

REACTIONS ON CATALYTIC PROBE SURFACE DURING OXYGEN PLASMA TREATMENT OF POLYETHER SULPHONE

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Abstract: Experiments on the behavior of a nickel catalytic probe during activation of the surface of polyether sulphone in oxygen plasma are described. The temperature of the probe mounted 30 cm apart from inductively coupled RF oxygen plasma was measured for the case of empty discharge vessel and the case a sample with the dimensions of 8 cm x 1.2 cm x 0.4 cm was mounted in the middle of the discharge coil. It was found that both the maximum temperature and the first time derivative of the probe was much higher in the case of loaded discharge vessel than in the case of empty vessel. Both effects were described in terms of a higher probability for recombination of radicals such as CO on the probe surface than the recombination of neutral oxygen atoms.

Reakcije na površini katalitične sonde med plazemsko obdelavo polieter sulfona

Ključne besede: sonde katalitične, sonde katalitične nikljeve, reakcije površinske, obdelava s plazmo, plazma kisikova, polieter sulfon, aktiviranje površine, jedkanje plazemsko, jedkanje suho plazemsko, RF razelektritve radiofrekvenčne, T-t karakteristike temperatura-čas

Povzetek: Prikazujemo obnašanje nikljeve katalitične sonde med aktivacijo površine polieter sulfona v kisikovi plazmi. Merili smo temperaturo sonde, ki je bila nameščena 30 cm od induktivno sklopljene RF kisikove plazme v primeru prazne razelektritvene komore in v primeru, ko smo v sredino razelektritvene tuljave namestili vzorec z dimenzijami 8 cm x 1.2 cm x 0.4 cm. Ugotovili smo, da sta tako največja temperatura, ki jo doseže sonda, kot tudi prvi časovni odvod temperature sonde po vklopu RF generatorja, precej večja v primeru, ko je v razelektritveni komori nameščen vzorec, kot v primeru, ko je komora prazna. Oba pojava smo tolmačili z večjo verjetnostjo za rekombinacijo radikalov kot je CO na površini sonde, kot je verjetnost za rekombinacijo nevtralnih atomov kisika.

1. Introduction

Oxygen plasma has become widely used for low temperature treatment of organic materials in research laboratories and industry. Technologies based on application of oxygen plasma include degreasing of different components /1/, plasma dry ashing /2/, activation of polymer surfaces for painting/printing /3/, and plasma ashing of biological samples /4/. Oxygen plasma for surface treatment of different samples is created in low-pressure discharges, such as microwave discharge (both non-magnetized and ECR modes), RF discharge (inductively and capacitively coupled) and a variety of DC discharges. Discharges are usually created in vacuum chambers made of a material with a low recombination coefficient for the reaction $2O \rightarrow O_2$, such as metals, which form thin films of stable oxides, glasses and ceramics. For different application, oxygen plasma with different parameters is used. By changing the type of the discharge, the discharge power, dimensions of the discharge vessel, pressure and pumping speed, one can obtain oxygen plasma with different parameters, i.e. the density and energy distribution of various particles created in plasma. In any case, the plasma is thermodynamical non-equilibrium. In most cases, the energy distribution function of each type of particles is close to Maxwellian, so the temperature is defined according to the rules of statistical mechanics. The electron temperature in plasma is usually several 10000°C (average kinetic energy of several eV), while the temperature of heavy particles is often close to the temperature of the inner wall of the discharge vessel.

Due to inelastic collisions with hot electrons, the density of excited states of oxygen molecules in the discharge differs significantly from the values found in thermodynamical equilibrium gas. The density of electrons and positive ions is often within $10^{15} - 10^{17} \text{ m}^{-3}$ bracket, the density of negative oxygen ions is usually an order of magnitude lower, the density of neutral oxygen atoms is often around 10^{20} m^{-3} and sometimes even one or two orders of magnitude higher. The same applies for the density of ozone molecules (O_3). Many particles are found in excited states. Molecules are found in high rotational and vibrational states and also in single electron excited states. Excited states are usually relaxed by photon emission so plasma is an effective source of radiation ranging from IR to UV light.

