# EFFECTS OF ADDITION OF HYDROGEN TO NITROGEN PLASMA DURING NITRIDING OF TITANIUM AND SACM645 STEEL USING SUPERSONIC EXPANDING PLASMA JETS

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## Abstract

Nitriding of Titanium and SACM645 steel using supersonic expanding pure nitrogen and nitrogen/ hydrogen mixture plasma jets at 30Pa in chamber pressure were carried out. The results are summarized as follows. Plasma jets had enough reactivity to form a hard and thick titanium nitride layer on the surface of a titanium sample by only a few minutes plasma jet irradiation even at 30Pa in chamber pressure, and addition of hydrogen to pure nitrogen plasma jets promoted the nitriding of titanium. Besides, though hard layer was not formed on the surface of the SACM645 steel in the case of pure nitrogen plasma jets use, hard layer was formed on the sample without any damages by only a few minutes plasma jets irradiation in the case of hydrogen/ nitrogen mixture plasma. According to the results of optical spectroscopic measurement, it is considered that these phenomena were caused by the chemical reaction owing to NH radical. From these results, this process was found to have a high potential for surface modification of steel.

## 1. Introduction

Direct-current arc jet plasma torches have many attractive characteristics, that is, simple structures and systems, and light weight. Since plasma jets have high energy density, plasma spraying is successfully used as a technique for protective coating. Furthermore, recently, surface modification process utilizing the reactivity of plasma jets like thermal plasma chemical vapor deposition (TPCVD) is noticed as a new surface modification method. However, since plasma jets were used only as heat sources in conventional plasma jet processes, surface modification under a low pressure below 3kPa had rarely been done.

In our previous study about the diagnostics of $N_2$+$3H_2$ plasma by means of optical emission spectroscopy [1], many kinds of molecular radical, such as not only $N_2$ but also NH, were observed near the outlet of the plasma torch. Therefore, $NH_3$ and/or $N_2$-$H_2$ gas mixture plasma are expected to be much more reactive than pure $N_2$ plasma also in thermal plasma jet.

In this study, in order to investigate the nitriding promotion effects of addition of hydrogen to nitrogen plasma jets, nitriding of titanium and SACM645 steel using pure nitrogen and hydrogen/ nitrogen mixture plasma jets were carried out at 30Pa in chamber pressure.

## 2. Experimental apparatus and procedure

Experimental apparatus for the surface nitriding, which is shown in Fig.1, consists of vacuum chamber, plasma torch, gas supply system, power supply system and vacuum pump. Sample holder was placed in the vacuum chamber and plasma torch has the optimally designed supersonic expansion nozzle for use at 30Pa in chamber pressure. Samples were set on the sample holder as shown in Fig.2. The sample at the left side is placed as the axial center of the plasma jet irradiates this sample. The discharge power was 6 kW (40V, 150A), and the mass flow rate of $N_2$ gas was 0.2 g/s in the case of the pure nitrogen plasma jets use. In the case of hydrogen/ nitrogen mixture gas use, mass flow ratio of hydrogen/ nitrogen in the working gas was 1/3 and discharge power was 7.5 kw. The nitriding

