Spatial Characteristics and Application of Atmospheric Pressure Microwave Nitrogen Plasma Torch

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Abstract. Microwave (MW) torches are typically used to produce equilibrium plasmas for various environmental or industrial applications. We use Litmas Red MW torch (2.45 GHz, 3 kW), which is able to generate plasma in a state close to Local Thermodynamic Equilibrium (LTE) in temperature range of 1000-5000 K at atmospheric pressure. We present spatial characteristics of the generated MW plasma and an example of its application. We employ optical emission spectroscopy (OES) as a main diagnostic tool. Thanks to the movement ability of the optical bench we are able to get spectra from various distances from the plasma axis and to analyze horizontal profiles of plasma after Abel inversion. We mostly observed NO, N_2^+ and CN spectra. From the measured and the Abel-inverted horizontal profiles we found out that the emissivity decreases with increasing distance from the plasma axis. Emissivity also decreases with increasing height, but the shape of the profiles is kept. As an example of atmospheric pressure microwave nitrogen plasma application we present the first tests of carbon benefication. The diagnostics of carbon samples was performed by SEM equipped with WDX element analyzer and FTIR spectroscopy. The plasma heat treatment causes a mass loss, a composition change and a structure change of the carbon waste.

Introduction

Atmospheric pressure microwave (MW) plasmas present considerable interest for a wide range of applications, such as air pollution control, surface treatment, or carbon nanotube growth [1].

MW torch generates plasma close to LTE conditions. In our previous works [2] we investigated the basic characteristics of atmospheric pressure MW nitrogen plasma torch. Here we present spatial characteristics of generated MW plasma and its application. After adapting the optical bench for vertical and horizontal movement, we record spectra from various positions from the plasma axis and we analyze Abel-inverted horizontal profiles to get the information about the spatial plasma distribution. We also present the first tests of the MW torch application for thermal treatment of carbon waste. The treated carbon is a product of pyrolysis of used tyres. Its benefication is needed to get rid of the volatile components causing its bad smell, and to make it reusable for other processes.

Abel inversion

Microwave plasma torch is a cylindrically symmetric light source of certain thickness. This is why, when recording the emission spectra, we get the spectrum integrated along the whole plasma diameter (line-integrated spectrum) and not a spectrum from one specific point. This leads to incorrect measurements of the light intensity, which seems to be stronger than it really is.

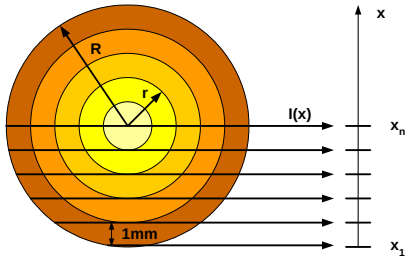

Figure 1. Abel inversion.

Abel inversion (Fig. 1) allows us to transform the measured line-integrated light intensity I(x) into the radial emissivity e(r).

$$I(x) = 2\int_r^R \frac{re(r)}{\sqrt{r^2 - x^2}}dr \qquad e(r) = \frac{1}{\pi}\int_r^R \frac{dI/dx}{\sqrt{x^2 - r^2}}dx .$$

Experimental setup

Litmas Red MW plasma torch powered by a 5 kW magnetron (supplied from special power generator) was used to generate atmospheric pressure nitrogen plasma with properties close to LTE. The magnetron has a maximum power output of 3 kW. The torch is able to generate plasmas in the temperature range of 1000-5000 K.