Several techniques have been used for determination of plasma parameters including electrical probes, magnetic probes, mass spectrometry, spectral intensities, line broadening, optical and ultra violet techniques, X-ray spectroscopy, far infra-red techniques, optical interferometry and microwave techniques /5/. For determination of the density of neutral atoms catalytic probes proved useful /6/.

Many oxygen particles created in plasma react with the organic samples treated. Oxygen atoms, for instance, can react with the surface of hydrocarbons either by being trapped on the surface causing oxidation of the material or forming volatile molecules (such as CO and OH) which leave the surface. In any case, plasma parameters are altered by the presence of organic

samples in the discharge vessel. It is clear that the density of oxygen atoms in the presence of samples is lower than in an empty discharge vessel. Some atoms are lost since they remain in the surface layer of the samples, and more are lost because they form light molecules (radicals as CO and OH finally form stable molecules - carbon dioxide and water). The change of the density of neutral reactive particles can be monitored by the use of a catalytic probe. In the present paper we show how the presence of a polymer sample alters the behavior of a catalytic probe.

2. Experimental

Experiments were performed in a glass discharge tube with the inner diameter of 36 mm and the length of 60 cm. Oxygen plasma was created at one side of the discharge vessel within a coil with the length of 15 cm, which was connected to an RF generator with the frequency of 27.12 MHz and the nominal power of 700 W. A catalytic probe was mounted on the other side of the discharge vessel. The probe is shown in Figure 1. The distance between the coil and the probe was 30 cm. The temperature of the probe after turn on of the RF generator was measured at different pressure. For the case of an empty discharge vessel, the temperature versus time is shown in Figure 2, 3 and 4.

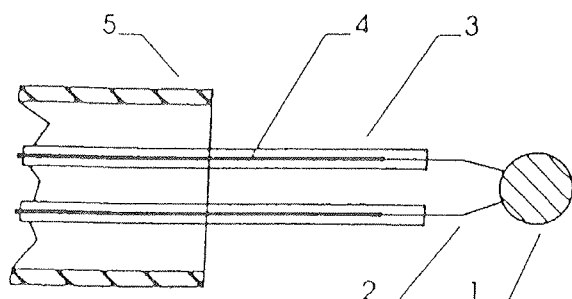


Fig. 1. Catalytic probe. 1 - nickel disc with the radius of 1 mm and the thickness of 0.2 mm, 2 - chromel - alumel thermocouple wires with the radius of 0.0625 mm and the length of 20 mm, 3 - thin glass tube with the outer diameter of 1.8 mm, 4 - kovar wire with the radius of 0.6 mm, 5 - glass tube with the outer diameter of 7 mm.

After the experiments with the empty vessel, a sample was mounted in the middle of the RF coil. The sample was made of polyether sulphone (PES) of a rectangular shape with the length of 8 cm, the width of 1.2 cm and the thickness of 0.4 cm. The temperature of the probe during the first 10 s after turn on the RF generator is shown in Figure 5, 6 and 7.

3. Results

Measurements of the temperature of the catalytic probe summarized in Figure 2 - 7 show that exothermic reactions take place on the probe surface when the RF

generator is on. For the first few seconds after turn on the generator, the temperature increases linearly with time, and after some time, a constant temperature is obtained. The time needed for reaching the steady temperature depends on the pressure in the vacuum system. In the case of empty discharge vessel, the constant temperature is obtained in 20 s at the pressure of around 100 Pa, and in 40 s at the pressure of about 10 Pa. When the sample is mounted in the discharge vessel, the measurements of the temperature were performed only during the first 10 s so not in all cases the constant temperature is obtained. Still, comparison of Figures 4 and 7 show, that the time needed to reach the constant temperature of the probe depends on what's in the discharge vessel. In the case of the PES sample in the discharge vessel, the time needed to reach the constant temperature is at least for a factor of 2 smaller than for the empty discharge vessel.

