OPTICAL EMISSION CHARACTERIZATION OF EXTREMELY REACTIVE OXYGEN PLASMA DURING TREATMENT OF GRAPHITE SAMPLES

KARAKTERIZACIJA EKSTREMNO REAKTIVNE KISIKOVE PLAZME Z OPTIČNO EMISIJSKO SPEKTROSKOPIJO MED OBDELAVO KOMPOZITA POLIMER – GRAFIT

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Characteristics of oxygen plasma during treatment of polymer graphite composite were monitored by optical emission spectroscopy. Plasma was created in a rather small volume of about 3×10^{-5} m^{-3} within a quartz glass tube by an electrode-less radiofrequency discharge in the H mode. The discharge was established using an RF generator with the frequency of 13.56 MHz and the output power of 550 W. The composite samples were discs with a diameter of 25 mm and the thickness of 8 mm. Plasma was created in pure oxygen and characterized by an optical spectrometer through an optical fiber. A low-resolution spectrometer Avantes AvaSpec 3648 was adjusted to the lowest acquisition time due to intensive radiation. The optical spectra revealed several atomic lines originating from radiative transitions from highly excited states, CO bands from 3rd positive as well as Angstrom transitions, and a broad continuum between 400 and 700 nm. Weak carbon atomic lines in the UV and infra-red part of spectrum were detected as well. The intensity of major spectral features was measured versus treatment time for 30 s. The results showed continuous decrease of oxygen lines and simultaneous increase of a CO line at 266 nm and C line at 911 nm. Spectral features were explained by intensive oxidation of the graphite sample. The unusually high intensity of CO bands were explained by interaction of highly excited oxygen atoms with graphite samples, while the appearance of the broad continuum was explained by partial overlapping of radiative transitions within CO molecule.

Keywords: optical emission spectroscopy, oxygen plasma, surface modification, functional groups, graphite

Z optično emisijsko spektroskopijo smo spremljali lastnosti kisikove plazme med obdelavo kompozita polimer-grafit. Plazmo smo ustvarili v razmeroma majhni prostornini približno 3×10^{-5} m^{-3} znotraj kvarčne cevi. Za vzbujanje plazme smo uporabili brez-elektrodno visokofrekvenčno plinsko razelektritev v H načinu. Uporabili smo radiofrekvenčni generator, ki je deloval pri frekvenci 13,56 MHz in izhodni moči 550 W. Kompozitni vzorci so imeli valjasto obliko s premerom 25 mm in višino 8 mm. Plazmo smo vzbujali v čistem kisiku, njene karakteristike pa merili z optičnim spektrometrom. Uporabili smo spektrometer Avantes AvaSpec 3648, ki ima nizko ločljivost v širokem območju med okoli 180 nm in 1100 nm. Zaradi izredne svetilnosti plazme smo uporabili najmanjši integracijski čas. Optični spektri so pokazali značilne črte, ki izvirajo iz atomskih prehodov, molekularne pasove, ki izvirajo iz prehodov v CO radikalih (3. pozitivni in Angstromov sistem), kakor tudi širok kontinuum v območju med 400 in 700 nm. Opazili smo tudi šibke črte, ki izvirajo iz prehodov v C atomih. Intenziteto najpomembnejših spektralnih vrhov smo spremljali med obdelavo vzorcev, ki je trajala 30 s. Rezultati so pokazali stalno padanje intenzitete kisikovih črt, obenem pa rast CO črte pri 266 nm in C črte pri 911 nm. Rezultate smo pojasnili z intenzivno oksidacijo kompozitnih vzorcev. Nenavadno visok CO vrh smo pojasnili z močno kemijsko interakcijo, ki je posledica prisotnosti visoko vzbujenih kisikovih atomov, medtem ko smo pojav kontinuuma pripisali prekrivanju spektralnih pasov, ki izvirajo iz različnih prehodov znotraj molekule CO.

