

# AN OPTICAL-EMISSION-SPECTROSCOPY CHARACTERIZATION OF OXYGEN PLASMA DURING THE OXIDATION OF ALUMINIUM FOILS

## KARAKTERIZACIJA KISIKOVE PLAZME MED OKSIDACIJO ALUMINIJEVIH FOLIJ Z OPTIČNO EMISIJSKO SPEKTROSKOPIJO

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A highly reactive oxygen plasma was applied for the oxidation of aluminium foils. The plasma was created within a radio-frequency discharge operating at a power of 300 W and a frequency of 27.12 MHz. Samples of Al foils with dimensions of (20 × 40) mm were placed into the discharge chamber. During the treatment of the foils with oxygen plasma, the optical spectra were measured simultaneously with an optical spectrometer. The predominant spectral features observed during the treatment were atomic oxygen lines at 777.4 nm and 844.6 nm, atomic hydrogen lines and an OH band at 309 nm. As the oxidation took place other spectral features appeared. The major lines were Na at 589.35 nm and K at 766.5 nm and 769.9 nm. The time evolution of the Na and K peaks showed well-defined maxima after about a minute of plasma treatment. These maxima depended on the pressure in the discharge chamber. At the lowest pressure of 30 Pa the maxima appeared after about 100 s, while at a pressure of 80 Pa the maxima appeared after about 50 s. At a pressure of 120 Pa these maxima appeared after about 125 s. This behaviour was explained by the segregation of Na and K on the surface of the foil and the rapid desorption into the gas phase.

Keywords: oxygen plasma, aluminium foils, oxidation, optical emission spectroscopy

Za oksidacijo aluminijevih folij smo uporabili visoko reaktivno kisikovo plazmo, ki smo jo ustvarili z radiofrekvenčno razelektivitvijo pri frekvenci 27,12 MHz in moči 300 W. Vzorce Al-folij dimenzij 20 × 40 mm smo položili v razelektivitveno posodo in obdelali s kisikovo plazmo. Med obdelavo smo istočasno snemali optični emisijski spekter z optičnim spektrometrom. Prevladujoča spektralna posebnost obdelave so bili atomski kisikovi vrhovi pri valovnih dolžinah 777,4 nm in 844,6 nm, atomski vodikovi vrhovi ter molekulski pas OH pri 309 nm. Po začetku oksidacije folij se je pojavila tudi emisija Na pri 589,35 nm in K pri 766,5 nm ter 769,9 nm. Časovni razvoj teh vrhov je pokazal na izrazit maksimum po eni minuti obdelave. Izkazalo pa se je, da je ta maksimum odvisen od tlaka v razelektivitveni posodi. Pri najnižjem tlaku 30 Pa se je maksimum pojavil pri 100 s, medtem ko se je pri tlaku 80 Pa pri 125 s. Tako vedenje smo pojasnili s segregacijo Na in K na površino folij in njihovo hitro desorpcijo v plinsko fazo.

Ključne besede: kisikova plazma, aluminijeve folije, oksidacija, optična emisijska spektroskopija

## 1 INTRODUCTION

Commercially available aluminium foils are nowadays widely used in different industries, including the electronic and food industries. Aluminium is characterized by good electrical and thermal conductivities, and since the material is relatively inexpensive its application is very broad. However, in some cases the surface of the aluminium foil should be modified. In many cases, for example, the material would perform better if a thin film of oxide is formed on the surface. Anodic oxidation ensures the formation of such an oxide film by a process that requires special equipment which is not always available. An alternative technique is the oxidation of metals using an oxygen plasma<sup>1-6</sup>. This technique proved to work very well for several metals, including stainless steel. Since the application of such a method is interesting for the electronics industry we performed research on a modification of aluminium foils with a highly reactive oxygen plasma<sup>7-10</sup>. It was found that a

thin film of the order of 10 nm is rapidly grown on such foils. The technology should not cause any other modification of the material. In order to see whether the micro-elements are not affected by the plasma treatment we performed a systematic study of the plasma characterization during a treatment of aluminium foils. Namely, the microelements that may be depleted from the foils are presented in such a tiny concentration that they are not visible with standard techniques for surface and thin-film characterization. On the other hand, metallic atoms have low excitation energies and are thus visible by optical emission spectroscopy, even when present in extremely low concentrations<sup>11</sup>.

