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大気圧プラズマを用いた窒化プロセス
Application – Nonequilibrium Plasmas: Nitriding Process by Atmospheric-Pressure Plasmas

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1. Introduction

Plasma nitriding is one of the widespread case hardening technologies, in which N atoms produced through plasma chemical reactions are thermally doped into the surface of steels or other metals to upgrade the tribological or functional properties, widely utilized in the automobile industry and the die/mold manufacturing. We have developed unique nitriding techniques with atmospheric-pressure plasmas while low-pressure glow plasmas are adopted in industry. Two sorts of nitriding are addressed with the pulsed-arc jet and the dielectric barrier discharge (DBD), where all the process is performed in atmospheric-pressure N_2 gas with a small amount of H_2 admixture [1]. Here, we discuss the two atmospheric-pressure plasma nitriding processes both from technological and academic viewpoints.

2. Technological Viewpoint

2.1 Plasma-jet nitriding: for low-volume production

In the plasma-jet nitriding, the plume formed from the pulsed-arc plasma is sprayed onto steel surface to dope N for ca. 1 h, resulting in the formation of surface hard layer of several 10 μm in thickness. As shown in Fig. 1, the treatment atmosphere can be maintained only with a simple cover to purge residual air and no air-tight container is necessary [2]. The N dose amount can be controlled by changing the fraction of H_2 gas added to the operating N_2 gas [3]. Fig. 2 shows typical nitrogen mapping of the sample cross-section for several f_h, the fraction of H_2 in the operating gas. We see that the N dose amount tends to decrease with increasing f_h.

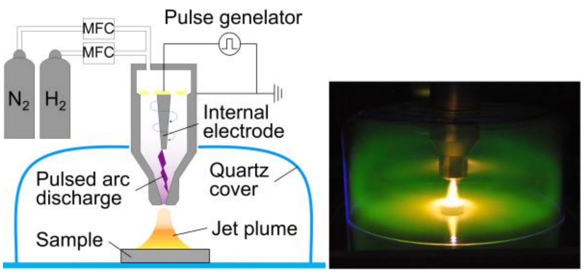

Fig. 1 Plasma-jet nitriding system.

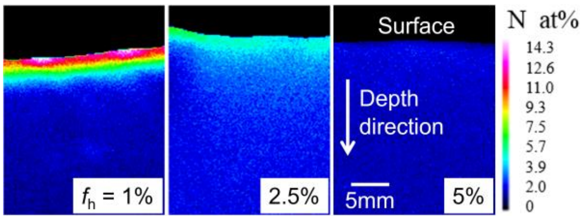

Fig. 2 EPMA nitrogen mapping of the sample cross-section for several hydrogen fractions.

The non-use of any vacuum equipment allows us very low-cost, timesaving nitriding processes compared to the conventional low-pressure processes. For this reason, the plasma-jet nitriding has a potential to offer a practical high-mix low-volume case hardening, which meets the requirement of Society 5.0.

2.2 DBD nitriding: for controlling treated area

Here we would like to employ a peculiar electrode system of the planar DBD shown in Fig. 3 where the upper electrode is a point electrode while the lower plane electrode is a steel sample to be nitrided. The adoption of the point electrode is to highlight “the DBD extension phenomenon under high temperature,” where the ignition area of DBD extends with increasing the ambient temperature beyond the sectional area of the point electrode as

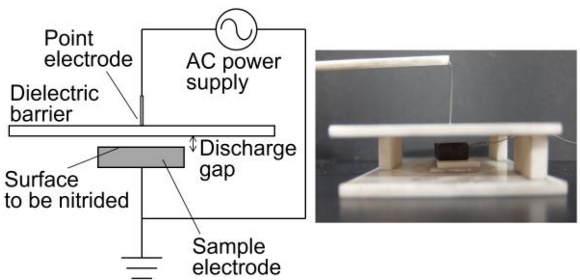

Fig. 3 DBD electrode system to exhibit the extension phenomenon under high temperature.

shown in Fig. 4 [4]. We found that the DBD extension can be changed by the applied voltage and the subsequent nitrided area also can be controlled. Fig. 5 shows the 2D hardness profile of the sample cross-section for high and low applied voltages. We see that the nitrided area becomes larger (smaller) for the high (low) voltage following to the ignition area of DBD. This fact indicates the future technology for a new mass production method without vacuum equipment and precise local treatment without masking.