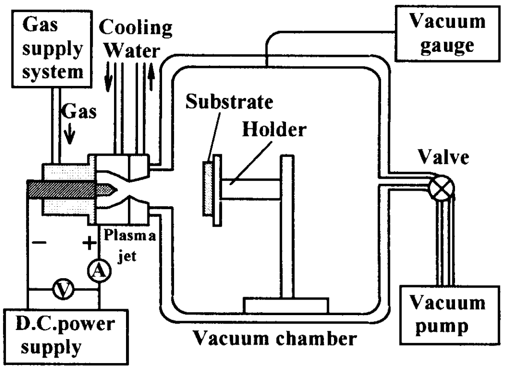


Fig.1 Schematic diagram of the apparatus for surface nitriding

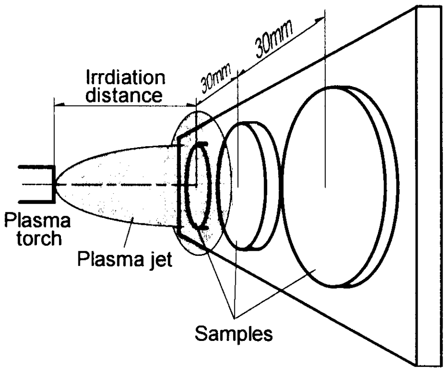


Fig.2 Schematic diagram of sample holder

time was 5 min in all cases. Samples are $\phi$ 25mm× 3mm$^t$ titanium and/or SACM645 steel. These samples had polished surface by #1000 sand papers in advance. Sample temperatures during operation are measured by CA thermocouple fixed on the other surface of the samples. The surface structures of nitrided samples were investigated by means of X-ray diffraction (CuK$\alpha$, 40kV, 30mA). The surface hardness of the nitrided sample was measured by Vickers hardness testing. Wear resistance testing using Block on Disk method was also conducted in the case of SACM 645. Fig. 3 shows schematic diagram of the wear testing apparatus. The disk was 200mm in diameter, the rotational speed was 1450rpm and the load was 500g. The surface of the disk was covered with #2000 sandpaper. The wear mass loss was measured every 3000m wear distance by the time that total wear distance reached 15000m.

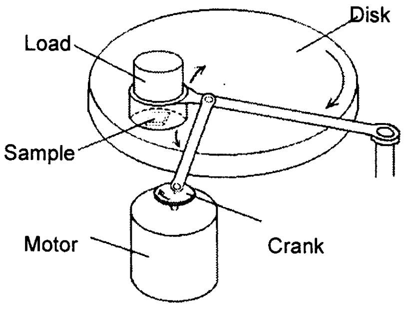


Fig.3 Schematic diagram of the wear testing apparatus sample holder

## 3. Results and discussion

### 3.1 Nitriding of titanium

*a) Nitriding using pure nitrogen plasma jets*

In our previous studies [2], [3], plasma diagnostic studies in a plasma torch at 30 Pa of chamber pressure were carried out by means of optical emission spectroscopy. Consequently, although temperatures of heavy particle species at the nozzle throat were about 10000K, the temperatures drastically fell down through the nozzle and vibration temperature and rotation temperature were 4000K and 2000K respectively at the nozzle outlet. It was found that the temperatures at the nozzle outlet decreased with decreasing pressure and that these temperatures at the nozzle outlet were much lower than those in the case of conventional thermal spraying and thermal plasma chemical vapor deposition.

In this study, in order to investigate the reactivity of such a low temperature plasma jet, nitriding of titanium using nitrogen plasma jet is carried out under a low pressure at 30Pa.

Fig. 4 shows XRD pattern of the surface of the nitrided sample at the center in the case that irradiation distance was 130mm. Since only TiN and $Ti_2N$ peaks were observed in this XRD pattern, it is proved that compound layer was constructed on the surface of the sample. Fig. 4 shows Vickers hardness of the sample as a function of depth from surface. The surface hardness of the sample is over 1000HV, and the thickness of the hard zone with hardness over 400HV below the surface zone was over 100$\mu$m. The conclusion derived from the data as shown in Figs.4, 5, were confirmed by microscopic examination. The white non-etchable zone, probably compound layer, and heterogeneous zone with thickness over 100$\mu$m below the white zone were clearly visible in the micrograph shown in Fig.6.

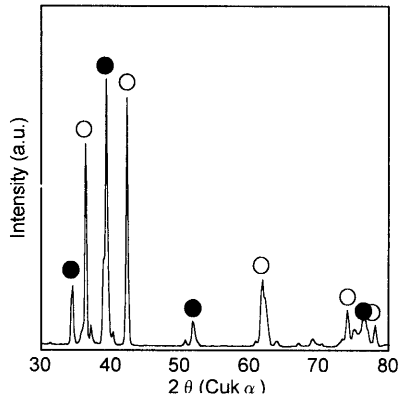


Fig.4 X-ray diffraction pattern of the sample nitrided at 30Pa with 130mm in irradiation distance. (○: TiN, ●: $Ti_2N$, ▲Ti)

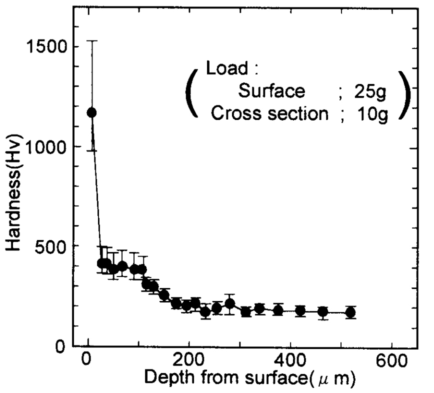


Fig.5 Vickers hardness of the sample nitrided at 30Pa with 130mm in irradiation distance.

