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Trial Application of Pulse-Modulated Induction Thermal Plasmas to High-Speed Nitridation with N_2/H_2 Injection

トーチ下流部から N_2/H_2 を混入したパルス変調誘導熱プラズマによる Ti 試料高速表面改質

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This report describes a trial application of pulse-modulated induction thermal plasma (PMITP) at 15 kW to high-speed surface nitridation of Ti. Influence of the pulse modulation (PM) of the coil current was investigated on the surface temperature and surface composition of the specimen. Gas composition was also measured by quadrupole mass spectroscopy (QMS). It was found that the PM could provide the high-speed nitridation of the specimen with low thermal damage.

1. Introduction

The inductively coupled thermal plasma (ICTP) is widely used for many materials processings [1, 2] because of its high enthalpy and high reaction activity. To obtain a further effective radical source for high-speed surface modification process, we have developed a pulse-modulated induction thermal plasma (PMITP) system [1, 3]. This PMITP system can modulate the coil current amplitude of the order of several hundreds amperes almost into a rectangular waveform. Until now, we found from the optical emission spectroscopy (OES) that Ar-N_2-H_2 PMITP can produce more excited nitrogen atoms into the reaction chamber with less heat flux compared to a non-modulated thermal plasma [3].

In the present report, we measured the gas composition around the surface position of the specimen irradiated by Ar-N_2-H_2 PMITP. For this measurement, a quadrupole mass spectrometer (QMS) with a water-cooled probe was used. In addition, the Ar-N_2-H_2 PMITP was actually irradiated to the Ti specimen with measuring surface temperature of the specimen. The surface composition of irradiated specimen was also analyzed by X-ray diffractometer (XRD).

2. Experimental setup and conditions

Fig. 1 illustrates a configuration of the plasma torch for PMITP. The plasma torch is composed of two coaxial quartz tubes with a 330 mm length. Argon gas was supplied as a sheath gas along the inside quartz tube. Nitrogen and hydrogen gas mixture was radially injected from eight holes in the frange. The distance between the holes and coil-end is 110 mm. Total gas flow rate including N_2/H_2 mixture was fixed at 100 slpm. Nitrogen gas flow rate Q_{N_2} was set to 2 and 4 slpm. Hydrogen gas flow rate was fixed at 1 slpm. Pressure in the chamber was fixed at 230 torr. The quantity "On-time", which is the time duration with higher current level (HCL), was set to 10 ms, and

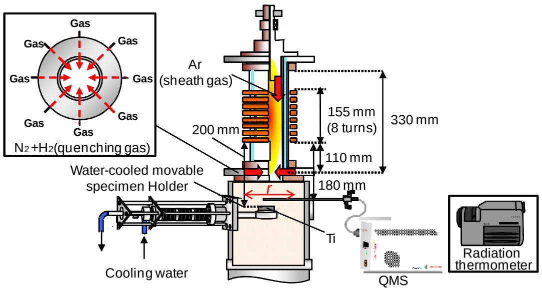

Fig. 1: Schematic of plasma torch and chamber.

"Off-time", the time duration with lower current level (LCL), was set to 5 ms for PMITP. We also defined the shimmer current level "SCL", as a ratio of LCL/HCL. A time-averaged input power was fixed at 15 kW for any modulation condition. A Ti specimen was located on the water-cooled specimen holder, which was installed downstream of the chamber. This holder was fixed at 200 mm below the coil-end. Surface temperature was measured using a radiation thermometer. Irradiation time of Ar-N_2-H_2 PMITP was set to 180 s.

For gas composition measurement, a capillary inside a water-cooled tube was installed at 180 mm below the coil-end. The water-cooled tube was used to avoid too much heat flux from the thermal plasma to the capillary. Another tip of this capillary was connected to the QMS, which measures mass spectra. The tip of capillary with the water-cooled tube can be moved in radial position to measure radial distribution of the gas composition.

3. Results and discussions

3.1. *Gas composition around downstream portion*

Irradiation of nitrogen atom to the specimen may have large effect for nitridation using thermal plasmas because the nitrogen atom has much higher density in a thermal plasma than nitrogen ion. Thus, we here focused on the nitrogen atom, which appears at m/z=14 in mass spectra. Fig. 2 shows the radial distribution of ion current for m/z=14 in mass spectra for Ar-N_2-H_2 PMITP with Q_{N_2}=4 slpm. The ion current of m/z=14 in mass spectra is considered to increase monotonously with nitrogen atomic density. In case of 100%SCL, the ion current becomes lower around the center axis of the reaction chamber (r=0 mm) than at other radial position. This means that the nitrogen atomic density is lower at r=0 mm because of ionization due to high temperature of the thermal plasma. On the other hand, reducing SCL increases the ion current at r=0 mm compared to those at other radial positions. Fig. 3 shows the ion current for m/z=14 in mass spectra at r=0 mm for Q_{N_2}=4 and 2 slpm as a function of SCL. This figure implies that the nitrogen atomic density at r=0 mm increases with reducing SCL, not only the excited nitrogen atom found from the OES measurement. This result indicates that the PMITP has a capability to provide more nitrogen atom onto the specimen.