Ključne besede: optična emisijska spektroskopija, kisikova plazma, modifikacija površine, funkcionalne skupine, grafit

1 INTRODUCTION

Oxygen plasma is a popular medium for modification of different materials.[1–10] Unlike normal oxygen in thermal equilibrium, non-equilibrium state of oxygen gas reacts with materials already at room temperature.[11] Such high chemical reactivity is often attributed to high dissociation fraction of oxygen molecules even at relatively low power density.[12–17] Oxygen plasma is particularly suitable for treatment of carbon – containing materials.[18–23] The reaction channels include oxygen incorporation onto the surface of carbon containing materials as well as slow etching by formation of CO molecules and CO$_2$ molecules which quickly desorb from the sample surface under low pressure conditions and are pumped away.[24] If a sample contains a substantial amount of hydrogen (like polymers or hydrogenated carbon deposits) the reaction products are also OH radicals and H$_2$O molecules.[25–26] In many cases the incorporation of oxygen onto the sample surface is sufficient in order to obtain desired modification of carbon containing materials.[27] In such cases, weakly ionized highly non-equilibrium plasma is applied. The technology based on application of weakly ionized oxygen plasma for modification of carbon-containing materials is often called surface functionalization.[28–31] In other cases, however, at

least a part of material should be removed in order to achieve appropriate results. Weakly ionized plasma is not reactive enough to allow for rapid removal of thick carbon films, so more aggressive plasma should be used. Typical examples of aggressive plasma include those created in relatively small volumes by rather powerful discharges, such as arc,[32] microwave[33] and radiofrequency discharges in the H mode.[34] Plasma created in such discharges is spatially limited by the existence of high electromagnetic fields and the power density may exceed 10^8 W m^{-3}. Such plasma is never cold – the neutral gas kinetic temperature is usually over 1000 K. Still, plasma is highly non-equilibrium since the dissociation and ionization fractions are much higher than in thermal equilibrium at several 1000 K. Such plasma often allows for intensive chemical reactions taking place on the sample surface and is suitable for development of technologies for rapid removal of carbon containing materials from samples.[35–37]

2 EXPERIMENTAL

Experiments were performed in a plasma reactor pumped with a two stage rotary pump with the nominal pumping speed of 80 m^3 h^{-1}. Suitable pressure is adjusted in the reactor by leaking oxygen into the system during continuous pumping (the pressure was set to 75 Pa of oxygen). This allows for rapid removal of any reaction compounds from gaseous plasma. Plasma is created within small volume inside a quartz glass tube with the inner diameter of 36 mm. The length of plasma column is effectively limited to about 8 cm using a short water cooled copper coil connected to a radiofrequency generator operating at the standard frequency of 13.56 MHz and the maximal power of 1200 W. The generator is matched to the coil via a matching network consisting of two variable vacuum capacitors. The network is adjusted in order to allow efficiency of about 80 %. The forward power of 550 W was used at current experiments. Plasma was characterized by optical emission spectroscopy. We used a low-resolution spectrometer Avantes AvaSpec 3648 with the following characteristics: spectral resolution of 0.8 nm in the spectral range from 180 to 1100 nm. The radiation emitted from plasma was conducted to spectrometer via a fiber optical FC-IR waveguide. The
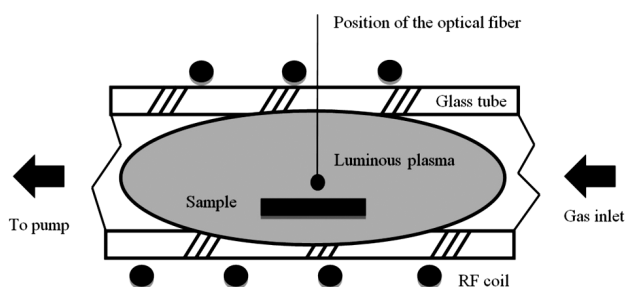
waveguide tip was mounted approximately 5 mm above the sample as shown in **Figure 1**. Samples were commercially available pure graphite samples. The samples were in form of disc of a diameter of 25 mm and a thickness of 8 mm. They were immersed into the centre of plasma as shown in **Figure 1**.

