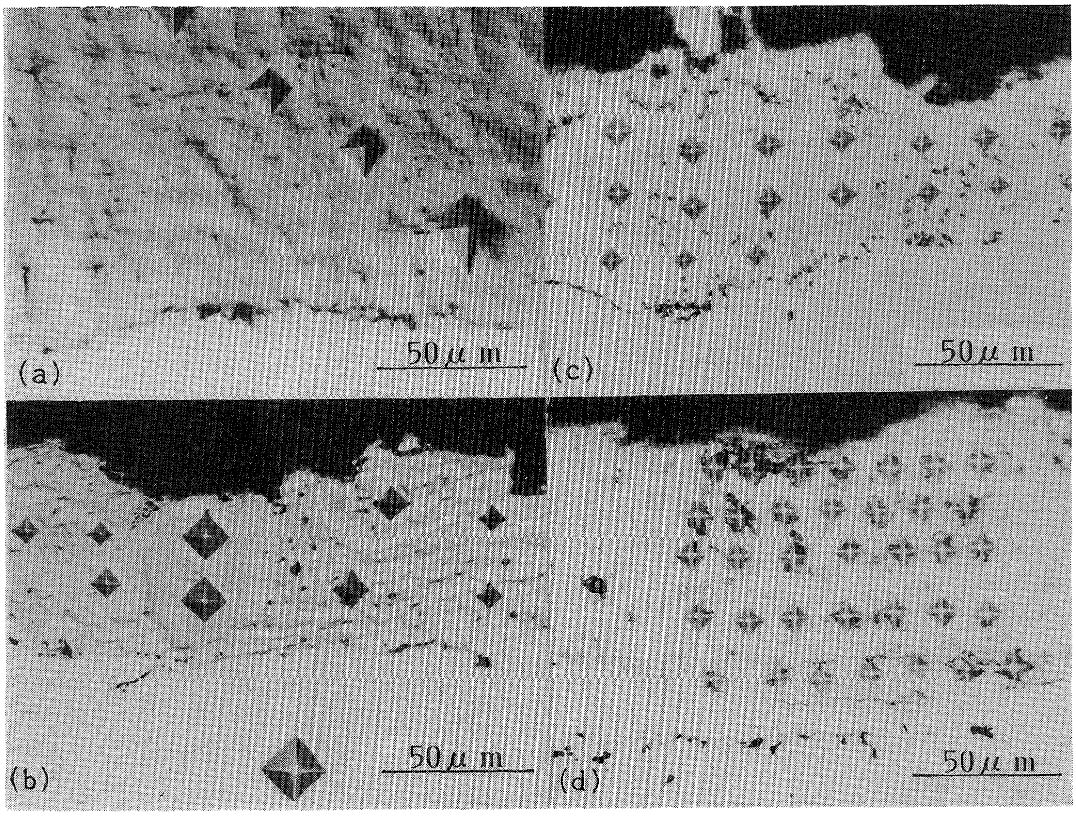


Fig. 8 Optical microstructure of Ti spraying coating a) Ar plasma sprayed in Ar atmosphere, b) N_2plasma sprayed in N_2 atmosphere, c) Type I (a), (b) (N_2plasma sprayed and laser irradiated in N_2 atmosphere) d) Type III (a), (b) (Laser-plasma jet sprayed and laser irradiated in N_2 atmosphere)

the section-photo of sprayed coating obtained by process Type 1 (a), (b) ; (d) shows the section-photo of sprayed coating obtained by process Type III (a) (b).

It can be recognized from comparing the section-photos in Fig. 8 with each other that the characteristic laminated structure exsisting in the sprayed coating has disappeared after irradiation by lasser beam due to melting of the laminated structure.

Figure 9 shows the section-photo of sprayed coating obtained by process Type III(a) in which the sprayed coating and the boundary between coating and base metal was bonded tightly together. Next item to be described is the effect of laser irradiation on the degree of nitridation of the sprayed coating.

