Visualizations with high speed framing camera of the evolutive phases related to the development of a microplasma in ionic solution

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This technical article presents experimental results of qualitative analyses by photos with high speed framing camera of the evolutive phases related to the development of a microplasma in ionic solution with a controlled electrical conductivity. These analyses became possible by the construction of an experimental device consisted of an electric voltage pulse generator electrically connected with the high speed framing camera and with two electrodes positioned in a micrometric distance from each other forming an electrochemical cell. The application of an electric voltage pulse between the electrodes in a predefined time in microseconds and under special experimental conditions using the generator triggers in the same time the high speed framing camera. This camera makes it possible to obtain extremely rapid various photos of the chemical and physical phenomena occurring between the electrodes. Through the obtained photos it can be verified that the development of a microplasma in ionic solution is firstly the direct result of the formation of a volumetric quantity of gas within the space between the electrodes. The intensity of the electric voltage pulse applied at the electrodes conduces to the “rupture” of the dielectric properties of this gas, thus producing a microplasma with special physical characteristics. It is also explained that the gas formed between the electrodes is hydrogen resulting from the electrochemical reactions developed in the ionic solution after the application of the electric voltage pulse between the electrodes.

Palavras-Chave: solução ionic solution, microplasma, high speed framing camera, electric discharge, pulse generator.

1. Introduction

A microplasma in form of a luminous electric discharge (“glow discharge”) with elevated thermal energy can be formed in liquid and gaseous dielectric contained between two electrodes positioned in a small distance from each other. For generation of this microplasma, special experimental conditions must be controlled, as for example, the total distance between the electrodes and intensity of electric voltage applied at them, so that an ionization process\(^1\) of the dielectric molecules can take place, consequently with the formation of electrons and ions with high kinetic energy. The elevated temperature produced with such microplasma is sufficiently high (~10,000°C) to provoke a localized melting of the electrodes’ materials, generating a microcrater. In some experimental cases, the total time referred to the “thermal contact” of the high energy of the microplasma with the electrodes’ surface can be precisely controlled by a special electronic device, as for example, a pulse generator. Certainly, the formation of a microplasma is directly connected with the development of important physical phenomena happening simultaneously. For example, a very strong emission of light in form of electromagnetic waves in the visible spectrum is also the result of these phenomena. Furthermore, the extremely high electrical conductivity of this type of microplasma as consequence of its great degree of ionization\(^2\) is a significant evidence of occurrence of physical phenomena related to the interaction of particles (electrons and ions). The spatial distribution of electrons and ions as well as the collisions between them given the final characterization of the microplasma, such as temperature, density of electrons, frequency (oscillations of electrons) and degree of ionization.

Another real possibility to rapidly generate a microplasma with the above mentioned characteristics is through the use of an electrically
non-conductive medium (an ionic solution) confined between two separated electrodes forming a very small electrochemical cell, with the application of an electric voltage at them. If the distance between the electrodes is very small, an elevated intensity of applied electric voltage primarily results in the development of a gas quantity in the ionic solution contained within the space between the electrodes, provoking an electrical isolation that conduces in the sequence to the formation of microplasma in form of an electric discharge. In this special case, there is firstly the induced production of a gaseous dielectric medium by electrochemical reactions between electrodes to immediately promote the extremely rapid generation of a microplasma with a defined duration in some µs.

The electrochemical/physical effects resulting of the generation mechanism of such important type of microplasma can be certainly used for the material removal from an electrically conductive workpiece with some special technical advantages. To exactly produce a microplasma in ionic solution it is necessary to use a pulse generator, whose electronic characteristics provide adequate technical conditions for the development of electrochemical and thermal phenomena between two electrodes positioned in a micrometric distance from each other.