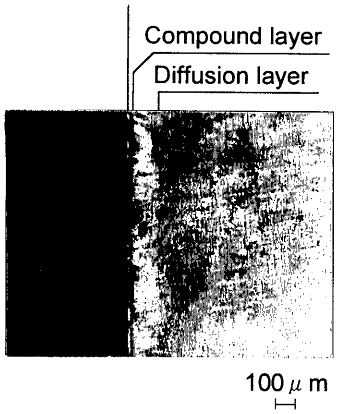


Fig.6 Optical micrograph of cross section of the sample nitrided at 30Pa with 130mm in irradiation distance.

Fig.7 shows the maximum sample temperatures during operation as a function of irradiation distance. Although the maximum temperature on the condition with 130mm irradiation distance were about 1400K, the temperatures gradually fell down with increasing irradiation distance to about 1170K, which was in the range of the temperature in conventional plasma nitriding, in the case that irradiation distance was 180mm. However, as shown in Figs.8, 9, nitriding rate and surface hardening rate fell down drastically as the irradiation distance was further. Finally, nitriding and surface hardening occurred scarcely in the case that irradiation distance was further than 160mm.

### *b) The Effects of addition of hydrogen to pure nitrogen plasma jet*

In nitriding process, nitriding rate was enhanced by hydrogen addition. Hence, plasma nitriding by using ammonia and/or nitrogen/ hydrogen mixture plasma, rather than pure nitrogen plasma, had been practically used in many industries. Generally, the effects of hydrogen addition to nitrogen plasma on the nitriding rate was thought that chemically reactive species, i.e. molecular radicals, generated by hydrogen addition to nitrogen promote nitriding.

Fig.10 shows the XRD patterns of the samples at the center on the conditions that irradiation distances were 160mm, 180mm and 200mm. nitriding was promoted in the case of hydrogen/ nitrogen mixture plasma jets with 200 mm in irradiation distance in comparison with the case of pure $N_2$ with 160 mm in irradiation distance, though the sample temperature on the former condition was lower than that on the latter one.

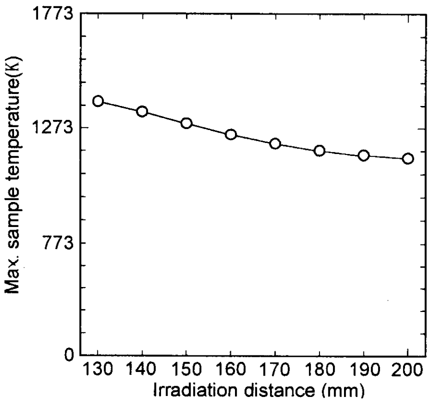


Fig.7 Maximum sample temperatures during operation as a function of irradiation distance.

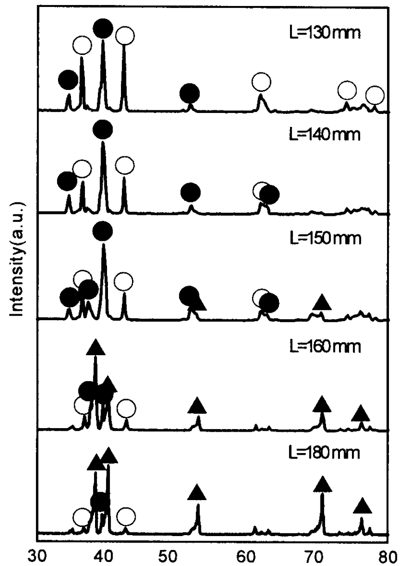


Fig.8 X-ray diffraction pattern of the sample nitrided at 30Pa. (○: TiN, ●: $Ti_2N$, ▲Ti, L: Irradiation distance )

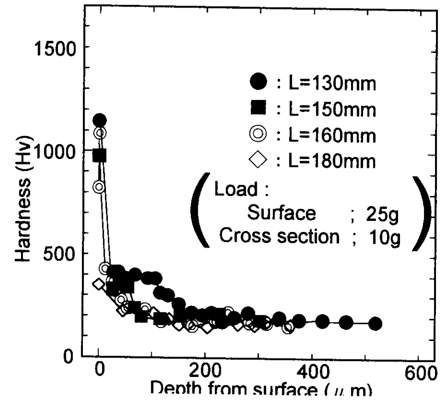


Fig.9 Vickers hardness of the nitrided sample as a function of depth from surface. (L : Irradiation distance )