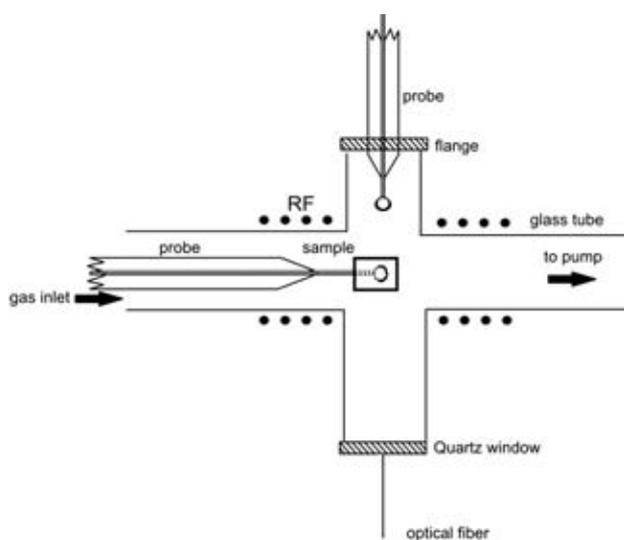
## 2 EXPERIMENTAL

The experiments were performed in a plasma reactor, which is schematically shown in **Figure 1**. The reactor is made from borosilicate glass with a low recombination coefficient for the reaction  $O + O \rightarrow O_2$ . The diameter of

the glass tubes presented in **Figure 1** is 40 mm. Two-sided tubes serve for the plasma characterization. One tube is terminated with a quartz window, while the other one is used for mounting a catalytic probe <sup>12-14</sup>. The samples are fixed on a thermocouple probe and placed in the centre of the discharge chamber, as shown in **Figure 1**. The RF coil is connected to the radiofrequency generator operating at a power of 300 W and a frequency of 27.12 MHz. On one side, the discharge chamber is pumped with a two-stage rotary pump with a nominal pumping speed of 16 m<sup>3</sup>/h, while on the other side commercially available oxygen is continuously leaked. The pressure in the experimental system is measured with an absolute pressure gauge. The ultimate pressure in the system is about 7 Pa. The residual atmosphere consists of water vapour and traces of other gases <sup>15</sup>. The optical emission spectra are detected through an optical fibre by an optical spectrometer (Ocean Optics HR 2000 CG-UV-NIR). The spectra were detected in the entire range from 200 nm to 950 nm. The spectra were taken at an integration time of 900 ms and a repetition time of 1 s. The spectral resolution of the spectrometer was 1 nm. The spectral sensitivity of the optical system was measured with a reference light source (LS-1-CAL, OceanOptics), and with a deuterium lamp for the range below 400 nm. The spectral sensitivity is almost flat in the region between 400 nm and 800 nm, but it drops significantly towards the edges <sup>15,16</sup>.

### 3 RESULTS

The samples were exposed to oxygen plasma at different pressures between 30 Pa and 120 Pa. The optical spectra were measured continuously during the plasma treatment, as explained above. Typical optical spectra are shown in **Figure 2**. **Figure 2** represents three characteristic spectra: after a) the first few seconds b)

