

UDC 517.958:596, 533.9.004.14, 621.039.6

Plasmatron with Renewable Carbon Nanostructured Covering of Electrodes

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DC arc air plasmatron with longlife electrodes protected by hydrocarbon gas was developed and tested. Atom and ions of carbon from near-electrode plasma deposit on the active surface of the electrodes and form electrode carbon condensate which operates as “actual” electrode. The electrode condensate was examined using Raman spectroscopy, scanning and transmission electron microscopy. It is found that the electrode condensate is composite carbonic stuff made of carbon nano-clusters which consists mainly of single and multi-wall carbon nanotubes and other carbonic forms including some quantity of the copper atoms intercalated to the carbonic matrix.

Keywords: plasmatron, hydrocarbon gas, electrode, carbon nanostructure.

PACS number(s): 81.05.Uw, 81.15.Pq

1 Introduction

Simplicity and reliability of the arc plasma generators (plasmatrons) using cylindrical copper cathode and air as plasma forming gas predestine their application at heat and power engineering for plasma aided coal combustion [1]. Life time of these plasmatrons electrodes is critical and usually limited to 500 hours. Considered in this paper the long life direct current (DC) arc plasmatron has the cathode life significantly exceeded 500 hours. To ensure the electrodes long life the process of hydrocarbon gas dissociation in the electric arc discharge is used. In accordance to this method atoms and ions of carbon from near-electrode plasma deposit on the active surface of the electrodes and form electrode carbon condensate which operates as “actual” electrode. To realize aforesaid the construction of electro arc generator of air plasma has been developed and tested. Fig.1 sketches the scheme of the plasmatron.

Using special orifices 2 propane/butane mixture is supplied to the zone of the arc conjunction to the copper water-cooled electrodes (cathode and anode). As a result inside the cathode cavity and internal surface of the anode medium of carbonic gas is formed. Linked with the arc in series, the magnetic coils 3 guaranty stabilization of the dis-

charge on the electrodes. The arc is initiated using oscillator and starting electrode 4. The processes of propane/butane molecules dissociation and carbon atoms ionization start with the rise in temperature. Arisen from ionization positive carbon ions deposit onto the electrodes surface under the influence of near-cathode decline in potential and form coating of the electrode condensate. This coating is “actual” cathode, deterioration of which is compensated by the flow of carbon ions and atoms. The coating thickness depends mainly on ratio of the flows propane/butane and air and the arc current.

To find out optimal compound of the hydrocarbon gas mixture with air and optimal diapason of the temperatures thermodynamic analysis of the mixture in equilibrium was fulfilled.

Software code TERRA [2] was used for thermodynamic analysis of the multi-component heterogeneous isolated systems (carbon + mixture of gases). TERRA has been developed to calculate high temperature processes. It has database of thermodynamic properties for more than 3500 chemical agents over a temperature range of 300 to 6000 K. The database includes thermodynamic properties of organic and mineral components of hydrocarbon fuels.

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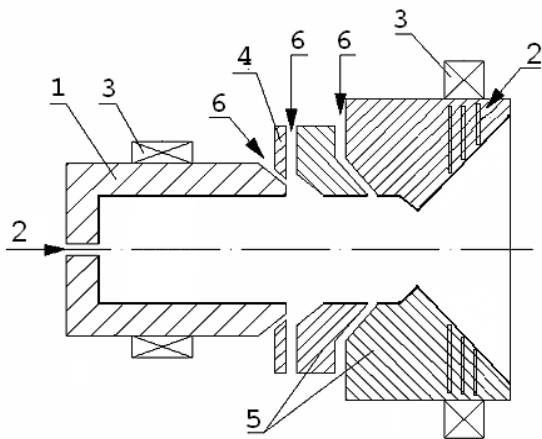


Figure 1 – The scheme of the long life DC arc plasmatron. 1 – Copper cathode; 2 – orifices for hydrocarbon gas supply; 3 - solenoid; 4 – starting electrode; 5 – copper anode; 6 – orifices for supply of plasma-forming gas (air).

2 Computation

The calculations showed that optimal compound of propane/butane/air mixture is as follows: 7.5% C_3H_8 + 7.5% C_4H_{10} + 85% air (Fig. 2). From the figure it is seen that molecular nitrogen concentration in temperature diapason from 300 to 5000 K is practically constant and it is 65 % in mass. With temperature increase its concentration decrease down to 52 % at temperature of 6000 K. Concentration of carbon monoxide (CO) in the temperature interval 1000-5000 K is practically constant too and it is about 30 %. Concentration of condensed carbon in the temperature interval 300-1000 K decreases from 11 % to 0.1 % in mass. At the further increase of temperature methane (CH_4) appears in gas phase. Its maximal concentration reaches 3.5 % at temperature 2500 K. At higher temperature it dissociates into atomic carbon and hydrogen. At temperature 3000 K hydroxyl (OH), nitrogen oxide and nitride (NO and CN) are observed in gas phase. At temperature higher than 4000 K in gas phase atomic nitrogen (N) is appeared.

The computation revealed that in accordance with maximal level of gaseous carbon concentration optimal diapason of temperature is 5000-6000 K.