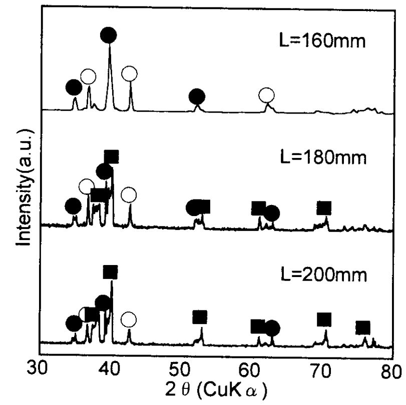


Fig.10 X-ray diffraction pattern of the sample nitrided at 30Pa. (○: TiN, ●: $Ti_2N$, ■: $TiN_{0.3}$, L: Irradiation distance )

From these results, plasma jet was thought to be have enough reactivity to construct a hard and thick titanium nitride layer on the surface of a titanium sample by only a few minutes plasma jets irradiation. Besides, the hydrogen addition to nitrogen plasma jet was proved to enhance nitriding of titanium.

### 3.1 Nitriding of SACM645 steel

Next, in order to obtain some useful information for practical use of this process, SACM645 steel was carried out.

*a) Nitriding using pure nitrogen plasma jets*

Fig. 11 shows radial profiles of surface hardness of the samples nitrided on the condition that pure nitrogen plasma jets were used. Though nitride layer was formed and surface hardening occurred on the sample on the same condition in the case of titanium, surface hardening hardly occurred in the case of the nitriding of the SACM645 steel. Fig. 12 shows X-ray diffraction pattern of non-nitrided and nitrided SACM645 sample. Nitride was not investigated on the surface of the sample, and surface hardening didn't occur by the nitriding using pure nitrogen plasma jet even in the case that the sample melted down during operation.

*b) The Effects of addition of hydrogen to pure nitrogen plasma jet*

In conventional nitriding processes, nitriding rate was enhanced by hydrogen addition to nitrogen or nitrogen plasma. Hence, nitriding by using $NH_3$ and/or $N_2$-$H_2$ mixture gas, rather than pure $N_2$, had been practically used in many industries. Generally, the effect of hydrogen addition to nitrogen or nitrogen plasma on the nitriding rate was thought that chemically reactive species, i.e. molecular radicals, generated by hydrogen addition to nitrogen promote nitriding. Fig. 13 shows Vickers hardness profiles of the nitrided SACM645 samples on the condition that $H_2/N_2$ mixture gas with 1/3 mass flow ratio was used as working gas. In this case, unlike the case of the nitriding using pure nitrogen plasma jets, surface hardening occurred and the hard layer which was over 800HV in Vickers hardness and over 50 μ m in thickness was formed on the surface of the sample by only 5 minutes operation. Especially, surface morphology of the nitrided sample was almost the same condition as that of the non-nitrided SACM645 sample though the surface hardening occurred drastically during operation (Fig.14).

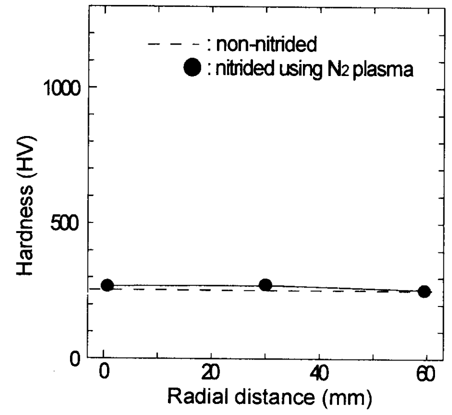


Fig.11 Radial profiles of surface hardness of an SACM645 steel and the sample nitrided by pure nitrogen plasma jets

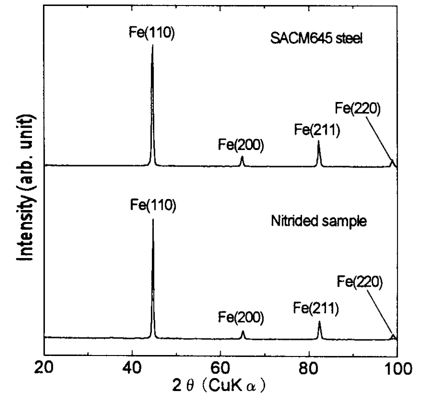


Fig.12 X-ray diffraction pattern of an SACM645 steel and the sample nitrided by pure nitrogen plasma jets