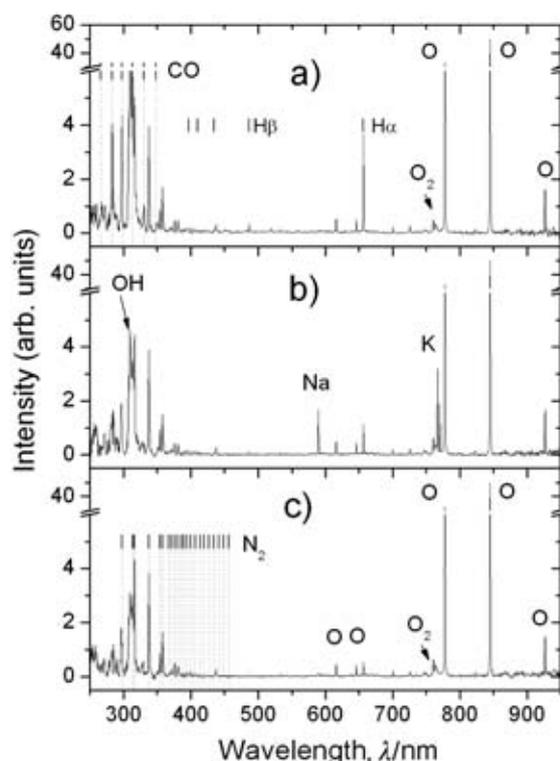


**Figure 1:** Schematics of discharge vessel  
**Slika 1:** Shema rezelektivne posode

after 50 s, c) after a prolonged treatment. The major spectral features are oxygen atom lines in the red part of the spectra and O<sub>2</sub> molecular band at 760 nm (b<sup>1</sup>Σ<sub>g</sub><sup>+</sup> – X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> (0,0)) <sup>17</sup>. Apart from these lines, additional lines of the atomic hydrogen Balmer series and the impurity molecular OH band at 309 nm <sup>18</sup>, the N<sub>2</sub> 2<sup>nd</sup> positive band, (C<sup>3</sup>Π<sub>u</sub> – B<sup>3</sup>Π<sub>g</sub>) around 315 nm <sup>19</sup>, and the CO Angstrom band 450–600 nm <sup>20</sup> are present. As the oxidation took place, other spectral features appeared. The major lines were Na at 589.35 nm (unresolved D-lines) and K at 766.5 nm and 769.9 nm. The time evolution of all these peaks during the plasma treatment of the Al foil is shown in **Figure 3** for the O, Na and K transitions, and in **Figure 4** for the other peaks: Hα, CO, O<sub>2</sub>, OH. All these experiments were performed at a pressure of 80 Pa. Note that the oxygen line's intensity exhibits a local minimum, while the Na and K lines are of maximum intensity. Another set of experiments was performed at different pressures. The time at which the maximum in the sodium peak was observed is plotted in **Figure 5**.

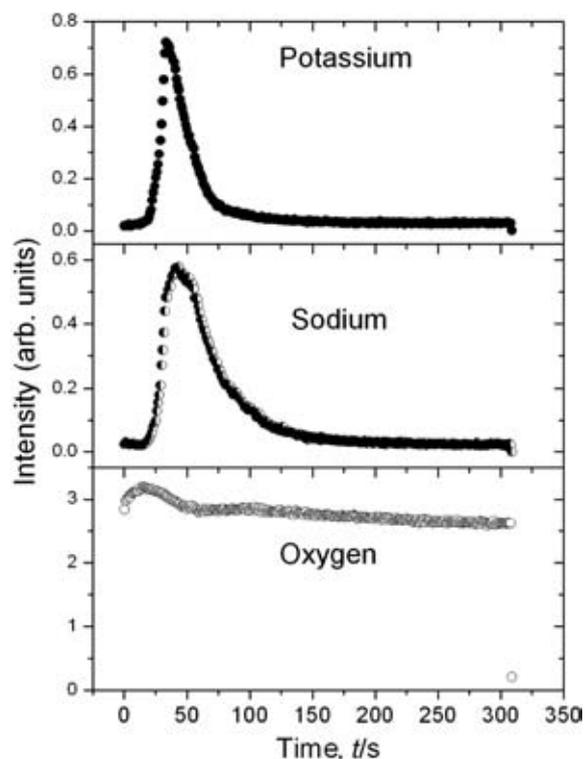
### 4 DISCUSSION

The spectrum presented in **Figure 2 a)** is rather typical for oxygen plasma created in an experimental chamber that is sealed with rubber gaskets and never



**Figure 2:** Typical optical emission spectra of the plasma in a) the first few s b) after 50 s, c) after a prolonged time (220 s). The oxygen gas pressure was 80 Pa and the discharge power 300W

