

Metallographic Comparison of Copper and Brass Plasma Reactor Electrodes After a Month of Operation

Sebastian Gnapowski ^{1*}, Elżbieta Kalinowska-Ozgowicz², Mariusz Śniadkowski³, Aleksandra Pietraszek⁴

Lublin University of Technology, Fundamentals of Technology Faculty; kalinowska-ozgowicz@tlen.pl (E. K. O.); m.sniadkowski@pollub.pl (M. S.); aleksandra.pietraszek@op.pl (A. P.)

* Correspondence: sgnapowski@wp.pl

Abstract

Researchers from around the world are looking for better and cheaper ozone production. One of the methods increasing the efficiency of ozone production is the use to a rotating electrode presented in this paper. Experiments were carried out which shows that the most important parameters are the materials used on the electrodes and the condition of its surface. The metallographic investigations of the electrodes after continuous monthly work was made, which show how the raids layers are formed. As a result of working in a highly oxidizing environment, the electrode is oxidized in the process of chemical corrosion. It is obvious that the layer of corrosion products created during the work of the plasma reactor isolates the surface of the electrode, which reduces the intensity of the electric field, causing a decrease in the amount of plasma generated, which is a direct cause of lowering the concentration of ozone during this process. The dynamics of plasma generation process and the type of electrode material working in changing process conditions are the decisive factors influencing the concentration of ozone produced. The influence of the medium, which is the electrode material, depends mainly on its resistance to corrosion in the environment of dynamically changing conditions, e.g. electrode rotation, oxygen flow through the rotating electric field and the long monthly working time of the plasma reactor.

Keywords: brass, Cu-Zn-Pb, raids layers, metals, electrode, ozone, plasma reactor

1. Introduction

The most common case of chemical corrosion is gas corrosion occurring in environments containing oxygen, air, nitrogen, sulfur and its compounds. Gas corrosion is the result of a chemical reaction of oxidation [1-3]. Heating metal products in the atmosphere of air causes their oxidation [4-6]. Oxygen from the air reacts with metal to form a thin layer of oxide separating the metallic surface from the gaseous environment. Depending on the nature of the structure of the oxide layer forming which determines the possibility of the oxygen atom's contact with metal atoms, four mechanisms of the formation of oxides on metals are distinguished [7-9]. The speed of elementary partial processes of the oxidation reaction of metals and alloys depends to a different degree on temperature and pressure. The slowest elementary process determines the speed of the entire reaction [10]. The oxidation times of individual metals in the air show significant variation - Table 1. The rate of oxidation depends to a large extent on the purity of the material, the condition of its surface and the pollution of the atmosphere. The condition of the metal surface significantly influences the rate of corrosion. In particular, acceleration of the corrosion course may be due to the preferential crystallographic orientation of the metal surface exposed to the oxidizing atmosphere. Larger dimensions and more irregular shapes of unevenness created as a result of inaccurate surface treatment of the metal or alloy make it difficult to evenly build up the scale and its plastic deformation without cracks and micro-scales. This promotes the acceleration of the gas corrosion process [11].

The composition of the atmosphere determines the nature of chemical reactions and the magnitude of corrosion damage. The presence of oxidants may be accompanied by aggressive vapors or other similar gases. The most common gas mixtures causing intensive corrosion are: air, steam, carbon compounds, e.g. mixtures ($\text{CO} - \text{CO}_2$), hydrocarbons, sulfur compounds, (H_2S , SO_2 and SO_3). exhaust gases containing mainly sulfur and ashes, as well as halogens, nitrogen and ammonia [9-10].

2. Materials and Methods

Ozone is widely used in industry and strives to ensure that its production is stable and as effective as possible [12-16]. The most frequent phenomena and processes during plasma generation were in the environment and explained. During these studies, decreases in concentration were observed [17-19]. The rotating electrode is not responsible for phenomenon phenomena, also observed in reactors of other types [20-23]. The factor that determined the investigations of electrodes used in the plasma reactor was the decreasing efficiency of the device during ozone production while maintaining constant process parameters [24]. The only noticeable change during the reactor operation was the change in the surface condition of the electrodes used and the decreases in the concentration of ozone produced in Figure 1, 2.



