An Atmospheric Pressure Microwave Plasma Torch

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Abstract: Microwave plasma sources at atmospheric pressure have a variety of different applications and therefore are object of intense research. This paper covers the spectroscopic investigation of an atmospheric pressure microwave plasma torch and experiments concerning the abatement of the perfluorinated compounds CF_4 and SF_6. By means of optical emission spectroscopy the gas temperature of a humid air plasma was determined to 3600 K by using the $A^2\Sigma^+$-$X^2\Pi$-transition of the OH radical. The electron temperature was determined to 5800 K by a Boltzmann-plot of atomic oxygen lines. The experiments concerning the decomposition of CF_4 and SF_6 showed that destruction and removal efficiencies (DRE) of over 99 % can be achieved and therefore the abatement of waste gases is a promising application of the presented microwave plasma torch.

Keywords: atmospheric pressure, microwave plasma, optical emission spectroscopy, decomposition of waste gases

1. Introduction

Atmospheric pressure microwave plasma sources have many applications in different industry sectors. On the one hand they can be used for treating surfaces like for example to clean, etch, or activate them to achieve better adhesion of paint, lacquer, or glue. On the other hand there are many applications in the field of chemical syntheses. Here the pyrolysis of methane to hydrogen and carbon and the decomposition of critical and harmful waste gases can be named [1-5]. Especially the decomposition of green house gases such as CF_4 and SF_6, which are widely used for etching processes in the growing semiconductor industry and which have very high green house potentials and therefore contribute in a great extent to the world climate change, has become an important task of mankind nowadays.

This paper presents spectroscopic investigations of an atmospheric pressure microwave air plasma. The gas rotational temperature T_{rot} is determined by using the $A^2\Sigma^+$-$X^2\Pi$-transition of the free OH radical while the electron temperature T_e is estimated by means of a Boltzmann-plot of atomic oxygen lines. A rough estimate of the electron density n_e is performed by using Saha's equation. Furthermore, experimental results concerning the decomposition of fluorocarbon and sulphur hexafluoride are presented, which show that the plasma source is suitable for this application. The raw and clean gases are analysed by quadrupole mass and Fourier transform infrared spectroscopy. The characterisation of the plasma again is conducted by means of optical emission spectroscopy providing information about species generated in the plasma. From these results possible reaction channels are deduced.

2. Experimental Setup

The microwave plasma torch, which is presented in this paper, is based on two axially symmetric resonators. Microwaves of 2.45 GHz are fed into a cylindrical resonator with a low quality via a rectangular waveguide. The other coaxial resonator is formed by a metallic nozzle below the cylindrical resonator. It is used for gas injection and has a low quality. The plasma is confined in a quartz tube and the gases can be fed in via tangential gas inlets or the metallic nozzle. Due to the combination of these two resonators this plasma source provides ignition of the plasma without any additional igniters and allows continuous, stable, and efficient plasma operation [6,7].

The plasma is characterized by means of optical emission spectroscopy. Therefore, the cylindrical

resonator is furnished with a slit at its front to have access to the plasma inside the resonator. The resonator has a height of 48 mm and is terminated with a water cooled metal plate, which is why optical diagnostics in axial direction z are only possible between z = 1 mm and 48 mm and again from z > 70 mm. The quartz tube has an inner diameter of 26 mm and therefore the plasma is limited to this extent in the radial direction r.

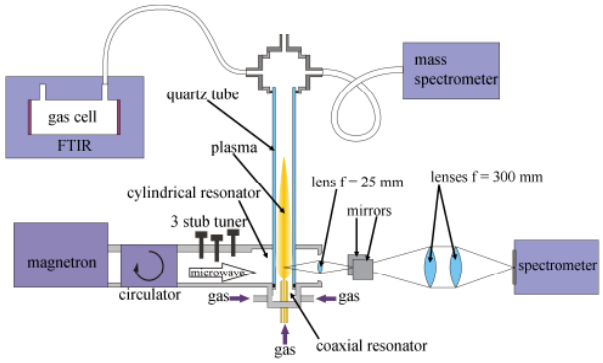

Figure 1. Scheme of the atmospheric pressure microwave plasma torch and of the experimental setup for the spectroscopic characterization of the plasma and for the experiments concerning the decomposition of CF_4 and SF_6.