Microwaves generated by magnetron are focused to the cylindrical plasma chamber made of a hardened teflon or Al_2O_3. The MW discharge is ignited by pneumatic insertion of a metal ignator into the plasma chamber. The brush-shaped ignator (synchronized with microwaves from the magnetron through the electronic unit) causes a local enhancement of the electric field resulting in a discharge ignition. The whole system is externally cooled with water and air. Contrary to the typical MW torch systems [3], in our case the gas is inserted downstream and tangentially through the two holes of the nozzle into the cylindrical plasma chamber. This is causing the swirl flow in the cylinder and generated swirling plasma is consequently blown out upstream through the central orifice of the nozzle. Blown out plasma is then analyzed by optical emission spectroscopy. Emitted light is guided through the optical bench containing an aperture, a fused silica lens and a beam-splitter positioned at 45° to divide the light beam to enter the two optical fibres of the Ocean Optics SD2000 spectrometer – Master which covers the spectral range of 200-500 nm and Slave 500-1100 nm. The optical bench is movable horizontally as well as vertically. Experimental setup and the basic torch characteristics are described in more detail in [2]. During the carbon benefication experiments the original carbon sample of typical weight 0.5g was placed on a stainless steel plate in the plasma about 1cm above the nozzle (Fig. 3). Approximate temperature of the plate, measured by a pyrometer, was 1500 K. The system was closed and exhausted because of possibly dangerous gases being emitted from polluted carbon samples. The carbon samples were heated for 5 or 10 minutes in nitrogen plasma of 13 l/min flow rate and 1.4 kW generator power. After plasma being switched off, the sample was cooled at a low N_2 flow 2 l/min to avoid oxidation.

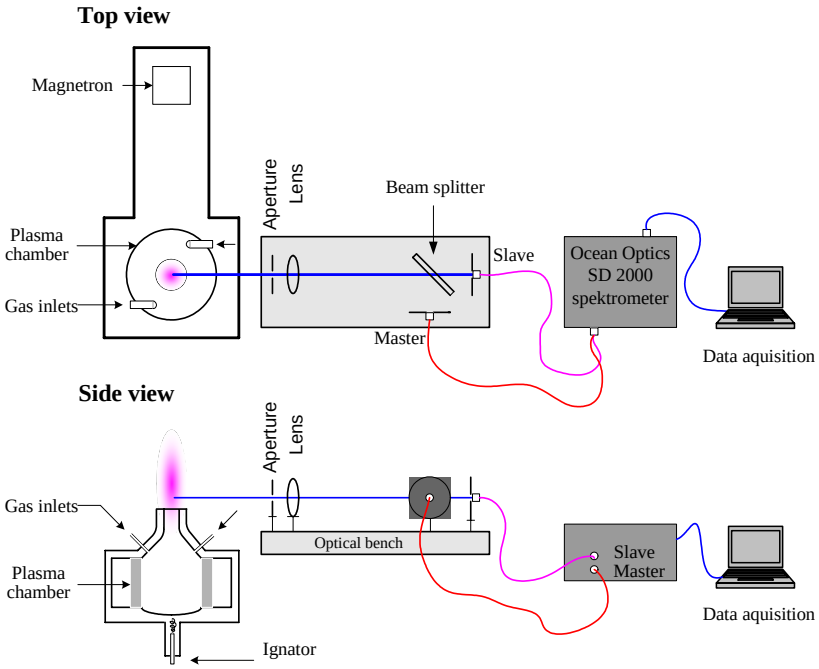

Figure 2. Experimental setup.

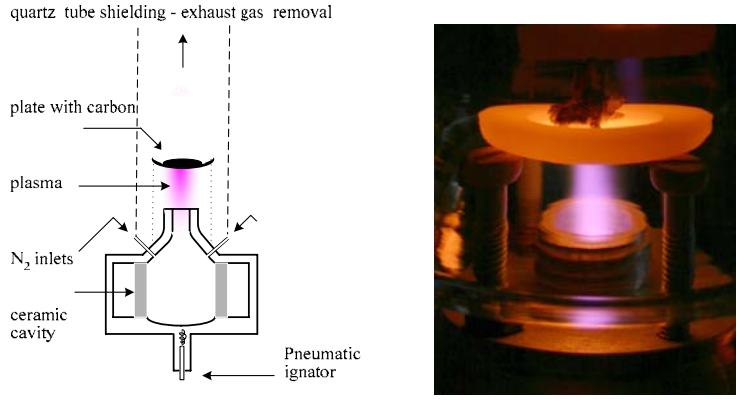

Figure 3. Treatment of carbon samples.