Figure 1. Photograph of electrodes for operation in a plasma reactor, a) copper electrode, b) alloy electrode Cu-Zn-Pb

Before exploitation, the electrodes were characterized by a shiny surface characteristic for the materials used, namely: copper and copper alloy (Cu-Zn-Pb) - Figure 1.

After one month of operation, the electrodes made of copper and Cu-Zn-Pb alloy had a matt surface with a dark coating indicating the presence of a layer of oxidation products – Figure 2.



Figure 2. Photograph of electrodes after monthly use in a plasma reactor a) copper electrode, b) Cu-Zn-Pb alloy electrode

Another effect was the decreasing concentration of plasma (ozone) produced on the registered Lissajouses figures (Figure 3) and on the curves of the ozone concentration over time - Figure 4.

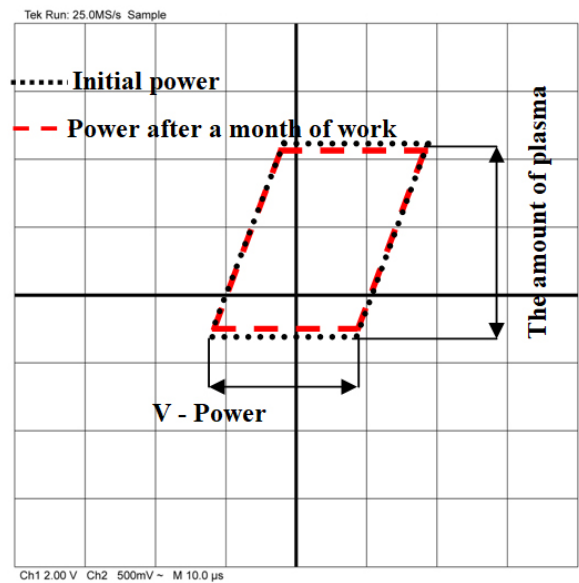


Figure 3 Lissajous figures on the first day of work and after a month of reactor operation

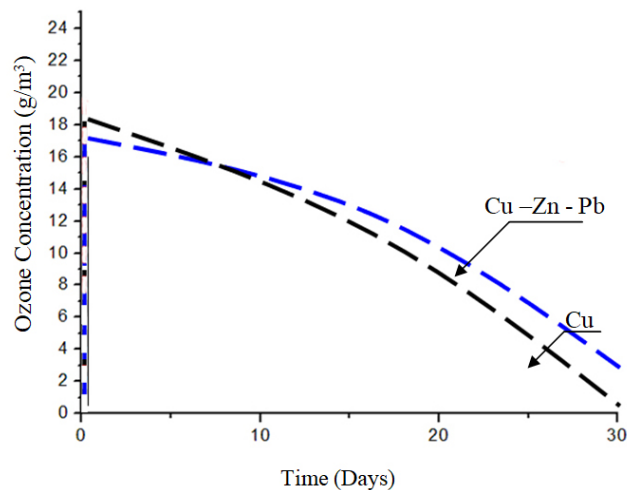


Figure 4. Relationships between ozone concentration and electrode working time

Table 1. Chemical composition of a copper electrode

Copper	Concentration of elements by % weight						
	Cu	Bi	O	P	Pb	Σ	No inclusions
CW004A* CuETP**	≥ 99,9	≤ 0,0005	≤ 0,04	---	≤ 0,005	≤ 0,03	Ag i O

* according EN

** according ISO

Table 2. Chemical composition of a copper alloy electrode (Cu - Zn - Pb)

Alloys	Concentration of elements by % weight						
	Cu	Pb	Almax	Femax	Ni	Snmax	Zn
Cu-Zn-Pb C34000 wg EN CW600Nwg.ISO	62,0 - 64,0	0,8-1,6	0,05	0,1	0,3	0,1	rest

The aim of the experiment was to determine the structural effects of the chemical corrosion process of the surface of rotating electrodes operating in the environment of dynamic oxygen flow and ozone in an electric field of a defined intensity.

The experimental material consisted of electrodes made of solid copper rod, copper alloy (Cu-Zn-Pb), Chemical composition of electrode materials are given in Tables 1 and 2.

