Acta Agrophysica, 2002, 80, 115-122

OZONE SYNTHESIS IN THE DIELECTRIC PACKING PRESENCE

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A b s t r a c t. Ozone synthesis process in the presence of various non-conducting materials placed in a discharge gap was studied. Experiments were carried out in two kinds of silent discharge type ozonizers. The higher ozone concentrations were obtained when the materials with high heat conductivity were used. The results of the average gas temperature measurements by the thermovision method are presented.

K e y w o r d s: ozone synthesis, dielectric material, heat exchange.

INTRODUCTION

Electroplasma ozone synthesis is a process treated in the literature as a completely monophase one. When analysing the process in detail even, 70 reactions [1-5] are considered, taking into account the various particles and their excited states. The commonly acknowledge mechanism of the process proceeding in pure oxygen includes five most essential reactions [6], separated among the time-lasting-diversified steps occur in succession:

step I: $O_2 + e \rightarrow O + O + e$ (R1)

step II: $O + O_2 \rightarrow O_3^*$ (R2)

$O_3^* + M \rightarrow O_3 + M$ (R3)

step III: diffusion processes, the heat exchange.

In the presence of ozone also competitive reactions proceed in the reaction zone:

in the step I: $O_3 + e \rightarrow O_2 + O + e$ (R4)

in the step II: $O_3 + O \rightarrow O_2 + O_2$ (R5)

The typical process proceeds in the narrow discharge gap (1-2 mm) between the electrodes with considerable surface area. Under those conditions the contact of the reagents (also the electrons) and the electrodes walls is absolutely natural. The walls participate among other in the energy stabilisation of an ozone excited

particle (R3). When the process proceeds in the presence of the active solid packing filling the discharge gap the packing surface may plays a significant role [7]:

$$O_2 + e \rightarrow O + O + e \quad \text{(R6)}$$

$$O_2 \rightarrow O_{2(ads)} \quad \text{(R7)}$$

$$O_{2(ads)} + O \rightarrow O_{3(ads)} \rightarrow O_3. \quad \text{(R8)}$$

The external surface of the packing participates also in the conduction on electric charges. The surface discharges are the subject of many penetrating studies [8-19]. In the presence of packing many significant process parameters change, i.e. the gas velocity and flow character which influence the average gas temperature in the gap.

The use of silica packing enables to obtain a significant increase (ca. 30%) in ozone concentration [20-23]. The studies carried out do not conclude the final explanation of the packing action [7, 19-26]. The results of macrokinetic calculations show a strong inhibiting effect of silica packing on ozone decomposition in the range of higher specific energies of the process [27]. The internal surface of silica may place a considerable role [21]. On the other hand, the information about ozone decomposition over SiO_2 is known [28]. That effect was observed when silica packing operates in the range of higher ozone concentration [29] and low active power values.

The internal surface of the silica packing does not play a significant role in electric charges passage, and the surface development does not cause an increase in ozone concentration [24]. It results from this that in the ozone synthesis process the grains external surface properties (influencing the charges passage) and the other dielectric features (the thermal properties) may have an essential meaning.

The studies carried out in a forced surface discharges type ozonizer with a gas flow arrangement in the gap [30] show the necessity of research on the influence of other materials on the ozone synthesis efficiency. The aim of studies is the analysis of the influence of individual non-conducting materials on ozone concentration obtained in oxygen under silent discharge conditions.

EXPERIMENTAL

Apparatus and measurement method

The measurements were carried out in two groups of non-conducting materials: the grain one (0.5-0.8 mm) and in the foil form (0.2-0.5 mm). The grain materials were examined in a tube Siemens type ozonizer with a gap double-side cooling system [31]. The foils were tested in an Otto type ozonizer with cooled metal electrodes separated with a glass dielectric (Pyrex 1.5 mm) [32]. In both ozonizers the starting discharge gap width was 1.5 mm. The measurements were

carried out at the cooling liquid temperature 25°C. Pure oxygen with ca. 0.8 ppm of water vapour was used.

Ozone concentration was analysed with a BMT 961TC (BMT Messtechnik Berlin) meter. The ozonizers were supplied with H.V. (up to 14 kV) electric current produced by an inverter operating at ca. 1 kHz. Active power consumed by an ozonizer was measured with an oscilloscope TDS 3032 (Tektronix).