To get a spatial resolution of the plasma, it was projected by an optical imaging consisting of lenses and mirrors on the entrance slit of a spectrometer. Two different spectrometers were used: A Mechelle 7500 spectrometer, which is sensitive in the visible and IR range, and an Acton SpectraPro-750i spectrometer. This spectrometer is sensitive in the visible range and is equipped with three different gratings (150 grooves/mm, 600 grooves/mm, and 1800 grooves/mm) and an ICCD camera having thereby already a one dimensional spatial resolution. Since the Mechelle spectrometer is sensitive in the IR range, it was used to determine the electron temperature using the atomic oxygen lines, which are located there. The Acton spectrometer was used to record high resolution spectra of the OH-radical between 306 nm and 310 nm. These spectra were used to determine the gas temperature.

For the characterization of the raw and clean gases a quadrupole mass and a Fourier transform infrared spectrometer were used. Furthermore, for these experiments a wet vent washer was installed behind the plasma torch. A schematic scheme of the atmospheric microwave plasma torch and the experimental setup is given in Figure 1.

3. Experimental Results and Discussion

The gas temperature as well as the electron temperature of an air plasma with a gas flow of 30 sl/min and a supplied microwave power of 3 kW were determined spatially resolved by means of optical emission spectroscopy.

The gas temperature is determined from high resolution spectra of the $A^2\Sigma^+$-$X^2\Pi$-transition of the OH radical. These spectra are compared to simulated ones from a databank, which have different temperatures, and the temperature of the one with the least square mean error to the measured one is chosen [8]. Figure 2 shows a typically measured spectrum and the simulated one, which fits best. Here the gas temperature was determined to 3140 K. The temperature was varied between 830 K and 9800 K in 30 K steps.

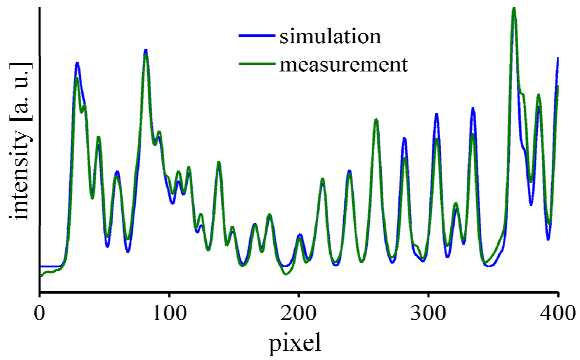

Figure 2. Determination of the gas rotational temperature by simulating the $A^2\Sigma^+$-$X^2\Pi$–transition of the free OH radical: A typically measured spectrum and the simulated spectrum, which fits best, are shown. Here the best fit results in a temperature of 3140 K.

The electron temperature was determined by using a Boltzmann-plot of atomic oxygen lines. In Figure 3 a Boltzmann plot of atomic oxygen lines, which can be observed in an oxygen plasma, is shown. The two lines at 777 nm and 844 nm are observed also in air plasma and therefore are used to determine the electron temperature in air plasmas.

Figure 4a) shows a photo of the plasma at a gas flow of 30 sl/min air and a microwave power of 3 kW confined in a quartz tube. In the lower part the cylindrical resonator with a slit at its front is located.

