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Ion nitriding of pure iron using high-density plasma beam generated by a tubular plasma source

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ABSTRACT

A tubular plasma source was developed to generate high-density plasma beam for nitriding using $N_2 + H_2$ mixture as working gas. The plasma source was demonstrated to be capable of generating a plasma plume with density of N_2^+ as high as ~$7.2 \pm 0.6 \times 10^{11}$ cm^{-3} in $N_2 + H_2$ mixed gases with N_2 content changed from 92.5% to 32.5%. After nitriding at 450 °C for 120 min, ~5-μm thick compound layers formed on the sample surface of pure iron with diffusion zone as deep as 0.4 mm, leading to 7.5– 8.5 GPa hardness. In addition, nitriding of pure iron could be realized at a low temperature as low as 250 °C, producing a compound layer with a thickness of ~2.5 μm. After nitriding for 120 min at temperatures of 330– 500 °C, the high-density plasma flow could produce a compound layer of 4– 5 μm with hardness of 10 GPa. N_2^+ and N^+ are suggested to be responsible for the nitriding of pure iron by the high-density plasma beam. The tubular plasma source allows us using $N_2 + H_2$ mixed gas with low hydrogen content for high-efficient nitriding. The gas temperature in plasma plume is ~300 °C, and thus is acceptable for low-temperature nitriding.

1. Introduction

Plasma nitriding is one of cost-effective methods for modification of steels and other metallic materials in wear and fatigue resistance. In industry, plasma nitriding has been commonly used, while exploration and improvement were successively reported in the past decades, with development of various novel plasma technologies, such as pulsed plasma nitriding [1], plasma immersion ion implantation (PIII or PI^3) or plasma source ion nitriding [2], ion beam nitriding [1,2], laser nitriding [2], and rapid nitriding by plasma jets [3,4]. Recently, discharges with highly constricted configuration received much attention due to their potential applications. For instance, microdischarges spatially confining the plasma to dimensions of 1 mm or less are able to generate stable glow discharges with an electron density as high as 10^{15} cm^{-3} at atmospheric pressure, thus are considered utility of plasma cathodes [5]. In addition, atmospheric pressure plasma jets (APPJs) are considered promising in low-temperature processing of materials [6–18] because APPJs are capable of easily producing plasma beams. APPJs were studied in applications of medical sterilization, surface modification, and synthesis of nano-materials. However, similar methods for plasma nitriding were not reported up to now.

As a matter of fact, microdischarges at atmospheric pressure and APPJs are both capable of inducing plasma beams into the inside of a metallic tube, and thus applicable to plasma nitriding for modification of tube internal walls. However, atmospheric discharges are of typical dielectric barrier discharge (DBD); and thus nitrogen plasmas are hardly created. On the other hand, oxygen is not easily avoided in the plasmas at atmospheric pressure. Therefore, we reduced the discharge pressure to 1– 200 Pa, at which a new type of tubular discharge is developed to generate high-density nitrogen plasma beams with an electron density as high as ~10^{12} cm^{-3} [19–21]. In addition, N_2 dissociation degree was found extremely high, as high as ~15% with gas temperatures lower than 700 K [19–21]. The high-density nitrogen plasma allowed us to fabricate amorphous silicon nitrides (a-SiN_x) at room temperature with a deposition rate relatively high [21,22]. In this work, the tubular plasma source was used for plasma nitriding of pure iron as a new technique meeting some special requirement. By changing the H_2 content in $N_2 + H_2$ mixed gases and temperature, the nitriding of pure iron was demonstrated using the plasma beam generated by the tubular plasma source. In addition, the species and gas temperature in the plasmas were studied using optical emission spectrum (OES).

2. Experimental methods

The plasma discharging was conducted in a 315-mm long quartz tube with inner diameter of 4.0 mm. A stainless-steel rod in 2-mm diameter was sealed in the bottom as one electrode. The chamber, which provided the vacuum environment for discharge of the tubular plasma, was used as the other electrode grounded. The experimental setup is schematically shown in Fig. 1(a) and (b) shows the typical photographs of nitrogen plasma. The plasmas were created using a low-

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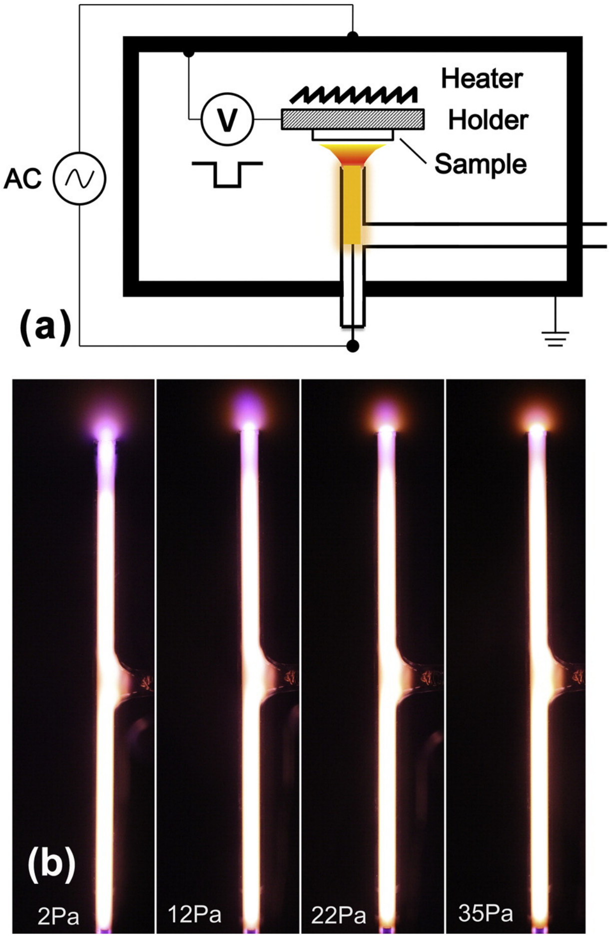