The diagnostics of carbon samples was performed directly by a scanning electron microscope (SEM) Tescan TS5136MM equipped with wavelength dispersive X-ray (WDX) INCA Wave analyzer, and on KBr pellets analyzed by Fourier-transform infrared (FTIR) spectrometer Perkin Elmer Spectrum BX. KBr powder to the sample ratio was 1:100.

Results and discussion

Measured spectra

We identified emission of N_2 molecules, N_2^+ ions and NO and CN radicals in the emission spectra. (Fig. 4)

Strong emissivity of N_2^+ (B-X) relatively to N_2 (C-B) transition was confusing at the first sight, because ionization process of N_2 requires more energy than excitation of N_2 to the C state. That is why we expected N_2 (C) state to be more populated than N_2^+ (B) state, but in this case the N_2 (C-B) emissivity would be stronger than that of N_2^+ (B-X). In addition, the N_2^+ (B) is not supposed to be formed by electron excitation, because generated plasma most probably does not contain electrons with such a high energies as needed for this process (~19 eV). Possible explanation was found in Boudam et al. [4]. This paper considers these reactions as the most probable way of the formation of N_2^+ (B) state:

$$N_2\ (X, \nu>15) + N_2\ (X, \nu>15) \rightarrow N_2(a') + N_2\ (X, \nu)$$

where $N_2(X)$ is ground electronic state of N_2 molecule and ν is its vibrational quantum number, $N_2(a')$ is metastable state of N_2 molecule. Then

$$N_2(a') + N_2(a') \rightarrow e + N_2^+(X) + N_2$$

which is called chemi-ionization process. Finally

$$N_2^+(X) + N_2\ (X, \nu>11) \rightarrow N_2^+\ (B) + N_2\ (X).$$

We assume that in our case this way of generation of N_2^+ (B) can be involved, which would explain the paradoxical ratio of the emissivity of N_2^+ (B-X) and N_2 (C-B) transitions.

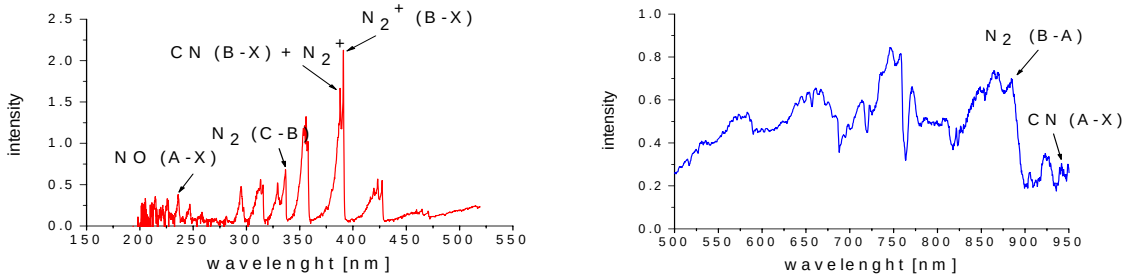

Figure 4. Measured spectra in UV and VIS region.

Spatial characteristics of microwave nitrogen plasma

Horizontal profiles in various heights were needed for the spatial characteristics. The experiments were carried out at 15 l/min flow rate and 1.46 kW magnetron power. The plasma temperature at these parameters, determined by comparing experimental and simulated (LIFBASE) CN spectra, was 4000±500K [2]. We measured the emission intensities in various positions from the plasma axis. The spacing between 2 points was 1 mm. We applied Abel inversion to these horizontal profiles. Abel-inverted horizontal profiles are presented in Fig. 5,6. Units for the measured intensity I(x) and Abel-inverted emissivity e(r) are: $\mu W.mm^{-2}.nm^{-1}.sr^{-1}$ and $\mu W.mm^{-3}.nm^{-1}.sr^{-1}$, respectively. We express the intensity in absolute units because the optical system was calibrated with optical standards: W and D lamps. Thanks to the cylindrically symmetric shape of the plasma (which is a condition for Abel inversion) we consider just one half of the profiles (Fig. 5). In the case of NOγ emission, the profile was not symmetric (Fig. 6) so both halves are shown. We expected the strongest emission of NO to be at the edge of the plasma, where heated nitrogen gets to the contact with surrounding air and reacts with O_2, which leads to the formation of NO. It was shown that the maximal emissivity is in the certain distance from the plasma axis and not at the plasma edge. The explanation is that the plasma was not ideally symmetric, but it could be spiral-twisted. This would also explain why the maximum of emissivity was not at the same distance from the plasma axis in various heights (h).