Results and Discussion

The non-conducting materials in a grain/foil form were examined from the point of view of their usefulness in ozone synthesis under silent discharge conditions. The results are presented in Table 1. The measurements were carried out in a range of low and high specific energy values at the active power P_A (0-25 W) and oxygen flow rate V (4-100 $Ndm^3 h^{-1}$). No correlation between the material electric properties (dielectric constant, electric strength, surface resistance) and ozone concentration was found. Therefore, an increase in ozone concentration is caused by the other properties of the packing. Besides the specific properties of the dielectric external surface (not examined up to now), its thermal properties are an especially important parameter. In all cases the ozone concentrations were higher than those obtained in an ozonizer with a non-packed gap. When the materials with a higher thermal conductance were used, the ozone concentrations obtained were higher than that obtained in the presence of silica packing. An especially clear effect was observed in the presence of alundum (96% Al_2O_3) and beryllium ceramics grains.

The packing presence in a discharge gap can influence the decrease in the gas temperature. This results from the better heat transfer conditions in the gap, connected with an increase in the gas linear velocity. Due to occupying a considerably part of the discharge space by the grains and forcing by them the change in the gas stream direction, the estimated linear velocity of a gas is several times greater than in a filled gap. This influences the convective heat-transfer coefficient value to the electrodes walls.

Table 1. The relative ozone concentration obtained in the presence of various non-conducting materials for limiting oxygen flow rate values and different discharge active power P_A values (reference: silica packing). Data in columns 2-4 from the ref. [33, 34].

Material	Heat conductivity, W/m K	Specific resistance, Ω cm	E	$c_{O3}/c_{O3(silica\ packing)}$			
				V = 4 Ndm^3/h		V = 100 Ndm^3/h	
				10W	20W	10W	20W
				2.5 Wh/Ndm^3	5 Wh/Ndm^3	0.1 Wh/Ndm^3	0.2 Wh/Ndm^3
1	2	3	4	5	6	7	8
Alfa-gel COH 4000 (foil 0.5 mm)	6.5	$5.7 \cdot 10^{12}$	-	1.00	1.02	0.98	0.95
Silicone composite with a ceramic filler (foil 0.5 mm)	1.5	10^{14}	5.9-6.2	0.99	0.95	0.96	0.95
Methyl poly (methacrylate)	0.18	$>10^{15}$	3.3	0.91	0.90	0.93	0.90
Polycarbonate	0.21	$>10^{17}$	3	0.94	0.95	0.93	0.96
Polyethylene LD (coating 0.2 mm)	0.32	$>10^{17}$	2.3	0.92	0.91	0.92	0.90
Polypropylene (coating 0.2 mm)	0.2	$>10^{17}$	2.25	0.91	0.92	0.89	0.88
Polyester resin 802 (coating 0.2 mm)	0.7	$>10^{12}$	6	0.93	0.93	0.92	0.95
Polystyrene	0.18	$>10^{16}$	2.4-2.65	0.93	0.89	0.88	0.90
Teflon (foil 0.5 mm)	0.25	$>10^{18}$	<2.1	0.9	0.85	0.92	0.91
SiO_2	1.3	10^{9}-10^{15}	3.5-6.5	1	1	1	1
Al_2O_3	2.1	$2 \cdot 10^{12}$-10^{14}	7-10	1.00	1.01	0.99	0.98
$BaTiO_3$	1.3	10^{11}	1500-2100	1.01	0.99	0.98	0.97
Cordierite		10^{12}-10^{14}	4.5-5.4	0.97	0.96	0.95	0.94
Boron-silica glass Pyrex	1.17	$2.5 \cdot 10^{7}$	5.07	0.95	0.97	0.97	0.96
Quartz glass	1.6	$4 \cdot 10^{9}$-$3 \cdot 10^{10}$	3.8	0.96	0.98	0.96	0.97
Alundum ceramics	10-35	10^{13}-10^{15}		1.05	1.04	1.06	1.08
Beryllium ceramics	71-196			1.05	1.03	1.06	1.12

In the presence of packing a heat transfer across the grains in the direction to the electrodes walls is also possible. Heat exchange between the gas and the grains surface takes also a place as a result of the gas linear velocity increase. In effect the average temperature in a gap decreases. Using the thermovision technique the changes in the gas average-mass temperature character in a gap were observed. These changes were produced by the changes in both the gas flow rate and the electrodes temperature during the ozonizer operation (Figs. 1 and 2). An increase in temperature seen in Fig. 2 (in reality the temperature of silica packing grains surface) caused by a 25-fold increase in the gas flow rate, and therefore the significant increase in linear velocity, is only ca. 5°C. This can indicate the not considerable effect of a packing on the heat exchange conditions. However, the technique used does not permit to control the gas flow rate and linear velocity exactly in the place of the temperature measurement. This results from the necessity of removing all the barriers in the way of the heat emitting surface – camera lens, which enables the gas to uncontrollably flow bypass the grains. This has a direct influence on the grains surface temperature, and can significantly underrate the measurement results. The temperature observed should be, therefore, higher. The results shown in Fig. 2 testify that such an explanation is well-grounded. When the electrodes temperature was 50°C the heat losses into the surrounding causes a considerably lower increase in temperature than that observed at 25°C.