3 RESULTS

A typical optical spectrum of oxygen plasma during treatment of a sample is shown in **Figure 2**. The spectrum presented has been corrected for spectral sensitivity of the spectrometer by means of a combined deuterium tungsten reference light source which allows for spectral calibration in the range from 240 nm to 940 nm (outside this range the calibration is unreliable due to low intensity of calibration lamp).[38] The spectrum is pretty rich. Apart from atomic oxygen and carbon emission lines very strong emission originating from excited states of CO molecules is observed. Also, a continuum is observed in the wide range from about 300 to 800 nm beneath the CO molecular emission. Insets show details of the UV part of the spectrum with resolved 3rd positive band of CO and IR part with a group of resolved C atomic lines. In UV region C atomic line at 248 nm is visible and a weak OH radical emission superimposed on (0,2) CO band.

The optical spectra were measured with an integration time of 7 ms (averaged 10 times) – effectively
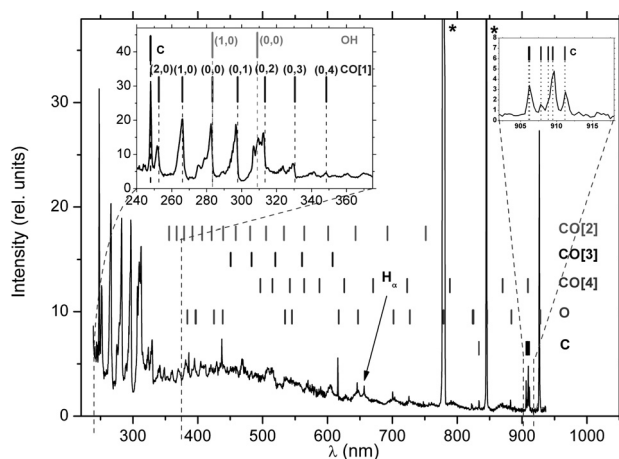
Figure 2: A typical spectrum of oxygen plasma during treatment of a composite sample. The spectrum was taken 30 s after initiation of plasma treatment. Stars denote spectral lines in saturation. Insets show details of the UV part of the spectrum with resolved 3rd positive band of CO and IR part with resolved C atomic lines. Abbreviations used: CO[1] = 3rd positive band, CO[2] = Triplet band, CO[3] = Angstrom band, CO[4] = Asundi band.

Slika 2: Značilni spekter kisikove plazme med obdelavo kompozitnega vzorca. Spekter smo zajeli po 30 s plazemski obdelavi. Z zvezdicami so označene emisijske črte, ki so bile v saturaciji. Vstavljeni sliki prikazujeta povečani del UV spektra z označenimi emisijskimi črtami 3. pozitivnega pasu CO molekule in povečani del IR spektra z označenimi atomskimi emisijskimi črtami C. Uporabljene kratice so: CO[1] = 3. pozitivni pas, CO[2] = pas tripleta, CO[3] = Angstromov pas, CO[4] = Asundijev pas.
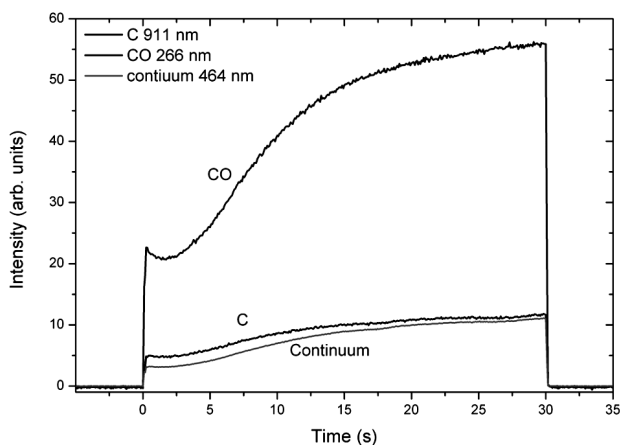
Figure 1: Schematic of the plasma reactor
Slika 1: Shema plazemskega reaktorja
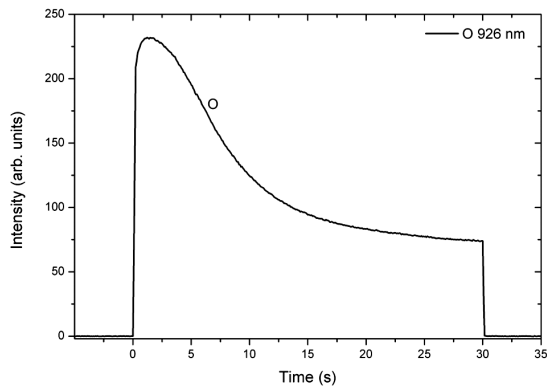
Figure 3: Spectral intensity time dependence of an atomic oxygen line at 926 nm
Slika 3: Časovna odvisnost kisikove črte na 926 nm