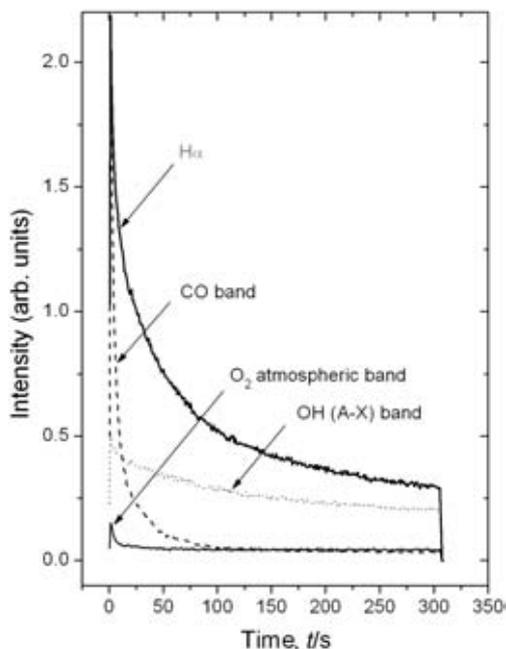
**Slika 2:** Značilni optično emisijski spekter plazme v a) prvih nekaj sekundah, b) po 50 s in c) po daljšem času (220 s) pri tlaku kisika 80 Pa in razelektivni moči 300W



**Figure 3:** Time evolution for Oxygen 777,4 nm, Sodium 589,35 nm and Potassium 766,5 nm intensities during a plasma treatment at 80 Pa of oxygen pressure

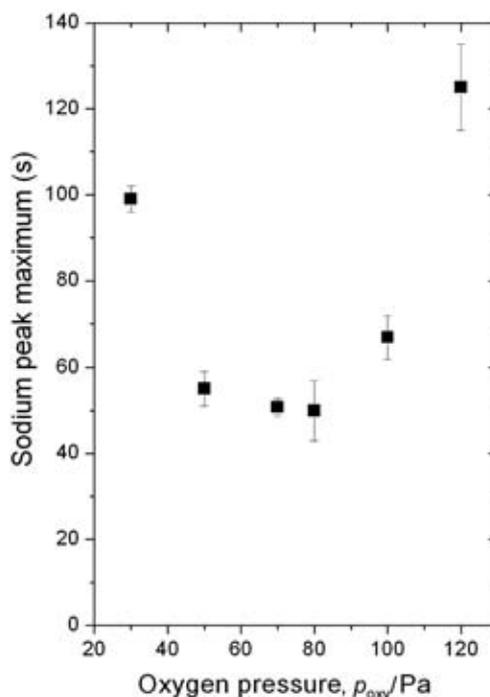
**Slika 3:** Časovna odvisnost intenzitet vrhov kisika O 777,4 nm, natrija Na 589,35 nm in kalija K 766,5 nm pri obdelavi v kisikovi plazmi s tlakom 80 Pa

backed<sup>15,21,22</sup>. Apart from the oxygen lines we could observe the OH band in the UV range as well as the molecular nitrogen and CO bands. The relatively strong emission from the hydrogen atoms is due to the dissociation of water molecules in our plasma. The nitrogen band probably comes from a small leakage of the system, while the CO band is probably due to the oxidation of traces of organic impurities. All these spectral features decrease in intensity with an increasing treatment time, as shown in Figure 4. Such a decrease is explained by the continuous pumping of the vacuum system and, also, the relatively good oxidation of the organic impurities. More interesting is the appearance of the Na and K peaks, as is clearly shown in **Figure 2 b)**. These elements do not come from the discharge chamber because they are not observed for the case of an empty chamber. The origin of these two metals is obviously the aluminium foil. A strong maximum of these peaks is observed versus the treatment time, as shown in **Figure 3**. Such maxima are explained by the heating of the aluminium foils during the plasma treatment. Namely, the aluminium foil interacts with the oxygen atoms that are present in a large concentration in the oxygen plasma. The interaction is both physical and chemical. The major physical interaction is a heterogeneous surface recombination. At the reaction  $O + O \rightarrow O_2$  the dissociation energy is released and observed as the internal energy of the aluminium foil. The recombination coefficient definitely depends on the surface properties of the aluminium foil, as well as its temperature.