Carbon benefication

After plasma heating of the carbon samples, we first observed that the sample did not smell anymore and its mass decreased (by 27% for 5 min and 48% for 10 min heating). We assume that some volatile substances, most likely aliphatic and aromatic hydrocarbons and their –OH and ether derivates were released from the carbon, which was confirmed by FTIR spectra (Fig. 7). An apparent

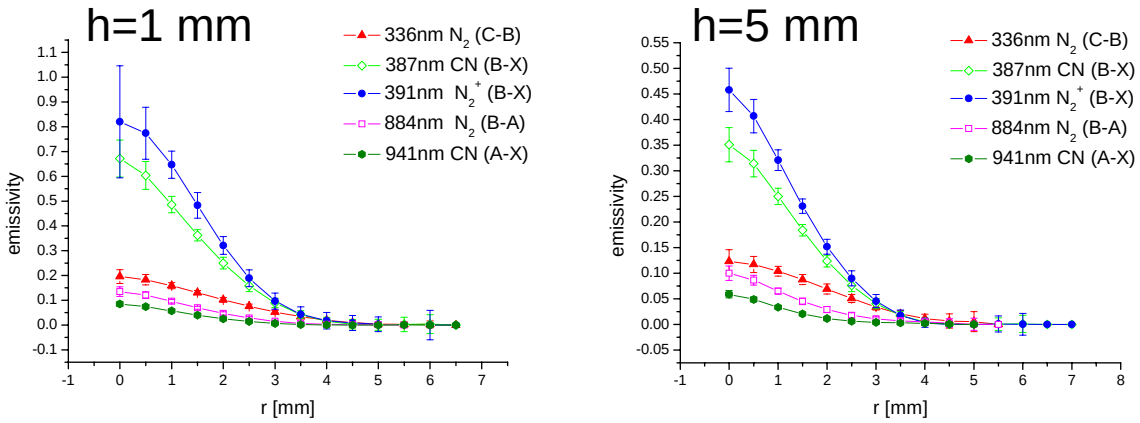

Figure 5. Abel-inverted horizontal profiles in h=1 mm and h=5 mm.

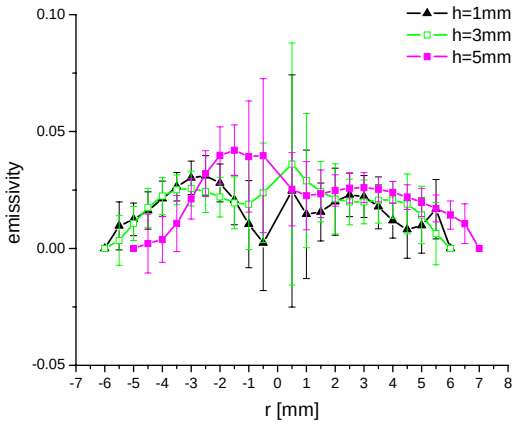

Figure 6. Abel-inverted horizontal profiles of NOγ.

reduction of CH_2, C-O-C, -OH, and aromatic C-H functional groups was observed. On the other hand, new compounds were created. We assume them to be metal oxides of trace elements found by WDX analysis. Detailed interpretation of the measured FTIR spectra requires further investigation.