Experimented electrodes in the form of rollers with a length of 100 mm and a diameter of 10 mm, had on the one hand an internal thread M6, and on the other, a hole \varnothing 6 mm with a milling for a fastening wedge on the drive shaft.

In order to determine the structure of materials used for electrodes and to comprehensively evaluate the metallographic effects of chemical corrosion on the surface of electrodes occurring during the plasma generation process, experiments were carried out using light microscopy, scanning electron microscopy and X-ray phase analysis.

Metallographic microscopic examinations were carried out on the material cut off from the electrodes after their 30-day operation. The cut material was embedded in a self-hardening resin and ground mechanically on aqueous abrasive papers. Polished teeth were polished mechanically using diamond pastes with different granulation. Polished copper and Cu-Zn-Pb alloys were cut in an iron chloride based reagent. Metallographic observations and grain surface measurements were performed using the OLIMPUS GX71 reflecting optical microscope using a computer image analysis system using magnification from 100 to 2000x.

X-ray experiments carried out with the diffractometric method included a qualitative X-ray phase analysis of the electrode surface after thirty days of use in a plasma generator. Electrode X-ray examinations were carried out using an Empyrean X-ray diffractometer from PANalytical. The experiments were carried out using a parallel beam technique in a configuration with a Pixcel detector Co08Keta cobalt anode at 35kV voltage and 25mA anode current. X-ray, qualitative phase analysis was carried out in the range of 2θ angles from 10° to 100° corresponding to the inter-planar distances between 1.027 nm and 0.11168 nm. The experiments ensured the conditions of the experiment in which the resulting diffractograms represent the material of the surface layer of the investigated electrodes. The phase composition of the layers formed on the surface of the investigated electrodes was identified based on the database of the International Center for Diffraction Data PDF - 4 + version 2015.

Using a scanning microscope was carried out to assess the structure of electrodes, as well as the chemical composition in micro-areas of raid layers formed as a result of the oxidation process. Observations were made on metallographic examinations using the SUPE 35 scanning electron microscope from the company ZEISS. In the research, a side detector and a lenticular detector were used, using secondary electrons detection. The chemical composition of the micro-areas of the raid layers was determined using the EDX system. The observation was carried out at an accelerating voltage of 20kV using a magnification up to 2000 times.

3. Results

Structural experiments of electrodes were carried out by metallographic observation using light microscopy, X-ray microanalysis as well as phase analysis using scanning electron microscopy. The subject of metallographic examinations was the assessment of the structure of the electrode material as well as the geometry of the raid layers on the surface of the electrodes after the monthly operation in the plasma reactor. The determination of the phase composition of the raid layers and their chemical composition in the micro-areas required the use of X-ray diffraction and the MAR method with high resolution.

The results of metallographic observations using light microscopy were included in micrographs - Figure 5-7, 11, 12. X-ray results were presented on the diffractograms - Figure 11, 16

and microanalysis made using the EDX attachment, scanning electron microscopy on micrographs (Figure 8, 9, 13, 14) and diagrams Figure 10, 15) and in Tables 3, 4.

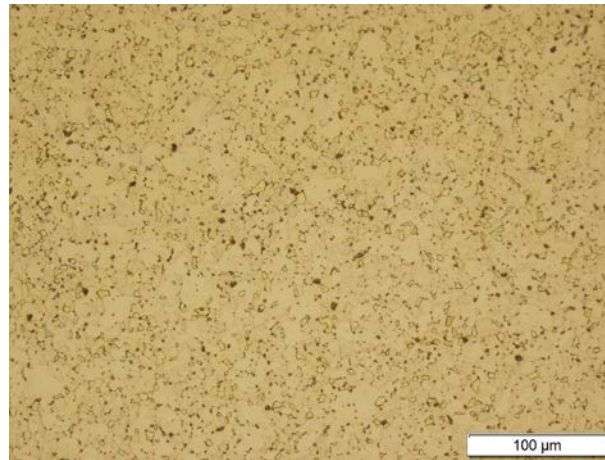


Figure 5. Heterogeneous phase α grains with lead separations in the Cu-Zn-Pb electrode structure

According on the results of metallographic examinations it was found that the layers occurring on the electrodes subjected to corrosive action of the aggressive environment of oxygen and ozone during the monthly operation in the plasma reactor, whose thickness does not exceed $10\mu\text{m}$, are characterized by the geometry corresponding to the raid layers. The electrode made of Cu-Zn-Pb alloy has a two-phase structure of non-homogeneous phase α particles (Zn solution in Cu) and pure lead in the form of precipitates – Figure 5, 6, 7. The average particle size of the α phase is from about 4 to $20\mu\text{m}$, and pure lead precipitations from about 1 to $4\mu\text{m}$ – Figure 8.