The technical content of this paper describes qualitative experimental investigations with the use of high-speed framing camera (HSFC) to correctly analyze the development phases of a microplasma in ionic solution contained between two electrodes. To possibility the realization of these experiments, a modern experimental device was constructed, where the HSFC electronically connected with a pulse generator has been precisely adjusted to take several photographic images of the above mentioned phases after being applied an electric voltage pulse between the electrodes. All results of these experiments are conveniently explained having as technical support the most important fundamentals of electrochemistry and plasma physic with their respective mathematical equations.

This paper initially presents in several details the technical characteristics of the experimental equipment developed to realize the experiments and, in the sequence, the experimental adjustments to possibility the generation of a microplasma in ionic solution.

2. Methods

2.1 Electronic and mechanical characteristics of the experimental device

Figure 1 presents the equipment (construction Robert Bosch GmbH, Bamberg) used to generate a microplasma in ionic solution under specific experimental conditions. This equipment is basically composed of a pulse generator, mechanical system (for holding and positioning of a workpiece and tool in a small distance from each other), high-speed framing camera (construction Institute IWS-Dresden, Germany) and oscilloscope (Gould 500 MHz).

The tool (tool-electrode) is positioned in the z-axle of the equipment with the possibility of executing precisely a positioning movement in the direction of the workpiece (workpiece-electrode) controlled through an electric motor. The functioning conditions of this motor are clearly defined by an open-loop controller in order to promote the correct feed movement of the tool-electrode along the z-axle without significant positioning deviations. For adjusting a very small distance ("gap") between the electrodes, the tool-electrode (a small cylindrical bar of hard metal with diameter of 1mm) is manually moved along the z-axle until its extremely light contact with the workpiece surface. In this moment the Haidenhain-system (a mechanical system to measure distances), which was mounted at the z-axle to possibility measurements of length, is exactly initialized with null value. In the sequence, the electric motor transmits through a command of the open-loop controller a driving force to the spindle of the z-axle, so that the tool-electrode fixed in this axe can be progressively moved in pre-defined distance over the workpiece surface. The gap resulting between the Electrode is also controlled by the Haidenhain-system to confirm the positioning coordinate of the tool-electrode along the z-axle previously adjusted by the open-loop controller. The gap is then completely filled with a small volume of ionic solution with controlled electrical conductivity.

The pulse generator (construction Robert Bosch, GmbH, Bamberg) is electronically connected by means of special electric cables with the workpiece and tool-electrode as well as with the high-speed framing camera, light source and oscilloscope. Through this generator an electric voltage pulse with a respective intensity in volts and periode of time can be applied between tool-electrodes and workpiece in order to generate a microplasma in the ionic solution contained within the gap. At the moment of the automatic application of a voltage pulse between the tool-electrode (with negative electrical polarity or "cathode") and workpiece (anode), an output electrical signal from the pulse generator automatically triggers at the same time the other electronic equipments which are connected with it in form of an electronic arrangement. The geometrical
form of the electric voltage pulse applied between the electrodes related to the formation a microplasma in ionic solution can be also visualized in details in the oscilloscope screen. A voltage divider transmits the signal of electric voltage pulse produced at the electrodes, whereas a current probe permits to obtain a signal of electric current in amperes in direct correspondence to this voltage pulse. The voltage divider and current probe are electronically connected with the oscilloscope and also mounted within the electronic circuit of the “pulse generator, tool-electrode and workpiece”.

Figure 1. Equipment for the experimental investigations related to the development phases of a microplasma formed in ionic solution.