Figure 5: Spectral intensity time dependance of H_α line at 656 nm and OH band at 309 nm
Slika 5: Časovna odvisnost H_α črte pri 656 nm in OH črte pri 309 nm

measuring about 13 spectra per second. Appropriate home made software developed within LabVIEW allows for tracking of selected spectral features versus time. The behavior of an oxygen line at 926 nm is presented in **Figure 3**. **Figure 4** reveals the behavior of CO band (1,0) at 266 nm, C atomic line at 911 nm and continuum contribution at 464 nm. Wavelength representing continuum emission was chosen such to avoid any known atomic or molecular spectral features. **Figure 5** is a plot of H_α and OH lines at 656 and 309 nm, respectively. Since both H and OH spectral features overlap with continuum contribution, latter was subtracted.
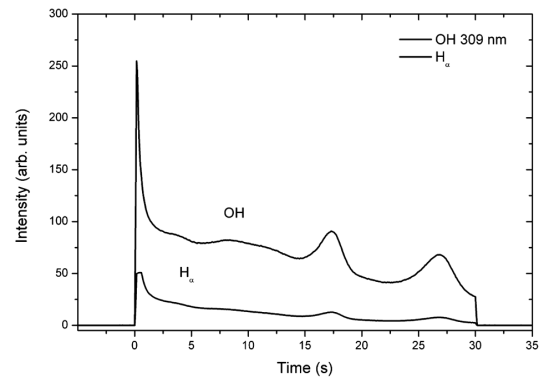
4 DISCUSSION

The optical spectrum presented in **Figure 2** reveals some interesting features that are worth discussing. As expected, the neutral oxygen atom lines prevail. The most intensive are the lines at 777 and 844 nm that correspond to transitions $3p\ ^5P - 3s\ ^5S$ and $3p\ ^3P - 3s\ ^5S$, respectively. Both excited states are characterized by a pretty high excitation energy which is 10.99 eV and

Figure 4: Spectral intensity time dependance of CO band at 266 nm, C atomic line at 911 nm and continuum at 464 nm
Slika 4: Časovna odvisnost CO črte pri 266 nm, C črte pri 911 nm in kontinuuma pri 464 nm

10.74 eV, respectively. The appearance of these lines has been observed by numerous authors[39–42] and is explained by multi-stage excitation of oxygen atoms. Namely, as the excitation energy is pretty high, the states are unlikely to be reached by electron impact excitation from the ground state. There are several metastable states of oxygen atoms that allow for such step-like excitation.