Figure 10 shows the results of X-ray diffraction of the sprayed coating obtained by process Type I (a) and (b) showed in Fig. 2. Figure 10 (a) and (b) show the result of X-ray diffraction of the sprayed coating irradiated by one and two times with a 500 (W) output laser and (c) shows the same test result of the sprayed coating irradiated two times with a 700 (W) output laser. If the result (a) is compared with the result (b), it can be recognized that nitridation of the sprayed coating is increased in correspondence with the irradiation times. This can be seen from Fig. 10 that the peak of TiN increased. It can

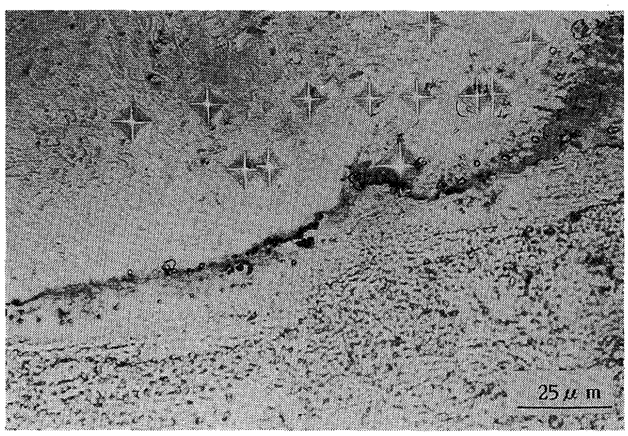


Fig. 9 Optical microstructure of Ti coating sprayed by Type III (a)

also be recognized by comparing the results of (b) and (c) that the nitridation is increased in correspondence with the increasing of laser output.

Figure 11 shows the effect of the laser irradiation condition on the hardness of the sprayed coating. In Fig. 11 (a) shows the value in the direct irradiated region and (b) shows the value in the vicinity of the irradiated region. These results indicated that the hardness of the sprayed coating is increased in correspondence both with

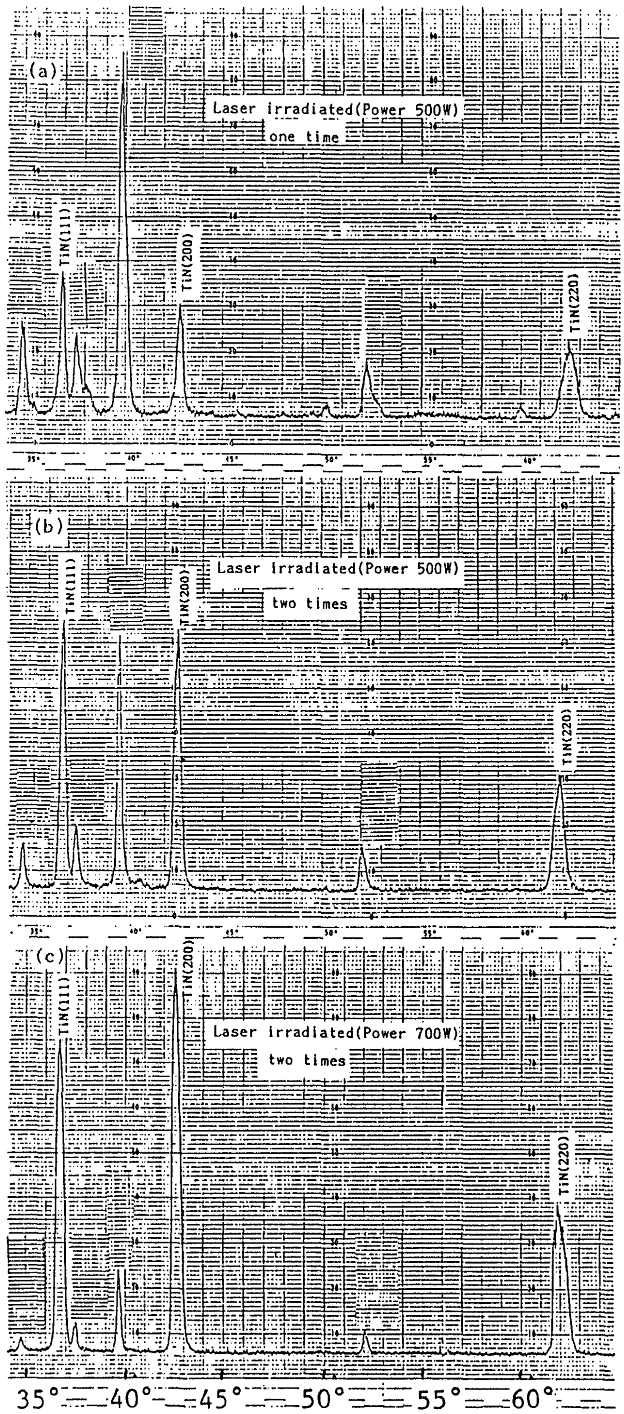


Fig. 10 Influence of laser irradiated conditions on X-ray diffraction pattern of Ti coating by Type I (a), (b)
(a) Irradiated one time by laser (500 W)
(b) Irradiated one two times by laser (500 W)
(c) Irradiated two times by laser (700 W)