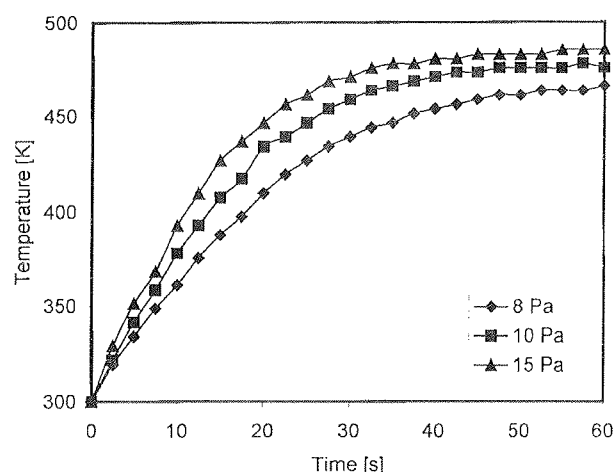


Fig. 2. Temperature of the nickel catalytic probe in empty discharge vessel during the first 60 s after turn of the RF generator at low pressure.

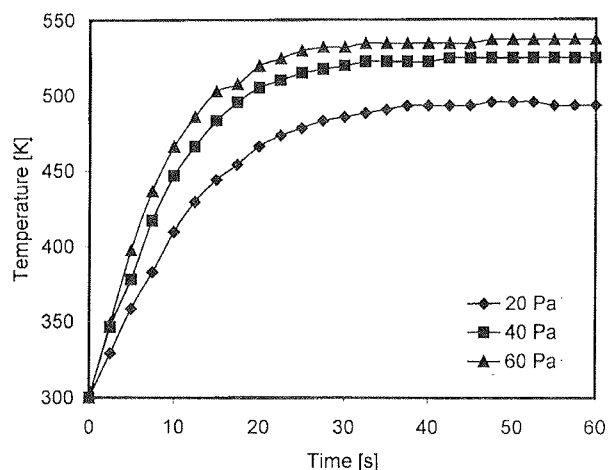


Fig. 3. Temperature of the nickel catalytic probe in empty discharge vessel during the first 60 s after turn of the RF generator at medium pressure.

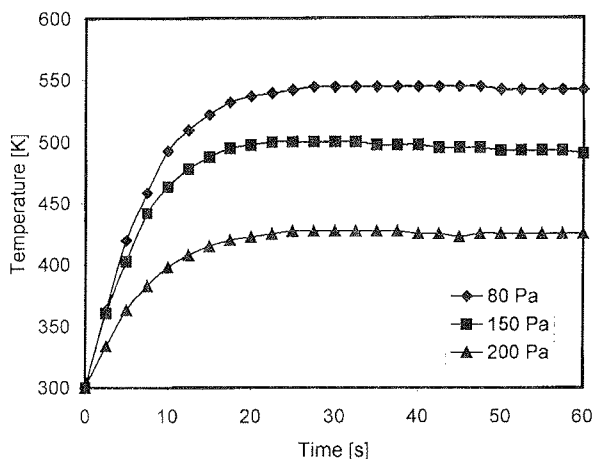


Fig. 4. Temperature of the nickel catalytic probe in empty discharge vessel during the first 60 s after turn of the RF generator at high pressure.

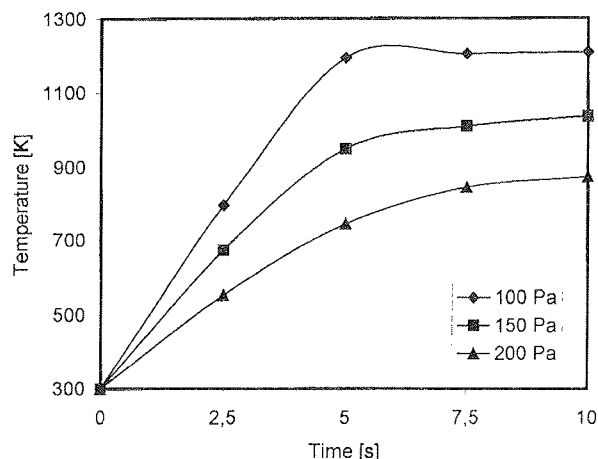


Fig. 7. Temperature of the nickel catalytic probe in loaded discharge vessel during the first 60 s after turn of the RF generator at high pressure.