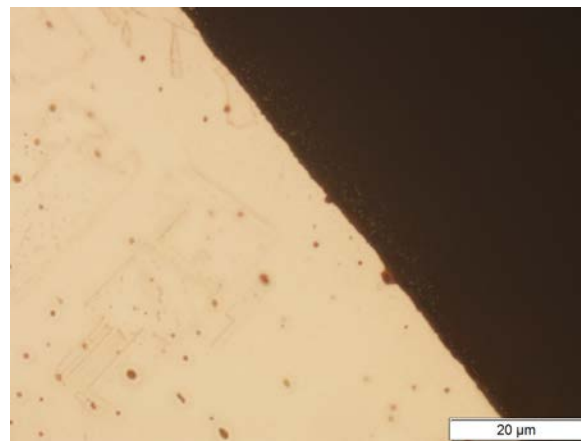


Figure 6. Discontinuous raids layer on the surface of the Cu-Zn-Pb alloy electrode (lateral transverse)

After a month of use, chemical corrosion products on the surface of the electrode form a discontinuous raids layer with a thickness of 2.3 to $4.0\mu\text{m}$ observed on lateral and longitudinal deflections - Figure 6, 7.

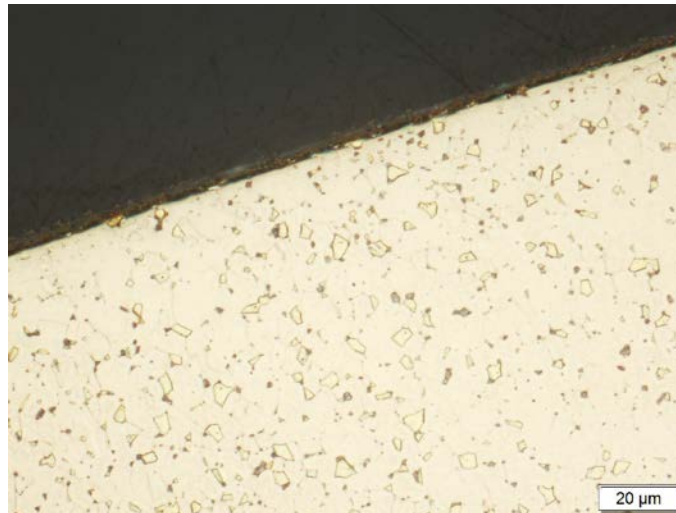


Figure 7. Discontinuous raids layer on the surface of the Cu-Zn-Pb electrode (longitudinal ripple)

Table 3. Results of quantitative chemical microanalysis in the raids layer of the Cu-Zn-Pb electrode at the points marked in Figure 9

Element	Point							
	1		2		3		4	
	% weight	% weight	% weight	% atom	% wag	% atom	% wag	% atom
OK	22,56	46,15	33,45	56,87	18,69	43,44		
AlK	17,68	21,44	22,99	23,18	06,46	08,46		
SiK	02,67	03,11	01,97	01,91	01,53	01,60		
CaK	00,78	00,63	01,87	01,27	01,17	01,08		
CuK	33,72	17,36	20,66	08,84	40,79	23,87	57,65	61,25
ZnK	22,59	11,31	19,06	07,93	40,79	14,71	35,31	36,46
PbL							07,04	02,29
SK					05,52	06,40		