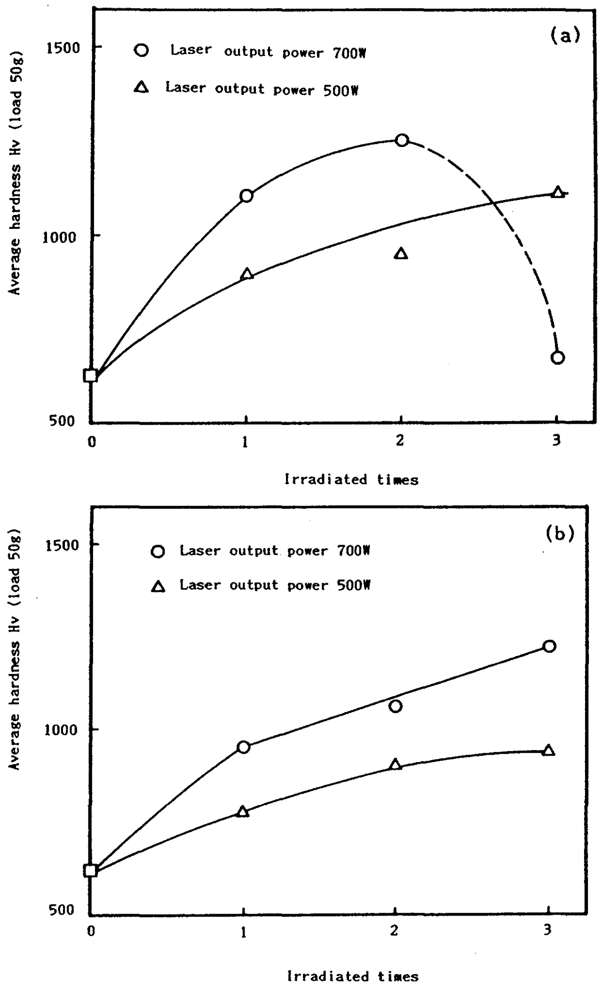


Fig. 11 Influence of laser irradiated conditions on hardness of Ti coating by Type I (a), (b)
(a) Irradiated range
(b) Neighborhood of Irradiated range

the increasing of irradiation times and the increasing of laser output. It becomes apparent from the above mentioned that the result of Fig. 10 corresponds exactly with that of Fig. 11. In other words, the hardness of the sprayed coating can be increased in proportion to the progression of nitridation.

5. Discussion

We have tried to confirm the effect of nitrogen contained in the compound sprayed coating on the progression of nitridation during irradiation. The compound sprayed coating obtained in the N_2 gas atmosphere by the sprayed condition showed in Fig. 4 and were irradiated with laser beam (200 - 600(W)) in Ar gas charged atmosphere. **Figure 12** shows the results of X-ray diffraction of the obtained sprayed coatings.

Figure 12 suggests us to recognize the progression of nitridation of sprayed coating. Moreover it can be considered that nitrogen contained in the sprayed coating either in solid solution state or in gas state which is reacted with remelted Ti due to laser irradiation and results in producing of TiN. In order to investigate detail mechanism of nitridation it is also evaluated whether the nitridation of the sprayed coating is activated with the nitrogen contained in the sprayed coating or is activated with abosrbed nitrogen from the charged gas atmosphere. For this purpose Ar-plasma spraying is carried out in Ar gas atmosphere and the sprayed coating was irradiated with laser beam in the nitrogen gas atmosphere in the same way as the above test.

Figure 13 shows the results of X-ray diffraction this result indicated less TiN in the sprayed coating. This result also means that a sprayed coating contained less nitrogen can not be nitrized even if it is irradiated with a CO_2 laser beam in the nitrogen gas. It can be considered that the nitridation of the sprayed coating irradiated with laser beam is caused by the activation of nitrogen has been contained in the compound sprayed coating and results in generating of TiN reaction.