3. Academic Viewpoint

The two sorts of atmospheric-pressure plasmas utilized here, the pulsed-arc jet and the DBD, possess drastically distinct characteristics from each other. The plasma jet is basically the afterglow of the thermal-equilibrium arc plasma, while the DBD is one of the most popular nonequilibrium plasmas. Such discrepancy will hopefully provide us different elementary processes for nitriding. We are planning to elucidate the nitriding capability of each nitrogen-related species by comparing the produced species and the nitriding efficiency of the two plasmas. As the first stage of the research, here we report optical properties of the two plasmas to discuss the possibility of the difference in their elementary processes.

3.1 Plasma-jet nitriding: NH radicals

We have been suggesting the possibility that NH radical is the key radical for the plasma-jet nitriding because the optical emission of NH radicals is always observed predominantly in the jet plume as shown in Fig. 6 [5]. Here the first result of the laser induced fluorescence (LIF) observation is presented. Fig. 7 shows the NH fluorescent signal from the jet plume taken by an iCCD camera for

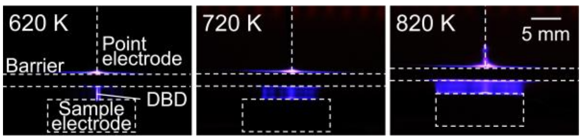

Fig. 4 Ignition area of DBD produced with a point electrode for several ambient temperatures.

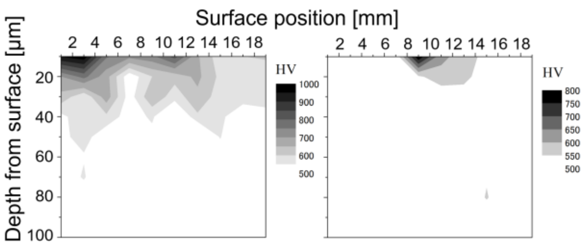

Fig. 5 Hardness profile of sample cross-section. Left: large-area ignition. Right: local ignition.

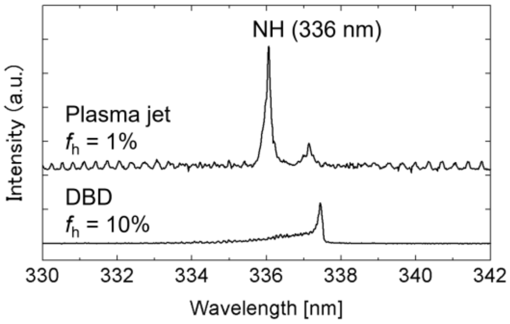

Fig. 6 Optical emission spectrum of each plasma.

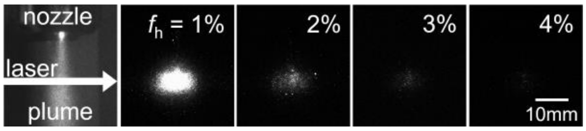

Fig. 7 NH fluorescent signal of the jet plume for several hydrogen fractions.

several f_h, where the laser wavelength irradiated into the plume is tuned to 305.05 nm and the fluorescent wavelength is ca. 336 nm. The fluorescent intensity decreases with f_h, indicating that the density of NH radicals in the ground state present in the jet plume decreases with f_h over 1%. Note that this tendency is qualitatively consistent with the N dose amount shown in Fig. 2. We consider that the result supports our suggestion on NH importance although other species have to be investigated.

3.2 DBD nitriding: other than NH radicals?

As shown in Fig. 6, we cannot detect NH emission from DBD even when H_2 gas is added. This fact supports the possibility that NH radical is not important for the DBD nitriding in contrast to to the plasma-jet nitriding. The LIF observation for DBD is currently projected.

4. Summary

Many of the nitriding researchers manage only one sort of plasma so that our situation is rare. We hope that our work leads us to thorough understanding of the plasma nitriding reaction.

Acknowledgements

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