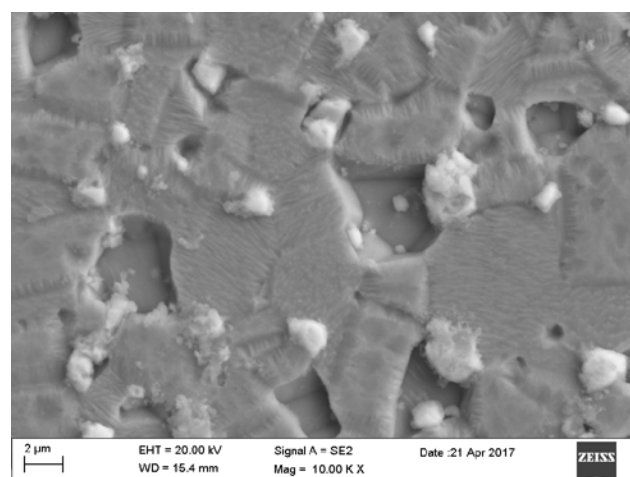


Figure 8. A phase grains with lead separations in the structure of a Cu-Zn-Pb alloy electrode

On the diffractogram made from the surface of the electrode there are diffraction lines originating from copper, lead, copper oxide and copper-zinc compounds (CuZn , $\text{Cu}_{0,67}\text{Zn}_{0,33}$) – Figure 10. The maximum number of diffraction lines with the highest intensity is observed from the

surfaces of the Cu_2O oxide phase, which indicates the majority of this phase in the layer under investigation. Diffraction lines originating from copper-zinc compounds (CuZn , $\text{Cu}_{0.67}\text{Zn}_{0.33}$) and small ones from pure lead are also characterized by high intensity - Figure 15.

Microanalysis in micro-areas of the raids layer of the investigated electrode allowed to state that in its chemical composition there are elements such as oxygen, copper, zinc and Al, Si, Ca, the amount of which is shown in Table 3.

The highest oxygen concentration of 56.87% occurs at the boundary layer of the atmospheric layer ozone and oxygen. As the distance from this limit increases to the electrode material, the oxygen concentration decreases significantly from 56.87% to 43.44% with increasing content of copper and zinc. The elements Al, Si, Ca, present in small amounts, appear in microanalysis, and their presence is probably an effect associated with the preparation of experiments preparations.

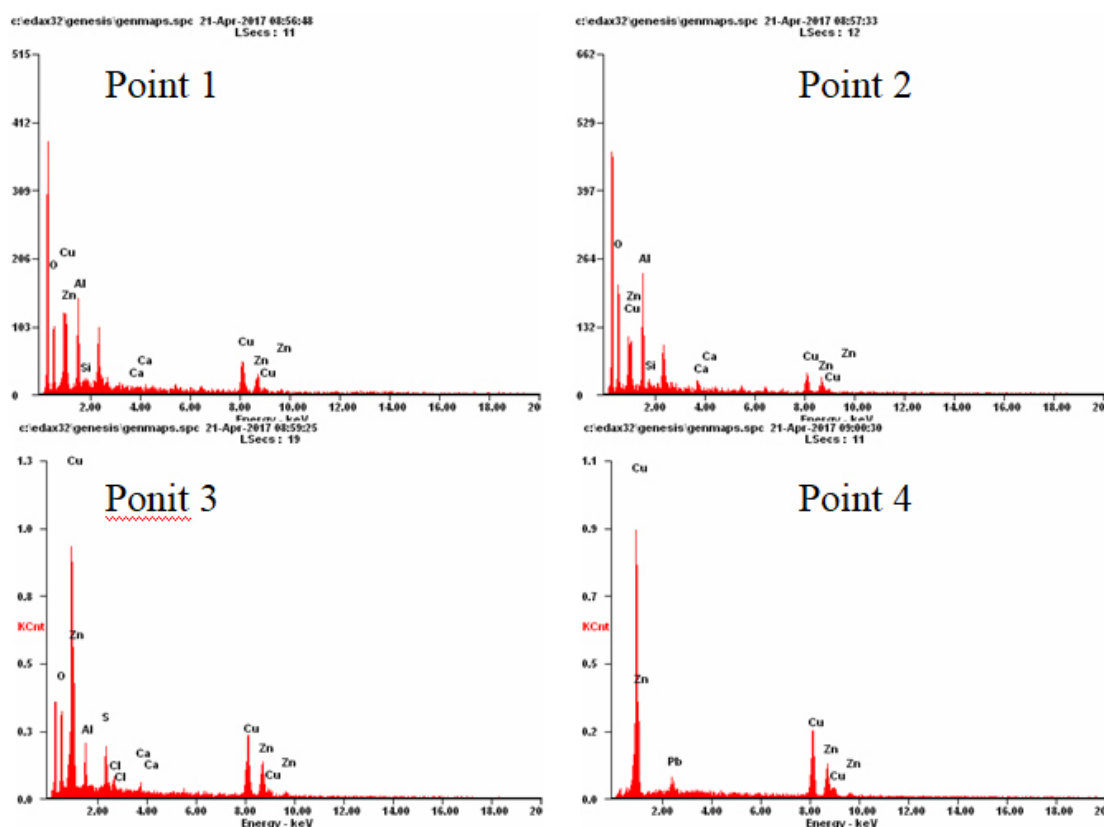
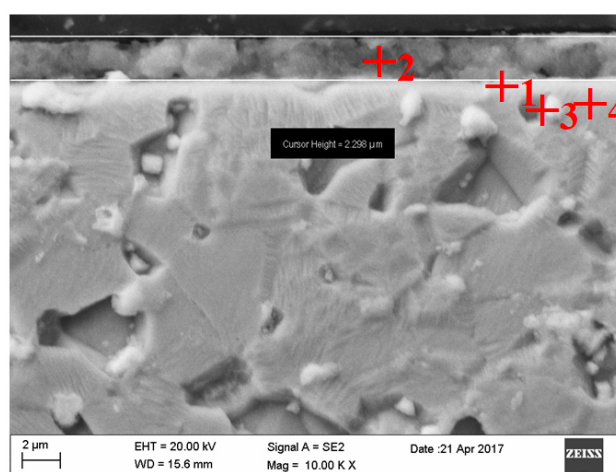


