Plasma Nitriding Performed under Atmospheric Pressure using Pulsed-Arc Plasma Jet

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Abstract: Plasma nitriding is achieved by spraying the nitrogen pulsed-arc plasma jet under atmospheric-pressure N\textsubscript{2}/H\textsubscript{2} mixture. The quality of nitriding is found to depend on the H\textsubscript{2} flow rate, which has an optimal value. We propose a simple mechanism of this dependence. Moreover, the amount of H\textsubscript{2} necessary for best nitriding can be decreased to 1/20 by changing the way of H\textsubscript{2} addition.

Keywords: nitriding, surface hardening, atmospheric-pressure plasma, plasma jet

Plasma nitriding is one of the surface-hardening technologies utilized for a number of mechanical products such as automobile components, dies, and cutting tools \cite{1-6}. As the treatment requires a vacuum system in conventional plasma-nitriding methods, the treatment is performed as a batch process and the capital cost becomes very high. To eliminate these shortcomings, we are developing a new plasma nitriding using atmospheric-pressure plasma technologies. As far as the authors know there are only a few literatures on successful surface hardening by atmospheric-pressure plasma nitriding, e.g., nitriding with a dielectric barrier discharge \cite{4}. Of a wide variety of atmospheric-pressure plasmas, we have adopted the pulsed-arc (PA) plasma jet for the following two reasons \cite{7}. First, the plume temperature of the PA discharge is suitable for nitriding. Second, the PA discharge can produce relatively high density reactive species.

Up to now, we have demonstrated that local nitriding is feasible with spraying the PA plasma jet onto a steel surface, provided that H\textsubscript{2} gas is added to the ambient N\textsubscript{2} atmosphere \cite{8}. Here, we report the detail of H\textsubscript{2} addition influencing the quality of nitriding. Moreover, a new method of H\textsubscript{2} supply is described in which the H\textsubscript{2} amount necessary for nitriding can be decreased drastically.

The jet nozzle is composed of a coaxial cylindrical electrode system as shown in Fig. 1. The grounded external electrode is 35 mm in inner diameter and has an orifice of 4 mm in diameter at the tip. The tip of the internal electrode has a curvature
radius of 4 mm. The electrode gap, between the internal electrode tip and the inner wall of the external electrode near the orifice, is 18 mm. N$_2$ gas of 99.99% in purity is introduced into the gap at 20 L/min. The low-frequency voltage pulse (4-5 kV in height and 21 kHz in repetition as shown in Fig. 2) is applied to the inner electrode using a high voltage power supply. The maximum of the discharge current is ca. 1 A. The afterglow of the generated PA plasma is spewed out from the orifice, forming the jet plume.

Nitriding is performed in a closed cylindrical container. The jet nozzle is inserted into the container from the upper end. Prior to the generation of plasma jet, the N$_2$ gas flow from the nozzle purges residual O$_2$ inside the container. Note that it is necessary for performing nitriding to add H$_2$ gas. Our conventional way is to add H$_2$ to the N$_2$ atmosphere through a container port (the atmosphere H$_2$ mode) [8]. Here we newly tried an alternative H$_2$ supply, i.e., to add H$_2$ through the jet nozzle with the working N$_2$ gas (the nozzle H$_2$ mode). The N$_2$/H$_2$ gas mixture flows out through the exhaust ports mounted at the lower end. The container is not fitted with any pumping system so that the N$_2$ pressure inside the container is kept at 1 atm.

The nitriding response is examined by spraying the jet plume onto the surface of disk-shaped samples (20 mm in diameter and 4 mm in thickness) of die steel JIS SKD61 which is frequently used to benchmark nitriding [3,6]. The sample is put on a ceramic heater to control the treatment temperature. The distance between the nozzle tip and the sample surface is 15 mm. The treatment temperature is 530ºC. The treatment duration is 2 h. The visible jet plume covers the entire surface of the sample during the treatment.

Fig. 3 shows a typical metallographic structure of a treated sample cross-section. The white layer is
the compound layer, which is mainly composed of $\varepsilon$-$\text{Fe}_{2.3}\text{N}$ phase. The dark zone beneath the compound layer corresponds to the diffusion layer. The hardness profile is shown later. Fig. 4 shows the nitrogen distribution of the cross-section obtained with EPMA. We can see that the compound layer of less than 10 $\mu$m contains a dense nitrogen and the diffusion layer (down to 70 $\mu$m here) also has a considerable amount of nitrogen. This indicates that the hardening is truly attributed to N atoms diffusing into steel surface.

Fig. 5 shows the hardness profile of nitried cross-section for several H$_2$ flow rates under the atmosphere H$_2$ mode. The results indicate that the quality of nitriding is low when the H$_2$ flow rate is too low, or too high. That is, there exists an optimal H$_2$ flow rate to provide the deepest hardened layer. In our experiments, the optimal value is 4 L/min. On the other hand, Fig. 6 shows the hardness profiles for the nozzle H$_2$ mode. One notices that this mode also gives a qualitatively same dependence on the H$_2$ flow rate. However, the flow rate necessary for nitriding is much lower than that for the atmosphere H$_2$ mode. The optimal H$_2$ flow rate, 200 mL/min, proves to be 1/20 of that for the atmosphere H$_2$ mode.

The optical emission spectroscopy revealed that the intensity of the NH radical is most prominent in the both H$_2$ modes. Fig. 7 shows the NH emission intensity as a
function of the H₂ flow rate. It can be predicted from the result that a low H₂ flow rate provides a high-density NH radicals and the density decreases with increasing H₂ flow rate under the both H₂ mode. This dependence might be due to that a high H₂ flow rate leads to the production of NH₃ rather than NH. It should be emphasized here that a substantially analogous NH emission intensity is obtained under the nozzle H₂ mode although the horizontal scale for this mode is 1/40 of that for the other mode. The effective NH production under the nozzle H₂ mode is most likely caused by the direct supply of H₂ to the discharge region involving active chemical reactions.

By considering the presented results comprehensively, we construct a likely mechanism of the plasma-jet nitriding as follows:

(A)  The HN radicals play a role of supplying N atoms to the sample surface.
(B)  The low-quality nitriding for too high H₂ flow rate under the both H₂ mode is due to the lack of N supply to the surface.
(C)  The low-quality nitriding for too low H₂ flow rate is caused by the surface oxidization by residual O₂ remaining because of a low H₂ reduction ability.
(D)  The efficient production of NH radicals under the nozzle H₂ mode provides the decrease in the H₂ amount necessary for nitriding to 1/20.

We hope that the PA plasma jet nitriding will offer an easy-to-use, economical hardening method to industrial and scientific fields.