The appearance of CO bands in the spectrum presented in **Figure 2** is explained by intensive oxidation of the samples. The third positive band belongs to transitions between b $^3\Sigma^+$ and a $^3\Pi$ states. The intensity of this band is much stronger than at experiments with less aggressive plasma.[43] The 3rd positive band dominates the UV part of the spectrum, while on other hand the central part of spectrum (300 – 800 nm) presented in **Figure 2** is dominated by a broad continuum. It is well known that this part of spectrum is dominated by overlapped bands of the Angstrom band – B $^1\Sigma$ – A $^1\Pi$, the Asundi a' $^3\Sigma^+$ – a $^3\Pi$ and Triplet (d $^3\Delta$ –a $^3\Pi$).[24] In the present case, they are definitely present but their characteristic spectral structure is only partially visible, and can only partially contribute to the continuum.

The appearance of a continuum in emission spectra can be due to the presence of a body with a high temperature, or the presence of excited multi-atom molecules. The continuum peaks at about 450 nm so the temperature of a body that would radiate this continuum should be about 7000 K. The sample is not that hot – if it were, it would glow so intensively that it would be visible with a naked eye, and would produce significant infrared part of the continuum. Also, as mentioned earlier, the optical fiber was mounted in such a way that the focus was about 5 mm above the samples. The hot body, if present at all, should be of microscopic dimensions, not visible by a naked eye. Such very small particles should be pretty dense in plasma to be capable of emitting the continuum observed in **Figure 2**. Since the system is pumped with a rather powerful pump the existence of such particles is not probable.

Three-atom molecules that might be present in plasma are CO_2 and H_2O and some more exotic ones.

The atoms may be formed at chemical reactions between oxygen reactive particles and the sample. The reactions definitely occur, but the molecules entering plasma are quickly dissociated in the rather powerful discharge. Namely, even the density of oxygen molecules in our plasma is pretty low. The discharge is just energetic enough to allow for rapid dissociation of molecules with moderate binding energy.

The continuum observed in **Figure 2** can be partially attributed to the specific properties of the spectrometer. As mentioned earlier, the resolution of our spectrometer is only about 0.8 nm. Any superposition of spectral features with a shift of less than 0.8 nm would appear as a broad line. A combination of such features would lead effectively to a continuum. The rather well defined lines in UV part of the spectrum continuum presented in **Figure 2** belong to the 3rd positive band. This band is frequently observed at plasma modification of organic materials, but is not the only one CO molecules can emit in the visible part of spectrum.[44] The Angstrom band is predominant in plasma with a rather low power density (or at least comparable to the 3rd positive band). In more powerful plasma, however, other transitions may become equally intensive, such as Asundi and Triplet band. If the spectral resolution of our spectrometer were better we would distinguish between spectral features arising from different bands. Low resolution of the spectrometer also prevents detailed characterization of spectral features that should allow for estimation of vibrational and rotational temperature of CO molecules. Nevertheless, the structure of ro-vibrational bands within the 3rd positive electronic transition in comparison to previous work[24] suggests existence of high rotational and vibrational temperatures which could partially contribute to the smeared out appearance of ro-vibrational structure. We note that time dependence of CO, C, and continuum emission is very similar pointing to the conclusion that continuum emission is of similar origin.

In the spectrum we clearly observe several neutral atomic carbon lines at 248 nm, 833 nm and around 910 nm. The right inset of **Figure 2** shows details of IR part indicating position of six carbon lines. Other C lines are not visible because they cannot be distinguished from the continuum in the visible part of the spectrum. The origin of C atoms can be sputtering of the sample by energetic ions from plasma. In our discharge configuration, however, no high DC voltages are present so ions are only accelerated in the sheath between unperturbed plasma and the sample which is kept at floating potential. The voltage drop across the sheath is only about 10 V so sputtering is practically absent in our plasma. Another possible explanation of the presence of C atoms in plasma is dissociation of CO molecules by electron impact. Since plasma is pretty energetic the density of electrons is high and they may even cause dissociation of the CO molecule although its binding energy is pretty high.