Despite the conductivity of the carbon samples being weak, it was good enough for SEM analysis at low magnifications. Microscopic pictures showed that the carbon has an amorphous structure with pores (Fig. 8a). Pictures of the treated samples revealed the steps-like shaped cleaving area (Fig. 8c), which compared to the smooth shape in the original sample (Fig. 8b) shows that material became more compact.

WDX analysis of all samples demonstrated C as a dominant element. Trace amounts of S, Ca and Zn were found in the original carbon sample and decreased after the heating, but new elements, such as Fe, Al, Si, K, Mg were found. We assume that some of these metals were released from the stainless steel plate during the heating.

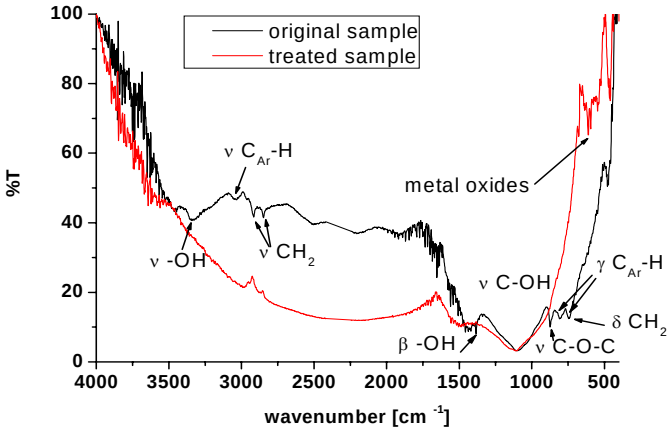

Figure 7. FTIR spectra of carbon samples.

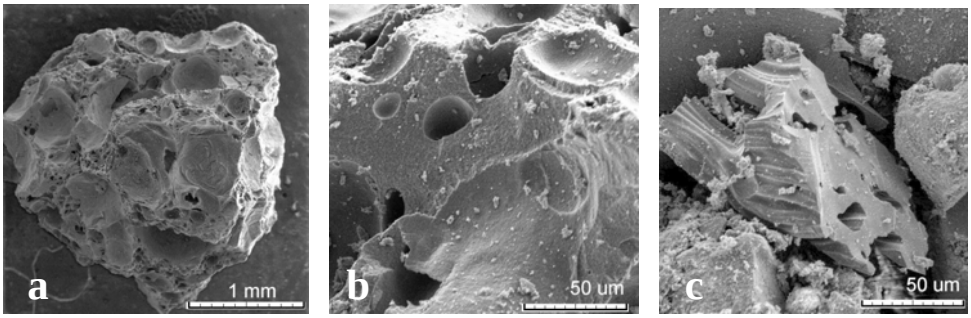

Figure 8. SEM pictures of carbon samples.

Summary and perspectives

We investigated spatial characteristics of microwave N_2 plasma at atmospheric pressure. OES was used as a main diagnostic method. We recorded the spectra in various distances from the plasma axis and in various heights and analyzed Abel-inverted horizontal profiles.

Emission of N_2, N_2^+ NO, and CN radicals was identified. Confusing strong emissivity of N_2^+ (B-X) relatively to N_2 (C-B) transition was explained by other way of formation of N_2^+ (B) state than electron excitation. Measured and Abel-inverted horizontal profiles showed that emissivity decreases with increasing distance from the plasma axis (except for the NOγ transition). In this case the maximum emissivity at certain distance from the plasma axis (not at its edge) was explained by the asymmetric plasma shape. Emissivity also decreases with an increasing height.

Atmospheric pressure nitrogen microwave plasma was also used as a heat source for used tyre carbon benefication. The plasma heat treatment causes a mass loss, a composition change and a structure change of the carbon. We are currently adapting the microwave torch system so that the

carbon powder could be inserted directly into the plasma chamber, which will provide a higher temperature compared to when the sample is heated on the supporting metal plate. The new setup will turn the plasma chamber upside down to enable the collection of the treated carbon powder. Because of the presence of pores we also plan further investigations of the treated carbon, such as measuring its adsorption capacity. This could be interesting for its potential use as an active carbon.

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