The gas temperature influencing the temperature of the surface (and interiors) of the grains, can influence their electric properties, among others the surface conductance.

It is generally accepted that the average gas temperature in a discharge gap is a „little" higher than the ambient one. The knowledge of the gas temperature has a meaning when the reactions occurring after the discharge decay are considered, especially ozone decomposition.

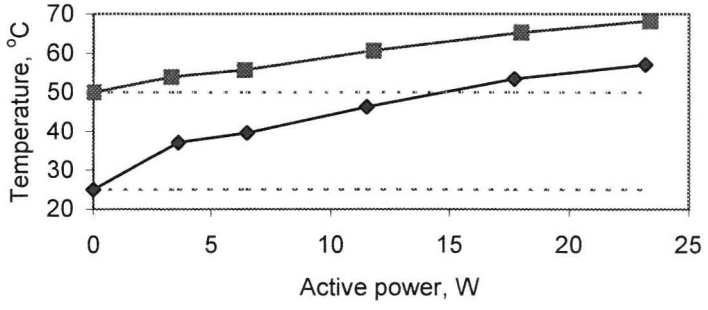

Fig. 1. Temperature in a discharge gap vs. discharge active power; a thermovision measurement. Oxygen flow rate 4 l/h, cooling liquid temperature 25°C and 50°C.

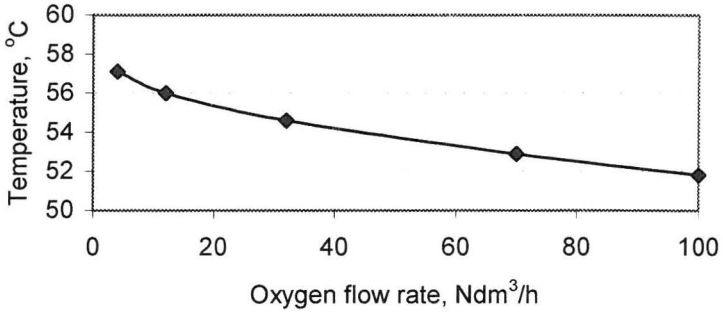

Fig. 2. Temperature in a discharge gap vs. gas flow rate; a thermovision measurement, cooling liquid temperature 25°C; P_A = 23.2 W (P_A/V = 0.23÷5.8 Wh/Ndm^3).

When an average gas temperature increases, reactions (R2-R3) are inhibited, whereas the reactions (R5) and (R9) are promoted, causing the ozone concentration decrease.

$$O + O = O_2 \qquad \text{(R9)}$$

The limitation of reaction (R4) participation should be moreover expected in the presence of packing, when ozone exists in the whole gap space and electrons passage takes place mainly on the dielectric surface.

SUMMARY

The studies confirm the usability of a fine-grained dielectric placed in a discharge gap for concentrated ozone synthesis in oxygen. Alundum and beryllium ceramics were the most useful materials. In the presence of them the ozone concentrations were higher than in presence of silica packing, studied in detail. Those materials are characterised by significant heat conductivity. The presence of a packing favours heat exchange between the gas and electrodes' walls, as a result of increase in the gas linear velocity. It seems probable that heat transfer from the reaction zone takes place to a significant degree directly between the dielectric grains and electrodes' walls. The results presented as well as those obtained in an ozonizer with a specially formed dielectric [30] show the necessity of undertaking attempts of using selected ceramics materials (instead of glass) for the ozonizer discharge barrier construction. This kind of materials, among others based on Al_2O_3, are characterised by high electric strength (30-50 kV/mm) and gas-leaktightness.

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SYNTEZA OZONU W OBECNOŚCI WYPEŁNIENIA DIELEKTRYCZNEGO

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S t r e s z c z e n i e. Badano proces syntezy ozonu w obecności różnych materiałów nieprzewodzących umieszczonych w szczelinie wyładowczej. Doświadczenia prowadzono w dwóch typach ozonatorów, w wyładowaniach cichych. Wyższe stężenia ozonu otrzymano dla materiałów z wyższym przewodnictwem cieplnym. Przedstawiono również wyniki pomiaru temperatury gazu przy wykorzystaniu technik termowizyjnych.

S ł o w a k l u c z o w e: synteza ozonu, materiały dielektryczne, wymiana ciepła.