Figure 3 represents time evolution of the oxygen atomic line at 926 nm (most prominent oxygen lines are in saturation). The line appears as soon as the discharge is turned on. In the first second it increases a little and then starts decreasing. The decreasing of the line intensity is due to loss of neutral oxygen atoms on the surface of the sample. The loss mechanisms include heterogeneous surface recombination and chemical reactions. The surface recombination often prevails[45], but not in our case. Namely, comparison of the oxygen line presented in **Figure 3** and CO line presented in **Figure 4** reveals complementarity. As oxygen line decreases, the CO and C lines increase. This complementarity indicates that the loss of O atoms as presented in **Figure 3** is due to formation of CO molecules rather than O_2 molecules. The increase of the CO and C lines intensity with increasing time is explained by increasing temperature of the sample. As mentioned earlier, the plasma is powerful and the neutral gas kinetic temperature is well above room temperature so the samples are heated by thermal accommodation of impinging gaseous particles. Other heating mechanisms include surface neutralization of charged particles, relaxation of metastables, surface recombination of radicals, and exothermic chemical reactions. The sample is therefore heated during plasma treatment. Since the probability for chemical reaction usually increases with increasing temperature, the production of CO molecules increases with treatment time as observed in **Figure 4**.

Another effect worth discussing is a pretty intensive CO emission just after turning on the discharge. Such an intensive line is rather unexpected since it is well known that the reaction probability for chemical interaction between oxygen plasma and organic materials is low at room temperature. The experimental system is, of course, at room temperature at ignition of the discharge. Surprisingly enough, the CO line is intensive even at the first spectra acquisition. Obviously, there should be a mechanism that allows for intensive oxidation at room temperature. Usually, temperature almost independent oxidation is explained by interaction of energetic ions with a sample. In our case, however, the ions have a low kinetic energy as discussed above. There should be other particles in plasma that allow for intensive oxidation even when the sample is at room temperature. The suitable candidates can be excited oxygen atoms in metastable states. They are definitely much more reactive than the atoms in the ground state and their density should be large in energetic plasmas. Unfortunately, very few experimental results on determination of the density of such particles are available, and they vary depending on the experimental setup. Wickramanayaka, found over 50 % of atoms in the first excited state in plasma very similar to ours[46]. Takeda, on the other hand, found orders of magnitude lower values[47].

Finally let us discuss the behavior of H and OH radicals as plotted in **Figure 5**. Both lines have an extreme at ignition of the discharge. This very short effect is often attributed to desorption of water molecules from the walls of the discharge chamber as well as from the sample. Namely, plasma radicals impinging the

surface supply quite a lot of potential and/or kinetic energy and cause desorption of water molecules. Since the supply is limited, the H and OH peaks drop in few seconds. They do not vanish, however, since the vacuum system contains adsorbed water molecules that slowly desorb from surfaces under vacuum conditions during plasma treatment. As mentioned earlier, water molecules quickly dissociate in plasma and this is the most probable explanation of rather high atomic H line observed in **Figure 5**.

5 CONCLUSION

Aggressive oxygen plasma was characterized during treatment of carbon containing samples. The systematic measurements revealed some interesting details. First, a broad continuum appeared in the range of visible light. Three different hypotheses that might explain the effect were presented and discussed. Consideration of physical and chemical effects as well as properties of our optical spectroscopy brought to a suggestion that the appearance of the continuum is partially due to relatively poor spectral resolution which prevents distinguishing between spectral features originating from different radiative transitions of CO molecules. Time evolution of the continuum radiation connects its origin with the origin of CO and C spectral emission. Second, the CO radiation was extremely high even just after igniting the discharge, when the samples are still at room temperature. This effect was explained by the presence of a substantial amount of neutral oxygen atoms in excited states. Metastable atoms interact with carbon at high probability even at room temperature and this explanation was suggested in the paper. The appearance of intense H atomic lines and OH band in the first second of plasma treatment was explained by desorption of water molecules from surfaces just after ignition of the discharge, while the decreasing of the oxygen atom line was explained by the loss due to chemical reactions.

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6 REFERENCES

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