3.2. *Surface temperature of Ti specimen*

Fig. 4 shows the surface temperature of a specimen after 180 s irradiation by Ar-N_2-H_2 PMITP as a function of SCL for different Q_{N_2}s. The surface temperature at 100%SCL reaches to almost 1300 °C. On the other hand, reducing SCL to 50% can decrease the surface temperature to about 1140 °C. This result indicates that PMITP can decrease the heat flux to the specimen, which can lower thermal damage.

3.3. *XRD analysis of Ti surface*

Irradiated surface of Ti specimen was analyzed by XRD. Fig. 5 shows the XRD results for different SCLs. The spectral peaks of TiN can confirmed to appear, and they were increased by using PMITP. On the other hand, the peak of α-$TiN_{0.3}$ was decreased. Here "TiN ratio" was defined as the ratio of TiN peak (2θ=42.6°) to α-$TiN_{0.3}$ peak (2θ=39.4°) in XRD spectra to evaluate the nitridation degree. Fig. 6 shows the result of "TiN ratio" versus diffraction angle for different Q_{N_2}s. We can see that reducing SCL from 100% to 63% increases "TiN ratio", and then further reducing SCL from 63% to 43% decreases it for Q_{N_2}=4 slpm. In this way, use of PMITP can promote nitridation of Ti surface compared to the conventional non-modulated thermal plasma. The PMITP can be a promising tool for effective nitridation process.

4. Conclusion

The experimental results showed that the PMITP provides more nitrogen atom density and less heat flux onto the specimen surface compared to conventional non-modulated thermal plasma. The XRD analysis indicated that nitridation of Ti was promoted around 63%SCL, i.e. the modulation condition. The above results imply that the PMITP can be a promising tool for effective nitridation process.

References

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[2] W. R. Chen, et al, Surface Coating Technol., 197, 109(2005).

[3] Y. Tanaka, et al, Appl. Phys. Lett., 89, 031501(2006).

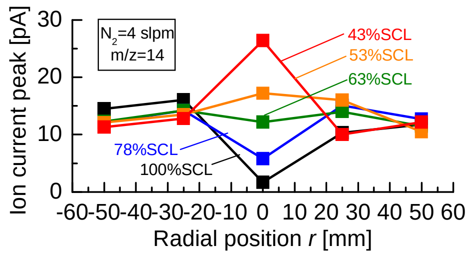


Fig. 2: Radial distribution of ion current for m/z=14 in mass spectra.

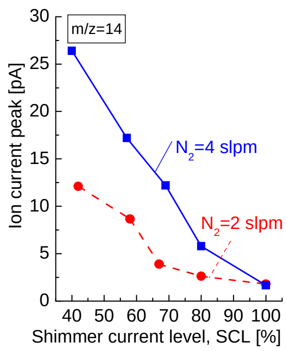


Fig. 3: Ion current for m/z=14 in mass spectra at radial position of 0 mm.

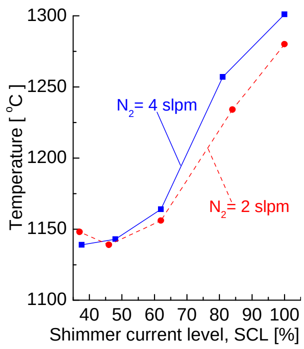
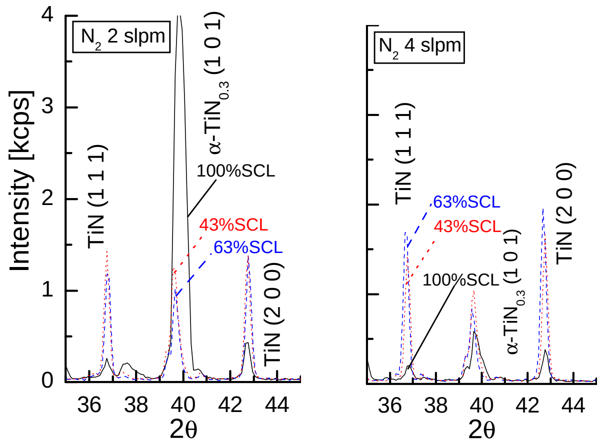


Fig. 4: Dependence of infrared radiation temperature of Ti specimen surface on SCL.



(a) N_2=2 slpm (b) N_2=4 slpm

Fig. 5: XRD diffraction diagram of Ti specimen.

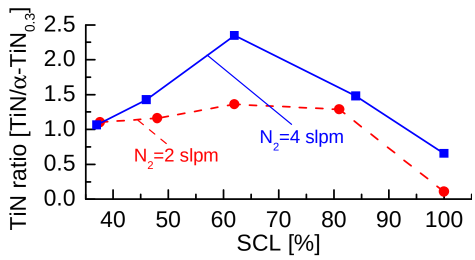


Fig. 6: The ratio of TiN peak (2θ=42.6°) to α-$TiN_{0.3}$ peak (2θ=39.4°) defined as "TiN ratio".