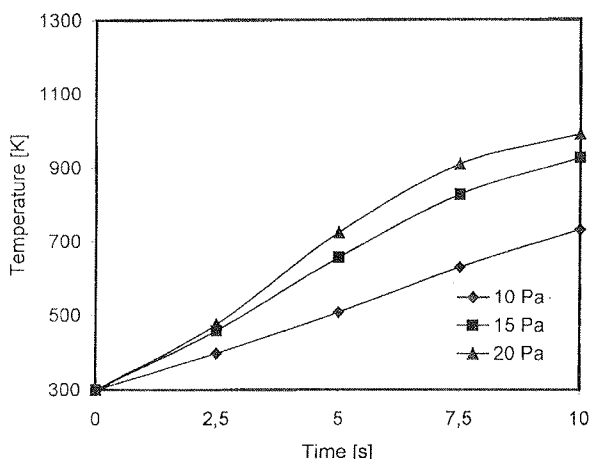


Fig. 5. Temperature of the nickel catalytic probe in loaded discharge vessel during the first 60 s after turn of the RF generator at low pressure.

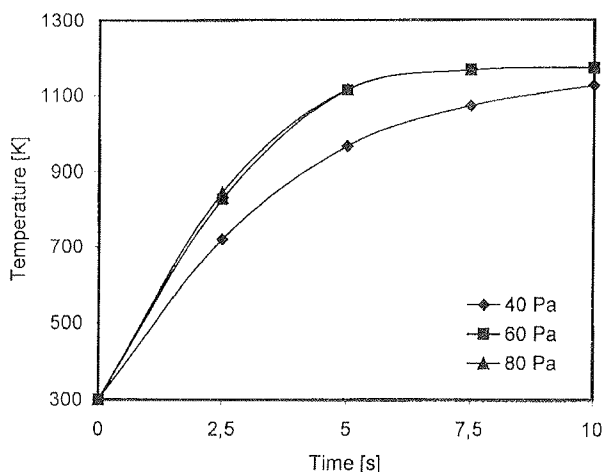


Fig. 6. Temperature of the nickel catalytic probe in loaded discharge vessel during the first 60 s after turn of the RF generator at medium pressure.

From the curves of the probe temperature versus time (Figure 2 - 7) the first time derivative after turn on the RF generator is calculated. The results are summarized in Figure 8. In the case of empty discharge vessel, the first derivative of the probe temperature is of the order of 10 K/s, while in the case of the discharge vessel with the sample it is an order of magnitude higher. In both cases, the derivative at low pressure increases with increasing pressure, reaches the maximum at the pressure of about 80 Pa and decreases with further increase of the pressure.

4. Discussion

Measurements of the first time derivative of the probe temperature give valuable data on the state of the gas in the vicinity of the probe [7,8]. If the gas is in the state of thermodynamic equilibrium, the temperature of the probe will remain unchanged, as the discharge vessel near the probe remains at room temperature. The rate of heating of the probe is therefore a measure of the non-equilibrium of gas in its vicinity. The higher the first derivative, the higher non-equilibrium of the gas. In the case of pure gas, the first time derivative of the probe gives semi-quantitative values on the density of neutral oxygen atoms in the gas [7]:

$$n_O = \frac{4Mc_p}{v\gamma W_D \pi r^2} \frac{dT}{dt},$$

where n_O is the O density near the probe, M the probe mass, c_p the thermal capacity of the material the probe is made of, v the average thermal velocity of oxygen atoms, γ the recombination coefficient for oxygen atoms on the probe surface, W_D the dissociation energy of oxygen molecule, r the probe radius and dT/dt first time derivative of probe temperature just after turn on of the RF generator. For the case the probe is made of nickel and its surface is covered with a thin film of nickel oxide, the constants in equation (1) are as follows: $M = 5.6 \times 10^{-6}$ kg, $c_p = 444$ J/kgK, $v = 700$ m/s, $\gamma = 0.04$,

$W_D = 5.12$ eV, $r = 1$ mm. Taking into account the measured values of dT/dt , which are about 10 K/s, the density of oxygen atoms in the vicinity of the probe is $1.4 \times 10^{21} \text{ m}^{-3}$ what is a reasonable result.

When a sample is placed in the discharge vessel, the density of oxygen atoms drops according to the discussion in chapter 1. However, the first derivative of the probe temperature did not drop at all. Moreover, the derivative increased for an order of magnitude, as can be seen in Figure 8. The result is certainly worth a discussion.