Figure 9. Results of point chemical microanalysis in the raids layer (point 1, 2,3) in the Cu-Zn-Pb electrode material (point 4)

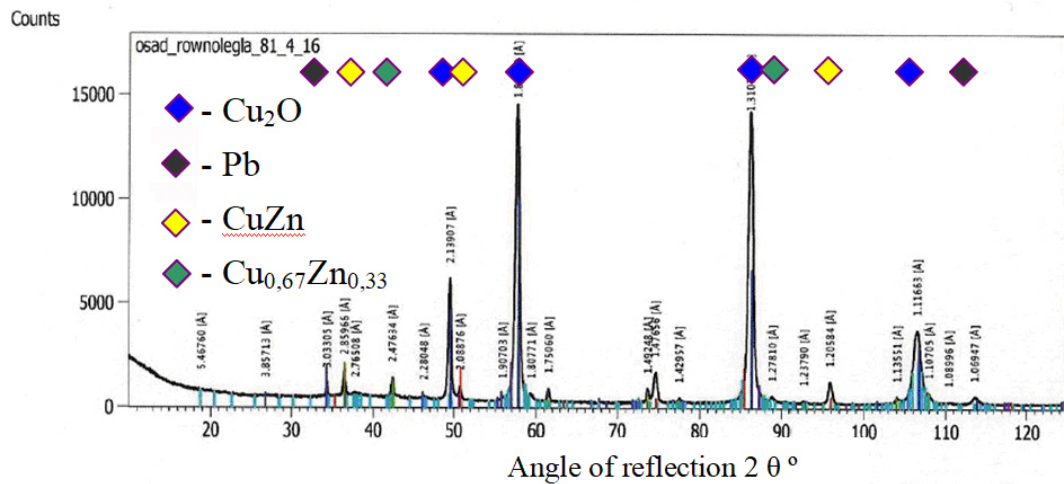


Figure 10. The diffractogram of the surface of the Cu-Zn-Pb alloy electrode

The structure of the electrode made of copper indicates the annealed condition of the material - Figure 11 - 12. The material is characterized by grains with average surface area in the range from 0.02 to 0.06 mm², inside which there are numerous twins – Figure 11. Oxidation products are located on the surface of the electrode in the form of a discontinuous raids layer - Figure 12. The thickness of the disclosed layer is from about 0.89 μm to 2.70 μm - Figure 12. The phase composition of this layer was determined on the basis of X-ray quality analysis - Figure 15.