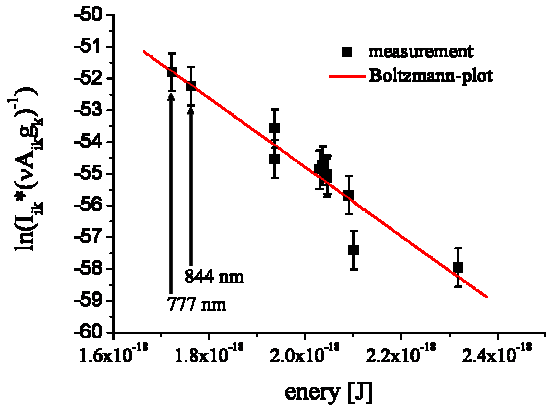

Figure 3. Boltzmann-plot of atomic oxygen lines observed in an oxygen plasma (gas flow 30sl/min, microwave power 3 kW). The two lines at 777 nm and 844 nm are observed also in air plasmas and therefore are used to determine the electron temperature in air plasma.

The plasma flame protrudes out of the 564 mm long quartz tube and has a length of approximately 600 mm. In Figure 4b) the spatial distribution of the gas temperature is shown. It can be seen, that the maximal temperature of about 3600 K is measured in the center of the cylindrical resonator. Even though the first lens was placed just behind the slit, inside the resonator only the radial region between r = -5 mm and r = 5 mm was accessible in the UV range explaining why only in this range the gas temperature could be measured. Above the resonator the gas temperature could be measured entirely in the whole quartz tube. In axial direction the gas temperature could be measured up to z = 370 mm where it has dropped to $T_g \approx 1970$ K.

The distribution of the electron temperature is shown in Figure 4c). It can be seen, that the maximum temperature of about 5800 K is about 2200 K higher compared to the gas temperature but also is measured in the center of the cylindrical resonator. However, the extent where T_e can be measured is much smaller compared to the range where T_g is measured. The electron temperature can be measured only up to z = 110 mm. Here it has dropped already to $T_e \approx 1760$ K. The fact that the gas temperature is about 2200 K smaller than the electron temperature can be explained by the fact that only the light electrons are heated by the microwave and the heavy particles are heated by collisions with the electrons.

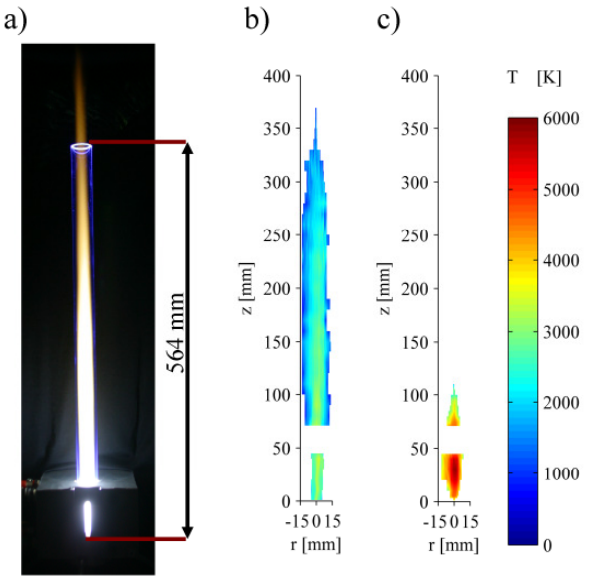

Figure 4. a) Photo of the plasma flame. Distribution of the b) gas and c) electron temperature at a gas flow of 30 sl/min air and a microwave power of 3 kW. The maximum temperatures of $T_g \approx 3600$ K and $T_e \approx 5800$ K are reached in the center of the cylindrical resonator.

A rough estimate of the electron density can be performed by using Saha's equation. With this assumption maximum electron densities of about $n_e \approx 2 \cdot 10^{20}$ m^{-3} are reached in the resonator center. Although the maximum electron density exceeds the cutoff density of $n_c = 7.4 \cdot 10^{16}$ m^{-3}, the microwave can penetrate into the plasma since at atmospheric pressure the plasma is collision dominated.