**Figure 4:** Time evolution for  $H_{\alpha}$  (656,2 nm), CO (519,3 nm),  $O_2$  (760,5 nm), OH (309 nm) intensities during a plasma treatment in 80 Pa of oxygen pressure

**Slika 4:** Časovna odvisnost intenzitet vrhov  $H_{\alpha}$  (656,2 nm), CO (519,3 nm),  $O_2$  (760,5 nm), OH (309 nm) pri obdelavi v kisikovi plazmi s tlakom 80 Pa



**Figure 5:** The treatment time at which the maximum of the Sodium 589,35 nm peak was achieved is plotted versus pressure

**Slika 5:** Čas obdelave v odvisnosti od tlaka, pri katerem je dosežen maksimum vrha natrija 589,35 nm

Although exact data are not available, it is generally accepted that the recombination coefficient increases with increasing temperature. This is the main heating mechanism. Apart from the physical reactions there is also a chemical reaction, e.g., the formation of a thin oxide film. Let us now discuss an extremely pronounced peak in the sodium and potassium lines versus the plasma treatment time. At first the sample temperature is low, so hardly any migration of Na and K from the bulk toward the surface is observed. However, as soon as the samples are heated to an elevated temperature, surface aggregation occurs and thus the intensity of spectral line increases with increasing temperature. After a certain treatment time the temperature is so high that the formation of an oxide film is accomplished. The oxide film represents a diffusion barrier for the migrating Na and K atoms so the concentration of these two metals in the plasma keeps decreasing. The drop in the Na and K lines is far from being sudden. This effect may be explained either by inhomogeneous oxidation or by poor pumping from the discharge region. Namely, both Na and K may adsorb on the surface of the glass chamber and desorb slowly during the continuous pumping. Let us now explain the very well pronounced minimum in the curve presented in **Figure 5**. At low pressure the density of the oxygen atoms is relatively low, so the heating by heterogeneous surface recombination is relatively poor. That is why the maximum is observed after about 100 s of plasma treatment. At high pressure, the oxygen atom density is high, but the treatment time is even longer. This effect can be explained either by good cooling of the sample due to pretty large drift velocity of the gas through our plasma reactor or by the lack of energetic ions. Namely, the kinetic energy of the ions reaching the surface of the aluminium foils depends on both the Debye length and the mean free path<sup>23,24</sup>. In the case of a short Debye length and a long mean free path the sheath around the sample is collision-less, so oxygen ions do not lose their kinetic energy. At the other extreme the ions suffer many collisions with neutrals in the sheath and lose practically all their kinetic energy. In our plasma the Debye length keeps increasing with the increasing pressure and the mean free path keeps decreasing with the increasing pressure. Obviously, the samples exposed to plasma at 30 Pa are bombarded with energetic oxygen ions, while this effect is missing at 120 Pa. In between these two extremes the ion energy is still high enough and the oxygen atom density is reasonably high to allow for rapid heating of the samples and thus the oxidation is achieved after about 50 s.

## 5 CONCLUSIONS

Samples of commercially available aluminium foils were exposed to a highly reactive oxygen plasma. The plasma was characterized by optical emission spectroscopy. We observed a rapid decrease in the concen-

tration of the impurities originally present in the discharge chamber. As the temperature of the samples was increasing we observed a rapid desorption of potassium and sodium from the samples. This desorption was explained by the migration of these two microelements from the bulk aluminium towards the surface. As an oxide film was formed on the surface, the diffusion was blocked and the intensity of Na and K spectral lines was decreasing with the increasing treatment time. Our results clearly show the applicability of optical emission spectroscopy for studying the migration of elements that are present in bulk aluminium at concentrations that cannot be detected with standard methods for the surface and thin-film characterization.

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