2.2 Adjustment of the high-speed framing camera and experimental parameters

To perform the experiments, the gap between the electrodes was adjusted in 50 µm and subsequently filled with an ionic solution chemically composed of NaCl and with electrical conductivity of 100 mS/cm. After these adjustments, an optical visualization of the gap could be made by a special focalization with use of specific electronics functions of the HSFC. This type of camera was specially developed for obtaining photos of extremely rapid phenomena at a speed 10,000 frames/s and in pre-defined exposure time of 100 nsec (table 1). Each channel of the camera (in the total 4) can be independently adjusted to take photos of the conditions of the gap after application of an electric voltage pulse between the tool-electrode and workpiece. Four sequences of experiments (repeated five times) were realized (see table 1). For example, in the sequence 1, the first channel of the HSFC captures images of the gap after 2 µsec of the application of a voltage pulse between the electrodes at a frame rate of 10,000 frames/s and with the exposure time as previously mentioned. The channel 2 takes various photos of the gap conditions after 6 µsec of the application of the voltage pulse between the electrodes, and so on. The several images recorded with these four sequences of experiments are stored in the HSFC and can be posteriorly played back in slow-motion. The great resolution and clarity of the obtained images is also guaranteed by the utilization of the light source (a strobooscope) that can be triggered together with the HSFC. The light source enables the correct illumination of the gap for the four channels of the camera during their operations.

3. Results and Discussion

Figure 2 presents a group of images obtained with the sequence of experiments described earlier. These images are the result of the development phases of a microplasma being formed in ionic at different spaces of time (ta, tb, tc and td) after application of an electric voltage pulse with intensity uc between the electrodes. It is possible here to identify that the voltage uc has as direct consequence the production of a volumetric quantity of gas at the tool-electrode surface (in ta). This gas quantity increases extremely rapid over the time in the direction of the workpiece surface. It is also explained that this gas volume comes from electrochemical reactions occurring in the gap. Because of the fact that the ionic solution contained in the gap is a chemical mixture between NaCl and deionised water with a low electrical conductivity, ions H⁺ are moved in the direction of the tool-electrode with a very rapid velocity in dependence on the electrical field applied in the gap as result of the voltage uc. At the tool-electrode surface, these positive ions receive electrons producing hydrogen gas (H₂) (eq. 1) through a chemical reduction process. At the workpiece, ions Cl⁻ are submitted to an oxidation reaction with the generation of a quantity of gas Cl₂ (eq. 2)[1]. The electrochemical mobility of the ions H⁺ and Cl⁻ defines the total rate of gas formation respectively at the tool-electrode and workpiece and strongly depends on the temperature and electrical conductivity of the ionic solution.

The intensity of electric current ic flowing in the electronic circuit “tool-electrode, ionic solution and
Because of the flux of electric current, the formation rate of the H$_2$ (g) at the tool-electrode and quantity of mass in grams removed of the workpiece are proportional to the current $i_c$. Due to the fact that ionic solution utilized in this experiments do not cause the formation of passive film of oxide on the workpiece surface, there is no lost of the current $i_c$, so that a elevated current density in A/cm$^2$ can be provided between the electrodes. The volume of hydrogen gas produced during a period of time $t_c$ can be expressed in terms of the electric current according to equation 3:

$$V(H_2) = I_c \cdot \frac{1}{0-t_c} \int I_c(x)dx$$

here, $V(H_2)$ = quantity of hydrogen gas formed at the tool-electrode as function of an average current $I_c$ related to the periode of time $t_c$; $I_c(x)$ = a mathematical function of the electric current $i_c$. Because of the flux of electric current $I_c$, the tool-electrode can be defined by an equilibrium potential $E$ (in volt) that is different of the tool-electrode potential $E^o$ in the ionic solution without the presence of an intensity of electric voltage applied between the electrodes. The mathematical difference between these two types of electric potentials is technically called of overpotential ($\eta$) and can be determined by the equation 4. The electric current $i$ (eq. 5) being generated only at the interface between the tool-electrode and ionic solution in dependence on $\eta$ is responsible for the development of the gas hydrogen. Such current significantly differs from $i_e$ and can be precisely calculated by the Butler-Volmer equation (Eq.5). The velocity related to the formation of the current $i$ is a consequence of the transport of ions in the ionic solution through convection, diffusion and migration (eq. 6). Each species of ion of the ionic solution is considerate to have a specific chemical potential:

$$\eta = E - E^o$$

$$i = i_0[\exp\left(-\frac{aF\eta}{RT}\right) - \exp\left(\frac{(1-a)F\eta}{RT}\right)]$$