As a selected application of this plasma torch the decomposition of waste gas was investigated. These investigations were performed in collaboration with the Fraunhofer Institut für Chemische Technologie (ICT) and the Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft (ISAW) of the Universität Stuttgart. An admixture of either SF_6 or CF_4 was added to a nitrogen gas flow and treated by the plasma. Optical emission spectra of these CF_4 containing nitrogen plasmas exhibited N_2,- N_2^+-, and CN-bands. When the gas mixture was moistened to offer reaction partners to the CF_4, additional NH- and NO-bands were observed. The raw as well as the clean gas was analyzed and the content of these agents was determined by quadrupole mass and

Fourier transform infrared spectroscopy. Thereof the destruction and removal efficiency (DRE) was calculated. In Figure 5 the DRE in dependence a) of the microwave power and b) of the gas flow is shown. It can be seen that SF_6 can be decomposed completely in the regarded parameter range of 1..3 kW and 25..50 sl/min. However, the DRE of CF_4 increases with an increase of the microwave power and decreases when the gas flow is increased. Nevertheless, DRE of over 96 % or even higher ones still can be reached for gas flows up to 40 sl/min nitrogen and at a microwave power of 3 kW.

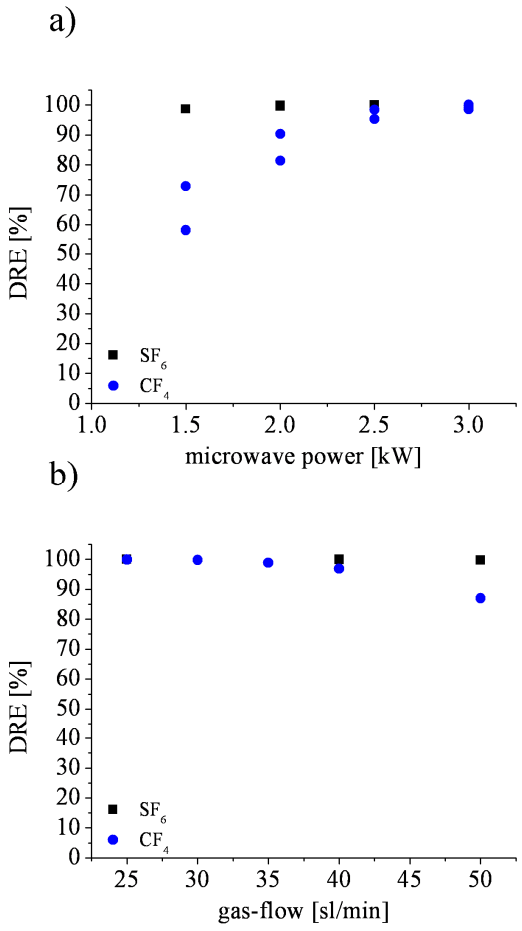

Figure 5. Destruction and removal efficiencies (DRE) of SF_6 and CF_4: a) in dependence of the supplied microwave power at a nitrogen gas flow of 25 sl/min and b) in dependence of the gas flow at a supplied microwave power of 3 kW.

Furthermore, the mass spectroscopic analysis showed that when dry nitrogen is used CF_4 is decomposed to SiF_3 where the silicon is originated from the quartz tube. When the gas mixture is moistened CF_4 is decomposed to CO, CO_2 and HF, which is turned into calcium fluorine by the wet vent washer. Fourier transform infrared analyses of the clean gas behind the wet vent washer showed, that in the case of humid gas mixtures only CO, CO_2 and very little amounts of nitride oxides are produced. Thus this plasma torch is well suited for the decomposition of perfluorinated compounds.

4. Summary and Conclusions

To summarize, the characterization of an air plasma revealed that the maximum temperatures of $T_g \approx 3600$ K and $T_e \approx 5800$ K are measured in the centre of the cylindrical resonator. The investigations concerning the decomposition of waste gases showed, that SF_6 and CF_4 can be decomposed completely and that no critical by-products are generated, which makes the presented plasma torch well suitable for this application.

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