6. Conclusions

1) Ti sprayed coating obtained by the low pressure nitrogen plasma process can be more nitrized by irradiation of CO_2 laser beam in the nitrogen gas atmosphere.

2) Ti sprayed coating obtained by the laser-plasma jet

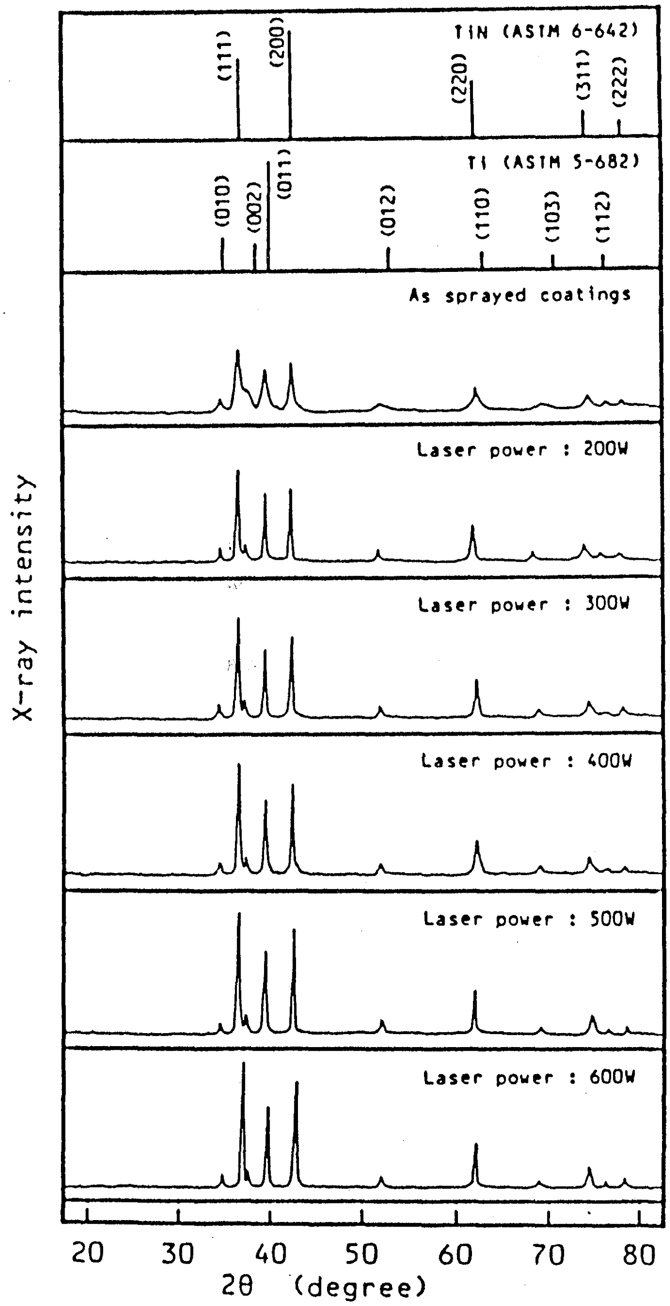


Fig. 12 Effect of laser power on X-ray diffraction of Ti plasma (N_2) sprayed coating irradiated in Ar atmosphere