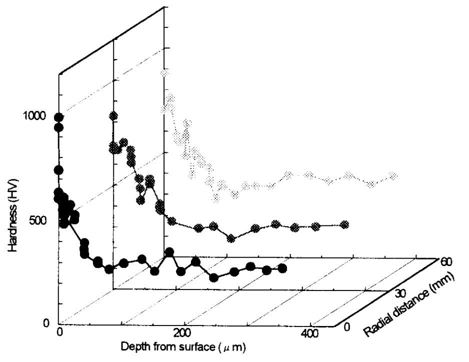
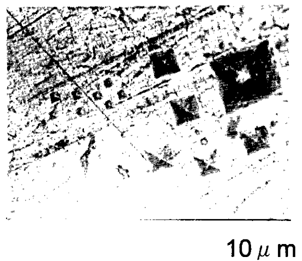


Fig.13 Vickers hardness profiles of the nitrided samples in the case of hydrogen/ nitrogen mixture plasma jets with 1/3 in mass flow ratio of hydrogen/ nitrogen.

a) non-nitrided sample



b) nitrided sample

Fig.13 Optical micrograph of cross section of the non-nitrided and nitrided SACM645 samples.

These phenomena were frequently investigated in the case that NH radicals generated in plasma jets contributed to the nitriding in the conventional nitriding processes.

Fig. 14 shows wear mass loss of a non-nitrided sample and the sample nitrided at the center. While the total wear mass loss of the non-nitrided sample at 15000m in wear distance is of mass 10.2 mg, the mass loss of the nitrided samples was of mass 2.6 mg. It could be confirmed that this process improved the wear resistance ability of SACM645 steel. However, though drastic surface hardening and improvement of wear resistance ability of SACM645 steel by nitriding using this process, peaks of nitride could hardly be observed in the X-ray diffraction patterns shown in Fig.15.

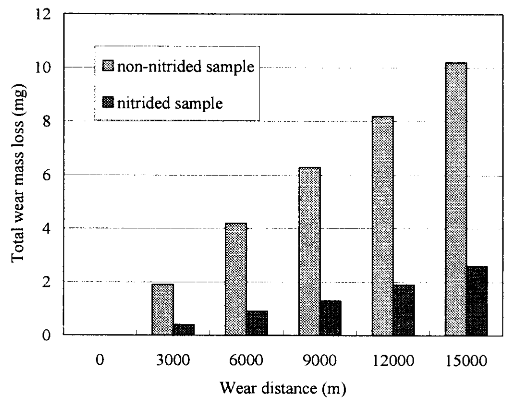


Fig.14 Wear test results on dry condition

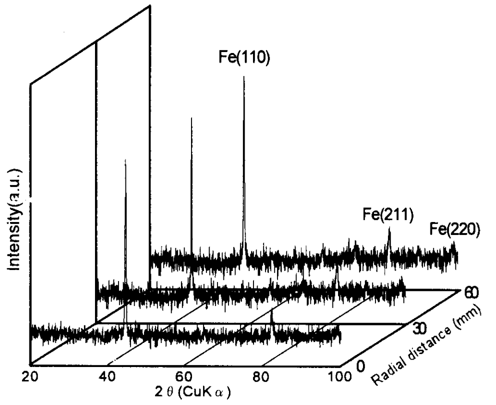


Fig.15 X-ray diffraction patterns of the nitrided samples in the case of hydrogen/ nitrogen mixture plasma jets with 1/3 in mass flow ratio of hydrogen/ nitrogen.

Hence, the mechanism of surface hardening in this process couldn't be revealed in this study though it is considered that the surface hardening in this process didn't occur due to nitriding or hydrogenation of iron but occurred due to nitriding of alloying elements.

## 4. CONCLUSION

In this study, in order to investigate the nitriding promotion effects of addition of hydrogen to nitrogen plasma jets, nitriding of titanium and SACM645 steel using supersonic expanding pure nitrogen and nitrogen/hydrogen mixture plasma jets at 30Pa in chamber pressure were carried out. Consequently, it was proved that super sonic nitrogen plasma jets had enough reactivity to form a hard and thick titanium nitride layer on the surface of a titanium sample, and addition of hydrogen to pure nitrogen plasma jets promoted the nitriding of titanium. Besides, though hard layer was not formed on the SACM645 sample in the case of pure nitrogen plasma jets use, surface hardening was promoted by hydrogen addition to pure nitrogen plasma. It was considered that the phenomenon occurred because NH radicals generated in plasma jets contributed to the nitriding, and we could estimate the evidence of this phenomenon from the result that the surface morphology of the nitrided sample. From these results, this process was found to have a high potential for surface modification even in the case of steel material like SACM645.

## REFERENCES

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