$$J_i = J_{\text{diff},i} + J_{\text{migr},i} + J_{\text{conv},i}$$

The process of hydrogen evolution is completed at the exact moment of the contact of the gas volume being formed at the tool-electrode with the workpiece surface. The period of time from the application of the electric voltage pulse between the electrodes until the contact of the gas volume with the workpiece surface (referring to $t_c$) is called electrochemical phase of the development process of an electric discharge in ionic solution. In this case, there is an electrical isolation of the space between the electrodes because the presence of a dielectric (hydrogen gas volume) with defined physical properties (for example, dielectric constant $\varepsilon$, permittivity and electric susceptibility $\chi$). The intensity of $u_e$ applied between the electrodes provokes the formation of an induced dipole moment $u$ (electrical polarization) in the dielectric (eq. 7)[7]. The gas molecules of the dielectric also have here linear, rotational and vibrational motion in defined degrees of freedom[8] with very low collisions and small electrostatic attractions by means of van der Waals’s interactions between themselves. Furthermore, thermodynamically, the dielectric gas confined in the space between the electrodes can be characterized as having a low pressure, volume and temperature:

$$\bar{P} = \chi_v \varepsilon_0 E$$

here, $P$ = electrical polarization of the dielectric; $\varepsilon_0$ = permittivity of free space; $E$ = intensity of the electric
field applied between the electrodes in dependence on $u_c$.

The electric breakdown of the dielectric permitting the generation of a microplasma between the electrodes occurs through a very rapid ionization process with formation of a great electron density$[9]$ in the gap. To correctly promote this ionization (by a process named as “impact ionization”), a small quantity of electrons with negative charges emitted from the tool-electrode surface due to “cold field emission” (eq. 8)$[10]$ is strongly accelerated in the direction of the workpiece surface by presence of the electric field. During this movement with high kinetic energy, some electrons frequently collide elastically and inelastically with neutral molecules of the dielectric gas, so that other electrons, positive ions and exited atoms are formed in the gap (eq. 9, 10)$[11]$. Now, positive ions are accelerated to the tool-electrode surface and electrons continue being moved to the workpiece, where consequently the electrical resistivity of the gap is gradually reduced due to a strong increase of the ionization degree of the dielectric gas (development of an “electron avalanche”)$[12]$.

The mechanical impact of the positive ions at high velocities with the tool-electrode and of electrons with the workpiece surface causes an increase of the thermal energy of these metals. In this case, a small quantity of electrons characterized by an electric current density is produced at the surface of the tool-electrode and workpiece through “thermal emission” (eq. 11)$[13]$. The formation of photons from excited atoms also determines the production of several other electrons in the gap. The collisions of photons with the surface of the electrodes are responsible by the generation of electrons through “secondary emission”. The very great quantity of electrons and positive ions produced by all these physical phenomena now identifies the gap as being completely ionized. This situation shows the total development of microplasma between the electrodes with high thermal energy. At this moment, the electric current flowing in the gap and the voltage between the electrodes are equalized respectively in values $i_D$ and $u_D$. The developed microplasma is only totally ended at the moment of the sudden elimination of the electric voltage source between the electrodes relative to the time period $t_D$.

$$\text{Eq. 8} \quad j(E) = K_1 \frac{|E|^2}{\Phi} e^{-K_2 \Phi^{1/2}/|E|}$$

here, $j(E)$= density of electric current emitted of a metallic surface by cold field emission in dependence on the electric field; $K_1$ and $K_2$= constants related to the material of the metallic surface; $\Phi$= local work function (“potential barrier”):

$$\text{Eq. 9} \quad e^- + H_2 \rightarrow H_2^+ + 2e^-$$

$$\text{Eq. 10} \quad e^- + H_2^+ \rightarrow H + H^+ + e^-$$

$$\text{Eq. 11} \quad j_s = AT^2 e^{W/RT}$$

here, $j_s$= density of electric current at the metallic surface, $A$= area of the metallic surface; $W$, $T$= “work function” and temperature of the metallic surface; $k$= Boltzmann constant.