Fig. 1. (a) Schematic experimental setup. (b) Typical photographs of the discharge operating at the given pressures.

frequency (20–80 kHz) AC generator operating at 55– 60 W and 25 kHz. A 0.5-mm thick sheet of pure iron with a purity of 99.99% was used as the samples for nitriding. The samples were cut into a size of 10 × 10 mm and placed right over the plasma plume at a 20 mm distance to the tube nozzle. A — 200 V pulsed-negative voltage was applied to the sample holder with a frequency of 35 kHz and a duty ratio of 1%. The sample holder was heated by a heater at the rear and the nitriding temperature on the sample surface was aligned using a thermal couple. Nitriding time was controlled at 120 min. Before discharging, the chamber was pumped to be better than ~1.0 × 10^{-3} Pa, and then 50 SCCM $N_2 + H_2$ mixed gas was injected in the quartz tube through a sidewall inlet, maintaining the pressure at ~20 Pa during discharging.

X-ray diffraction (Bruker D8) was used for study of the phases in the nitriding samples. Cross-sectional samples were prepared for measurement of nitriding layers by optical microscopy and electron probe mass analysis (EPMA-1600). Hardness evaluation was carried out on a microhardness tester (DMH-2LS) with Knoop's indenter (HK) under the loads of 10, 25, and 50 g. On the other hand, Nano-indenter XP was used to study hardness profile of diffusion zone using the cross-sectional samples. The plasmas were studied using plasma OES collected in spectral range of 200–1100 nm using a spectrometer (Acton, Pro-2500i) with a 1200 mm^{-1} grating. The slit entrance was set to be ~10 μm, providing a spectral resolution of ~0.05 nm. An OES fitting program [20] was used for determining the vibrational and rotational temperatures (T_{vib} and T_{rot}) of plasmas. The electrical characteristics of discharge were measured with a 1:1000 high-voltage probe (Tektronix P6015A) and a current probe (Pearson 6600) via a digital storage oscilloscope (Tektronix TDS 2012B). In addition, the density and temperature of electrons were measured using a Langmuir double probe placed at the plume center ~5 mm away from the tube nozzle.

3. Results and discussion

3.1. Iron nitriding

Before nitriding, the tubular plasmas were studied using discharge waveform. Similar to nitrogen discharging [19,21], the tubular source in $N_2 + H_2$ mixed gases also exhibited mixed discharge consisting of AC discharge and pulsed discharge, as shown in Fig. 2. The sine waveform is similar to that loaded by the AC generator, and the pulsed discharge has similarity to spark discharge, which was created probably by an additional gas breakdown outside the tube [19,21]. The pulsed discharge appeared periodically in per positive circle with an as high as ~1 A intensive pulsed current that is varied circle to circle and depends on the H_2 content ambient. As the quartz tube is very thin, the pulsed discharges produced an instantaneous power density extremely high (~250 W/cm^3); thus high activity of plasma is expected. Addition of H_2 produced a decrease in the average power of discharge, but the pulsed discharges were enhanced considerably, as shown in Fig. 3. It is of interest that the average power (P_{ave}) maintained at a constant of ~55 W for the H_2 content varied from 7.5% to 67.5%, but the pulsed power (P_{peak}) increases with the increase in H_2 content, indicating that H_2 is helpful for enhancement of the pulsed discharge. In our previous study [19–22], the pulsed discharge was found helpful for ionization and dissociation of N_2, and thus, was of benefit to nitriding either. The characterization demonstrates that the tubular source of discharge is special in generation of plasma different from conventional glow discharge, which has been widely used in nitriding facilities. More details for the tubular plasma discharge can be found in our previous study [19–22].

Using the tubular plasma source specially designed, ion nitriding of pure iron was demonstrated using the plasma beam. Because H_2 was

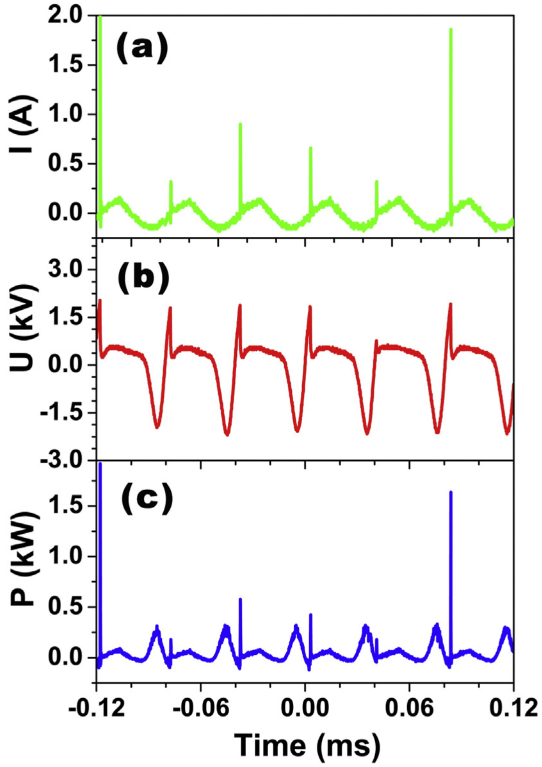

Fig. 2. Typical discharge waveforms, (a) current waveform, (b) voltage waveform, (c) instantaneous power. The discharge was operated in a 315-mm long quartz tube driven at 20 Pa, 25 kHz, and 60 W.