Correlational Study on Ground-State NH Radical Density and Nitriding Capability using Atmospheric-Pressure Plasma

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To evaluate the importance of NH radicals to plasma nitriding, we compare the operating-gas dependence of NH radical density present in the atmospheric-pressure pulsed-arc plasma jet and the nitriding capability of the relevant plasma jet. Here, the laser-induced fluorescence is adopted to measure the relative density of the ground-state NH radicals. On the other hand, the nitrogen concentration doped onto the steel surface is investigated to estimate the nitriding capability. As a result, both the NH density and the nitrogen concentration exhibit an exponential decay when the hydrogen fraction of the operating nitrogen-hydrogen gas mixture increases from 1 to 4%. Note that the NH density and the nitrogen concentration shows very close the $1/e$ decay constants. The similarity of the two values likely indicates a deep correlation between the NH radicals and the nitriding capability.

1. Introduction

NH radical has been mentioned as an important or an effective species for plasma nitriding treatment. For example, NH radicals are considered to play a key role in the radical nitriding, one of plasma nitriding techniques with the operating gas of ammonia and hydrogen mixture [1]. The existence of NH radicals in plasmas, however, has been investigated mainly by the optical emission spectroscopy [2], by which the ground-state species cannot be taken into account even though that should be the major species to govern plasma chemical reactions.

Incidentally, we have developed a unique nitriding technology by using the pulsed-arc plasma jet generated under atmospheric-pressure nitrogen-hydrogen gas mixture. For now, the plasma-jet nitriding has proved to enable surface nitriding of steels [3], titanium alloy [4], and diamond electrode [5]. Note that the plasma-jet nitriding possesses two properties important to the study reported here. First, the optical emission of excited NH radicals at 336 nm is predominantly observed in the jet plume [2], implying that the plasma jet contains considerable amount of ground-state NH radicals. Second, the nitrogen dose amount is very sensitive to the hydrogen fraction of the operating gas [3]. These two properties made us conceive a comparative study of the NH density and the nitriding capability using the plasma jet, where the relative NH density is measured by the laser-induced fluorescence (LIF) to take account of the ground-state species.

2. Experimental

2.1 Pulsed-arc plasma jet

Figure 1 shows the atmospheric-pressure pulsed-arc plasma jet. The jet nozzle is composed of the coaxial inner and the outer electrode with the discharge gap of ca. 20 mm. The nitrogen-hydrogen gas mixture with the hydrogen fraction f is introduced into the nozzle at 20 slm and the voltage pulses of ±5 kV and 21 kHz is applied to the inner electrode to generate pulsed-arc discharges in the gap. The afterglow is spewed out from the orifice of 4 mm in diameter to produce the jet plume.
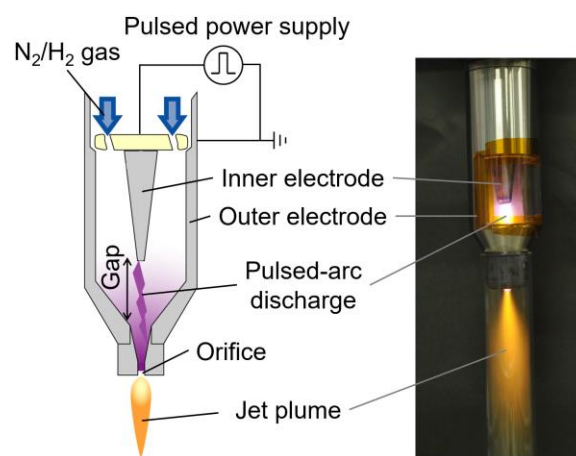

Figure 1 Electrode nozzle of pulsed-arc plasma jet.

2.2 Laser-Induced Fluorescence

Figure 2 shows a schematic of the LIF system. The jet plume is produced in a steel container to replace the air of the ambient atmosphere with the operating gas by gas purging. The container is fitted with four quartz windows on each side for LIF observation. Nano-second pulsed laser of ca. 305 nm in wavelength is generated by an OPO laser source for the transition of NH from the ground level $X_3\Sigma^-(v{=}0)$ to the excitation level $A_3\Pi(v{=}1)$, resulting in the fluorescent emissions of ca. 336 and 337 nm corresponding to the A-X(0,0) and A-X(1,1) vibrational bands [6]. The laser diameter is ca. 5 mm, the pulse energy is ca. 6 mJ, and the repetition is 10 pps. The NH fluorescence is detected with a spectrometer and an ICCD camera fitted with a bandpass filter of 337 ±5 nm. A delay generator adjusts the timing of the discharge current, the laser irradiation, and the gate of the spectrometer/ICCD camera.