The development process of the microplasma after the ionization period conduces to the formation of other important phenomena between the electrodes, such as the recombination of electrons and ions with the generation of electromagnetic waves or the mutual neutralization of positive and negative ions. In the first development phase of the microplasma, the electric voltage $u_c$ exponentially decreases over the time to $u_D$. During this period of time the electric current flowing between the electrodes is concentrated with high density due the “skin-effect” practically only at the external surface of the microplasma. After the moment that the voltage at the electrode is $u_D$, the electric current now flows between tool-electrode and workpiece in the whole cross-section of the microplasma. In this situation, because of the “pinch-effect”, the microplasma becomes radially compressed. This compression conduces to a highest level of the thermal energy related to the microplasma simultaneously generating a melting process in the surface of the electrodes. The material quantity being melted at the electrodes in the form of microcrater is not the same because of the different kinetic energy of electrons and positive ions in the microplasma. There is also here a strong dissipation of thermal energy from the microcrater into the material of the electrodes and from the microplasma to the ionic solution. Furthermore, it is also expected that during the development of the microplasma further production of electrons takes place due to the strong interaction of various photons with high energy (electromagnetic waves with high frequency)$[14]$ and neutral gas molecules. The presence of these photons in the microplasma is certainly responsible for the intensive emission of light that the can be clearly visualized in the figure 2.
The microplasma mentioned can be here considerate as a “non-thermal or cold plasma” because the temperature of electrons (\(T_e\)) is much higher than that of the ions (\(T_i\)) and neutral gas (\(T_{gas}\)) (\(T_e \sim 9700 \, ^\circ C \gg T_i \sim T_{gas} = 27 \, ^\circ C\)). The degree of ionization of this non-thermal plasma is normally estimated in the practice between \(10^{-6} - 10^{-4}\) as an immediate consequence of a “rate of ionization” of neutral molecules at a defined frequency (eq. 12). The electrical conductivity \(\sigma\) of the microplasma produced by this degree of ionization as function of the high density of electrons \((10^{16})\) can be precisely calculated by the equation 13. Here is supposed the quantity of electrons the same of the ions, so that the microplasma is also defined as “quasi-neutral”. Moreover, other important physical parameters used to clearly define some characteristics of the microplasma shown in the figure 2 are the Debye length (eq. 15) and plasma frequency (eq. 16).

\[
\text{Eq. 12} \quad \frac{dn_e}{dt} = n_e v_i
\]
\[
\text{Eq. 13} \quad \sigma = \frac{e^2 n_e}{m v_m}
\]
\[
\text{Eq. 14} \quad n_e = n_0 \exp(e \phi / kT_e)
\]

where, \(n_e\) = electron density; \(v_i\) = rate of ionization of the microplasma; \(v_m\) = effective electron collision per second; \(m\) = electron’s mass \((9.01 \times 10^{-31} \, \text{kg})\); \(e\) = electric or elementary charge of the electron; \(\phi\) = electrostatic potential; \(n_0\) = equilibrium electron density when \(\phi = 0\):

\[
\text{Eq. 15} \quad \lambda_D = \sqrt{\frac{\varepsilon_0 kT_e}{n_e e^2}}
\]
\[
\text{Eq. 16} \quad \nu_p = (\frac{e^2 n_e}{\varepsilon_0 m})^{1/2}
\]

here, \(\varepsilon_0\) = vacuum’s permittivity; \(\lambda_D\) = Debye length; \(\nu_p\) = plasma frequency;

The result of the combination of all these important characteristics of the microplasma is the development of a very high temperature between the electrodes. This temperature has as consequence a melting process of materials of the electrodes forming a micro-crater with special geometrical forms (fig. 3), where the material being melted during the development of the microplasma is quickly expelled from the microcrater into the surrounding gas volume by special forces after eliminating the voltage source applied between the electrodes. The expelled material is also solidified in form of a small white layer. This microcrater resulting in the surface of the electrodes after switching off the electric voltage between them presents normally two different regions due to a cooling process through the ionic solution. The two regions receive the technical denomination of “thermal influenced zone”. The first region of this thermal influenced zone is defined as “white layer”, as result of the high temperature of the microplasma.