Figure 11. Grains with twins in the structure of a copper electrode

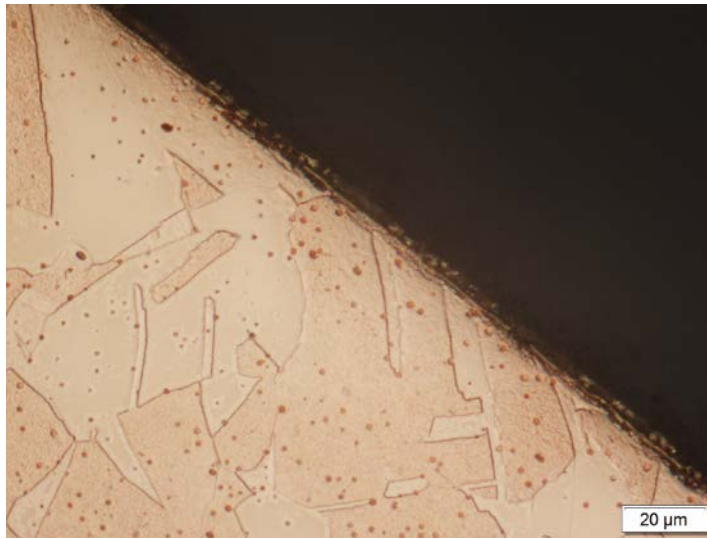


Figure 12. A discontinuous raids layer on the surface of a copper electrode

On the diffractogram made from the surface of the Cu electrode, the presence of diffraction lines of high intensity originating from the copper planes and of lower intensity than the surfaces of the Cu_2O oxide was found. The presence of oxygen and copper was found in the chemical composition of the raids layer analyzed point wise. In the analyzed points 1 and 2, the oxygen concentration is 12.84% and 10.41% respectively – Figure 14, Table 4.

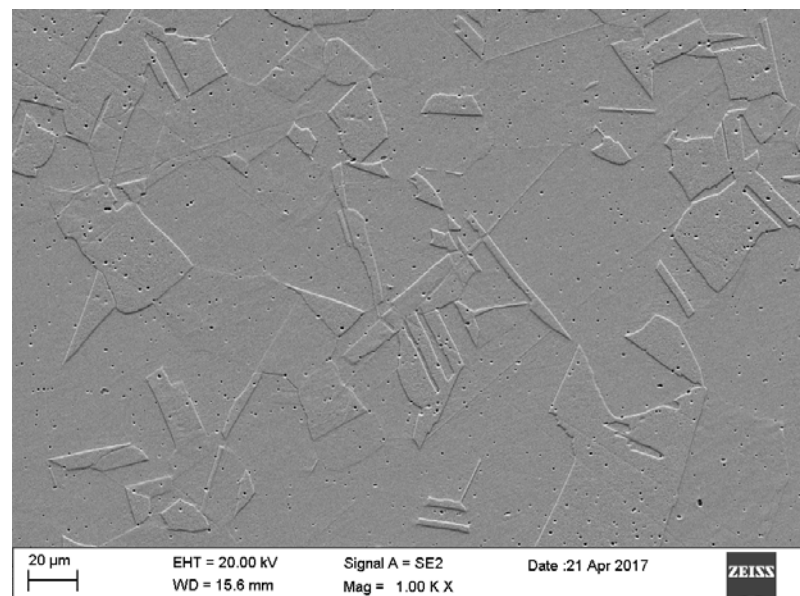


Figure 13. Displaced Cu grains in the structure of a copper electrode.