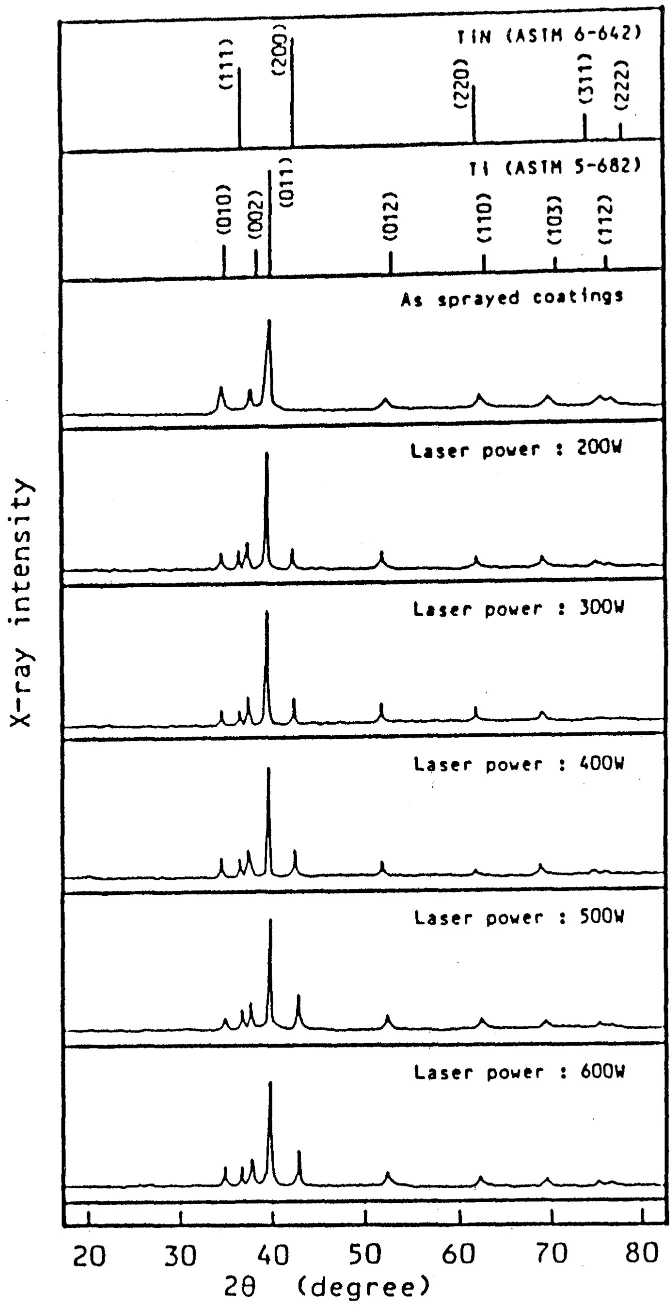


Fig. 13 Effect of laser power on X-ray diffraction pattern of Ti plasma (Ar) sprayed coating irradiated in N_2 atmosphere

combined spray in the nitrogen gas atmosphere is nitrized and results in producing of TiN. As the result of this change, the Ti nitrized sprayed coating shows about 1300 Hv as the mean hardness and shows gold colour in appearance.

3) The nitridation of the sprayed coating is increased in correspondence with the increasing of the laser output and the irradiation times of the laser beam.

References

1) P. C. Wold, F. N. Longo: "Vacuum plasma spray process and coatings" Proc. of the 9th Int. Thermal Spraying Conf. Hague, 1980, 187-196
2) M. F. Smith, R. C. Dykhuizen: "The effect of chamber pressure on particle velocities in low-pressure plasma spray deposition" Proc. of the 1st National Thernal Spraying Conf. Orlando, U. S. A., 1987, 21-24
3) N. Asahi, Y. Kogima: "A study of metallurgical characteristics of low pressure plasma titanium coatings" Proc. of the 7th Intl. Conf. on Vacuum Metallurgy, Japan, 1982, 305-312
4) F. Kassabji, F. Tourenne, A. Derradji, P. Fauchais: "Aluminium and aluminium nitride deposition by low pressure nitrogen arc plasma spraying" Prof. of the 10th Intl. Thermal Spraying" Conf. Essen, 1983, 82-84
5) R. Sivakumar, B. L. Mordike: "Laser melting of plasma sprayed ceramic coatings" Surface Engineering Vol. 4 No.2, 1988, 127-140
6) Y. M. Zhu, Y. H. Li, M. C. Liang, Z. R. Tian: "Laser processing of plasma-sprayed chromium oxide ceramic coatings" Proc. of TMS Fall Meeting in USA, 1988, 1-9
7) H. Bhat, R. A. Zatorski, H. Herman, R. J. Coyle: "Laser treatment of plasma-sprayed coatings" Proc. of the 10th Intl. Thermal Spraying Conf., Essen, 1983, 21-23
8) N. P. Bolotina, V. P. Larionov, T. V. Argunova, V. D. Tyunin, M. P. Lebedev: "Laser processing of plasma sprayed coatings" Proc. of Intl. Symp. on ATTAC'88, Japan, 1988, 217-221