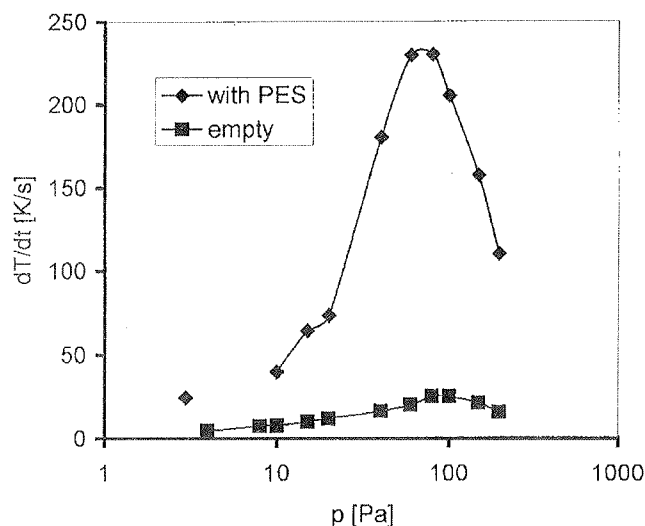


Fig. 8. Time derivative of the temperature of the catalytic probe after turn on the RF generator at different pressure in the case of empty and loaded discharge vessel.

In the case of empty discharge vessel, the probe is heated mainly due to recombination of neutral oxygen atoms on its surface. The probability of recombination (i.e. the recombination coefficient) for this reaction is rather low: $\gamma = 0.04$ [9] and the O concentration in the vicinity of the probe rather high (of the order of 10^{21} m^{-3} , as calculated above).

When the sample is mounted into the discharge vessel, the density of neutral oxygen atoms drops as they react chemically on the sample surface forming molecules like OH and CO. So one would expect that the derivative of the probe temperature would drop as well. However, newly formed molecules may also chemisorb on the probe surface and react with other particles reaching the surface. The most probable reaction taking place on the probe surface is $\text{CO} + \text{O} \rightarrow \text{CO}_2$. Other exothermic reactions may also occur on the probe surface. Due to all these reactions, the energy dissipation on the probe remains high although the density of O atoms is lowered.

The energy dissipated on the probe surface at the reaction $\text{O} + \text{O} \rightarrow \text{O}_2$ is similar to the energy dissipated at the reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2$, i.e. few eV. If the probability of both reactions is the same, the time

derivative of the probe temperature will not change much for the cases of empty and loaded discharge vessel. The experimental results, however, showed that the derivative of the probe temperature increased for an order of magnitude when the sample was mounted into the discharge vessel. Therefore, one can conclude that the probability of oxidation of carbon monoxide on the probe surface is much higher than the probability of the recombination of oxygen atoms.

5. Conclusions

Experiments on the behavior of nickel catalytic probe placed in the discharge vessel were described. The time dependence of the temperature of the nickel catalytic probe was measured at different pressure for the case of empty discharge vessel and the vessel loaded with a sample of polyether sulphone of a rectangular shape with the length of 8 cm, the width of 1.2 cm and the thickness of 0.4 cm. The measurements showed that for the first few seconds after turn on the plasma source the temperature of the disc rose linearly with time, and after about 10 s the constant temperature was obtained. The constant temperature of the probe depended on pressure and whether the discharge vessel was loaded with the sample or not. For the case of the loaded vessel, the constant temperature of the probe rose over 1000 K at any pressure between 40 and 150 Pa, while at higher and lower pressure the constant temperature was less than 1000 K. For the case of the empty discharge vessel, the maximum temperature of nearly 550 K was obtained at the pressure of 80 Pa. The first time derivative of the probe temperature after turn on the plasma source was of the order of 10 K/s for the case of empty discharge vessel, and of the order of 100 K/s when the sample was mounted into the discharge vessel. In both cases, the derivative increased with increasing pressure up to the pressure of about 80 Pa where the maximum value of about 25 and 230 K/s, respectively, was reached, and decreased with further increase of the pressure. It was suggested that the higher rate of heating of the probe in the case of the sample placed in the discharge vessel was due to a higher probability of reaction of CO and OH molecules on the probe surface than the probability of recombination of oxygen atoms on the same surface.

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