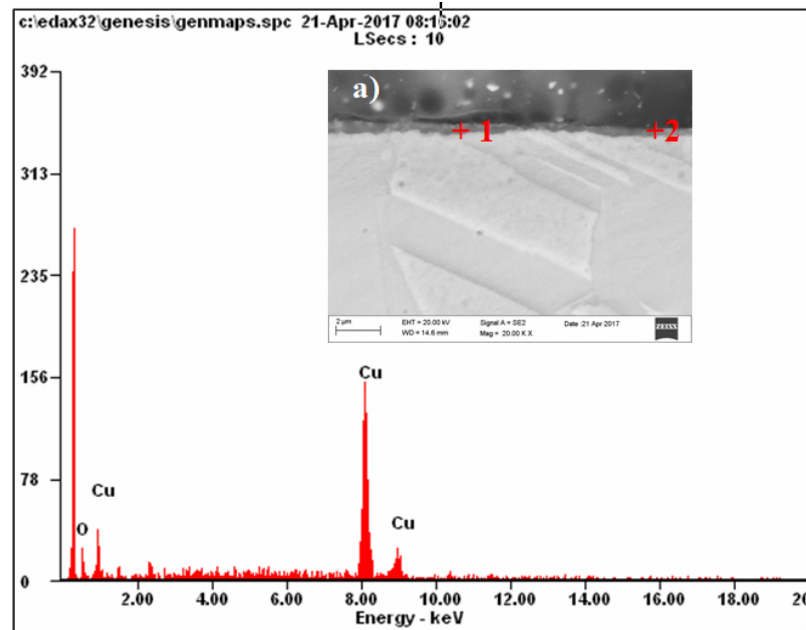


Figure 14. Results of microanalysis of the chemical composition from area 2 marked on the micrograph (a), (Cu electrode)

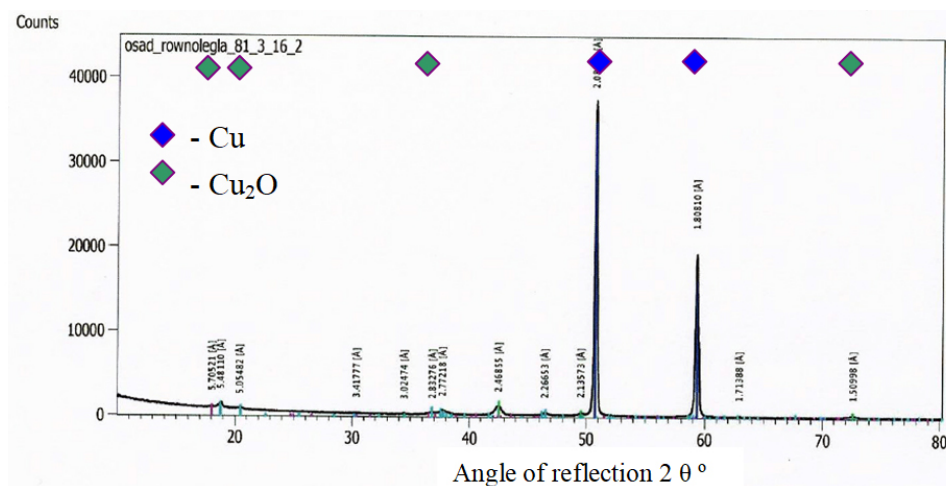


Figure 15. A diffractogram from the surface of a copper electrode

Table 4. Results of the quantitative microanalysis of the chemical composition in the areas of the raids layer on the copper electrode, marked on the photomicrographs (a) - Fig. 14.

Element	Point			
	1		2	
	% weight	%atom	% weight	% atom
OK	03,58	12,84	02,84	10,41
CuK	96,42	87,16	97,16	89,59

5. Conclusions

In the ozone production process, the plasma reactor electrode works in an aggressive environment of ozone generated and oxygen being ionized and recombined. As a result of working in such conditions, the electrode is oxidized in the process of chemical corrosion. The dynamics of

plasma generation process and the type of electrode material working in changing process conditions are the decisive factors influencing the concentration of ozone produced. The influence of the medium, which is the electrode material, depends mainly on its resistance to corrosion in the environment of dynamically changing conditions, e.g. electrode rotation, oxygen flow through the rotating electric field and the long monthly working time of the plasma reactor. The electrodes were made of materials characterized by similar corrosion resistance, namely Cu-Zn-Pb alloy and copper. Corrosion products formed on the surface of individual electrodes after 30 days of work in the plasma reactor showed different geometry, structure and chemical composition in the micro-areas of the raids layers. After one month of exploitation, corrosion products with a thickness of up to 20µm, typical for raids layers have been found on the surface of the electrodes [11]. On the surface of the electrode of Cu-Zn-Pb alloy and pure copper, the thickness of the resulting film is from approx. 4µm to 20µm respectively. The raids layers are characterized by discontinuities revealed both on longitudinal and lateral decouments - shade 6, 7, 12.

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