\[\text{Figure 3: Geometry of the discharge crater in the electrodes’ surfaces as result of the high temperature of the microplasma}\]

The white layer, whose thickness can be correctly visualized in details by application of metallographic techniques, is very hard and also present its external surface with geometrical characteristics totally irregular, containing some microcracks and porosities resulting of the contraction of melted material during its solidification. As consequence of this, the white layer is extremely brittle and has residual stresses. Furthermore, beside of the white layer, in direct contact with the non-affected electrode’s material through the high temperature of the microplasma, the second region of the thermal influenced zone is defined by heating above a temperature of 900 °C and the subsequent and sudden cooling of material of the electrode at the temperature of the ionic solution contained in the gap related to the moment of the implosion of microplasma. The metallurgical characteristics of this second region substantially depend on the chemical elements of the electrode’s material.

5. Conclusions

The qualitative results presented in this paper with use of high speed framing camera and a special experimental equipment clearly show all the principal phases referring to the development of a microplasma in electrolytic solution. The microplasma is generated in a gas volume of hydrogen produced through electrochemical reactions and confined in a very small capillary.
space under adjustment of an electric voltage and distance between electrodes as well as an intensity of electrical conductivity of the ionic solution. These experiments certainly open up new possibilities in the technical field of the plasma physic for a better comprehension of the generation mechanism of electric discharges in electrically non-conductive medium with the appropriate utilization of specific experimental conditions. The very high temperature of the electric discharge in the form of a microplasma induces to the formation of a microcrater in the surface of the electrodes with a thermal affected zone. Through the control of the periode time and electric current of the electric discharge the geometrical form of the microcrater can be defined in extremely small dimensions. The possibility for development of a microcrater in metallic materials by a microplasma developed in ionic solution certainly creates a new and important technological principle to produce surfaces with special geometrical forms and mechanical properties.

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6. References


Resumo:
Este artigo técnico apresenta o resultado experimental de análises qualitativas que mostram através de fotografias com câmara de alta velocidade (high speed framing camera) as fases evolutivas referentes ao desenvolvimento de um microplasma em forma de uma descarga elétrica gerado em solução iônica com condutividade elétrica controlada. Estas análises tornaram possibilidades pela constrição de um aparatão experimental constituído de um gerador de pulsos de tensão elétrica que foi conectado eletronicamente com uma câmera de alta velocidade e com dois eletrodos posicionados em uma distância micrométrica um do outro formando uma célula eletroquímica. Aplica-se um pulso de tensão elétrica entre dois eletrodos pelo gerador de pulso em um pré-definido espaço de tempo ajustado em poucos microsegundos sob condições experimentais definidas, acionando ao mesmo tempo a câmera de alta velocidade. A câmera permite de modo extremamente rápido a obtenção de diversas fotos dos vários fenômenos eletroquímicos e físicos que ocorrerem entre os eletrodos. Através das fotos obtidas verifica-se que o desenvolvimento de um microplasma em solução iônica é primeiramente o resultado direto da formação de uma quantidade de gás dentro do espaço entre os eletrodos. A intensidade do pulso de tensão elétrica aplicada entre os eletrodos favorece em seguida a ruptura da rigidez elétrica deste gás que se formou, onde é produzido assim um microplasma com características físicas especiais. Explica-se neste artigo que o gás formado entre os eletrodos trata-se de hidrogênio resultante de reações eletroquímicas desenvolvidas na solução iônica após a aplicação do pulso de tensão elétrica entre os eletrodos.

Palavras-chaves: solução iônica, microplasma, câmera de alta velocidade, descarga elétrica, gerador de pulso.