2.3 Plasma-jet nitriding

Nitriding treatment is performed by irradiating the jet plume on the cold-roll steel JIS SPCC ($25 \times 25 \times 1.2$ mm^3). The irradiation distance from the nozzle tip to the sample surface is 7 mm, providing the diffusion temperature of ca. 1000 K. The nitriding duration is 15 min and the sample is eventually quenched by water blasting. The treatment is
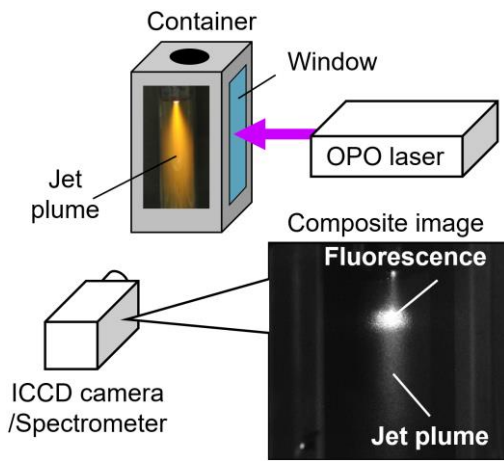
Figure 2 Schematic of laser-induced fluorescence measurement for evaluating NH density in plasma jet.

Figure 3 Comparison of normalized NH density n_{NH} and doped nitrogen concentration c_N for several f.

operated in a quartz cover to replace the air of the ambient atmosphere with the operating gas by gas purging. The nitrogen concentration is evaluated from the shift of X-ray spectrum of retained Austenitic phase.

3. Results and Discussions

Two spectral peaks of ca. 336 and 337 nm is observed from the jet plume only when the laser of 305.05 nm is irradiated, indicating that these signals are the fluorescence from the ground-state NH. The NH fluorescent intensity is obtained from ICCD images shown in Figure 2. No fluorescence is detected for $f = 0\%$, being consistent with the fact that hydrogen, which is an essential constituent of NH, is not introduced in the plasma. The fluorescent intensity monotonically increases with f up to $f = 0.5$-1%. On the other hand, further increase in f, in turn, provides a rapid, exponential-like decrease in the fluorescent intensity.

To discuss the reason for the f dependence of the NH density, we briefly describe here results of a zero-dimensional calculation of chemical reactions with COMSOL Multiphysics where the reaction set of an N_2/H_2 plasma system in Reference 7) is used. NH is produced in the arc through thermal equilibrium. The produced NH then suffers recombinations with other species in the plume to decrease its density. The major partners of recombination are H_2, H, and NH itself. Moreover, the calculated NH density exhibits an exponential decay with respect to increasing f similarly to the LIF observation for f over 1%. We consider from the results that the recombinations with hydrogen cause the decreasing tendency of NH density with increasing f. The detail of the calculation study will be reported somewhere else.

The quantitative measurement of nitrogen concentration doped on the steel surface by the plasma-jet nitriding shows that the concentration rapidly decreases with increasing f from 1 to 4%. A decreasing tendency of the nitriding capability with f has been observed qualitatively before [3], but the quantitative dependence is first obtained. Here, the nitrogen concentration also exhibits exponential-like dependence on f.

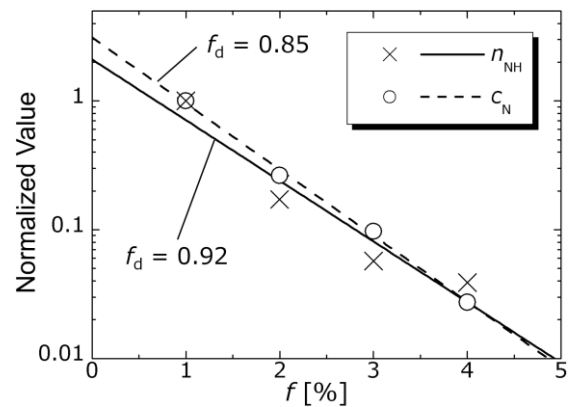Figure 3 compares the f dependence of the normalized NH density n_{NH} and nitrogen concentration c_N within the range of f from 1 to 4%. Both the NH density and the nitrogen concentration exhibit an analogous exponential-like decay with respect to f as mentioned above. Note that the values of the decay constant f_d of n_{NH} and c_N are 0.92% and 0.85%, respectively, where the plots are fitted with $\exp(-f/f_d)$. The two values are extremely close although they may take a value from the infinite range as a candidate.

4. Summary

In the plasma nitriding system with the pulsed-arc plasma jet, both the NH density in the plasma and the nitrogen concentration doped by plasma nitriding exhibit an exponential decay when f increases from 1 to 4%. Importantly, the NH density and the nitrogen concentration shows extremely close f_d. We believe that this similarity indicates a strong relationship between the NH density and the nitriding capability of plasma nitriding.

Acknowledgments

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