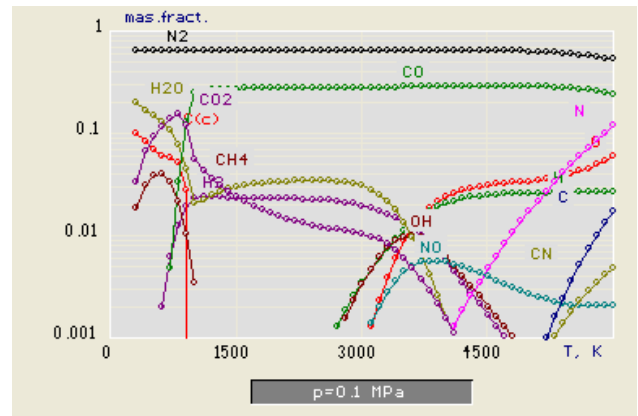


Figure 2 – Species concentrations versus temperature for the mixture 7.5% C_3H_8 + 7.5% C_4H_{10} + 85% air.

3 Measurements

This paper reports the results of complex physicochemical investigation of phase, structure and element compound of the material of carbon nanostructural coating which is generated from propane-butane mixture on the cathode of the plasmatron.

Some measurements of the long life plasmatron work regimes are gathered in Table 1. It is seen that when power of the plasmatron was in interval 76 – 132 kW and propane/butane flow in range of 0.4 – 0.7 l/min thermal efficiency of the plasmatron (η) reached 90 %. At that mass averaged temperature at the exit of the plasmatron (T) increased to 5000 K.

Table 1 – The results of the experiments.

N	I, A	U, V	Q _{gas} , l/min	η	T, K
1	200	380	0.4	0.9	3500
2	300	360	0.4	0.89	4100
3	400	330	0.4	0.88	4800
4	300	360	0.7	0.89	4800
5	300	380	0.7	0.9	5000

Fig. 3 demonstrates photos of the cathode spots of the arc conjunction made during some experiments. Square of the cathode spots depends not only on the power of the plasmatron but also on propane/butane mixture flow.



Figure 3 – Cathode spots of the arc conjunction at different regimes.

During the work of the plasmatron a film of the cathode condensate is formed in accordance with the processes of propane/butane molecules dissociation and carbon atoms ionization. Arisen from ionization positive carbon ions deposit onto the cathode surface under the influence of near-cathode decline in potential and form the film of the electrode condensate. It was determined the following parameters of the films. The film consists of carbon of 96.74-98.47 mass %, hydrogen of 1.24-2.26 mass % and cuprum of 0.30-1 mass %. Interplanar spacing is 0.333 (100%), 0.207 (1%), and 0.168 (5%). Specific electrical resistance of the electrode condensate is less than $10^{-8} \Omega \cdot m$. Thus the film of the cathode condensate is current installing polycrystalline graphitic material.

Fig. 4 presents Raman-spectra of the cathode condensate film. The specter was received using infrared laser with wave-length of 1.064 mkm. Black side, which was faced to the orifice of propane/butane supply, was analyzed. Carbon condensate is mechanically firm film of carbon. The surface of the film is black, its structure is flocculent and filiform. Carbon fibers are oriented in parallels with each other and normally to the surface of the cathode. The surface faced to arc zone of the plasmatrone is shiny, continuous and of a gray colour. In the Raman-spectra (Fig. 4) there are three intense bands of 1290.0 cm^{-1} , 1581.9 cm^{-1} , and 2564.5 cm^{-1} with their intensity 0.04, 0.05, and 0.05 of relative unit respectively. The first two intense bands are lines of Raman-spectrum of the first order. They are known as D- and G-lines of nanocluster graphite correspondingly. Abnormally strong band 2564.5 cm^{-1} is the first upper partial of the main D-oscillation at 1290.0 cm^{-1} and it is Raman-spectrum of the second order. Accordingly, the band 3191.23 cm^{-1} is the first upper partial of the G-line. The band 2876.64 cm^{-1} is also Raman-spectrum of the second order, but it is the main tone generated at composition the main oscillations (D + G) of nanocluster

carbon. Weak band 1335.58 cm^{-1} can be inclusion of diamond-like carbon into the cathode condensate.

Comparison of the Raman-spectra of the condensate with the spectra of carbon materials known from Ref. [3, 4] gives their coincidence with Raman-spectra of multi-walled carbon nanotube (MWNT) with some injection of the other forms of carbon, including single-walled carbon nanotube (SWNT). Some quantity of copper atoms falling into the carbon condensate is a catalyst for producing of carbon nanotubes.

Note that in the low-frequency region of the Raman-spectrum the bands at 169.74 cm^{-1} , 203.98 cm^{-1} , 240.57 cm^{-1} , 273.02 cm^{-1} etc. are registered. They concern to so-called radial breathing mode (RBM). Knowing value of the frequency (ν) of these RBM, and using formula $\nu = 223.75/d$ any can calculate carbon nanotubes diameter (d) [5]. The diameter of the nanotubes from the cathode condensate calculated using this formula is varied from 0.82 nm to 1.32 nm.

Now it is well known that physical-chemical properties of carbon nanotubes are unique. Their conductivity is better than conductivity of all conventional conductors and nanotubes can withstand current density 102-103 times more than metals. Also they have high heat conductivity, they are very mechanically firm, 1000 times more firm than steel and they gain the properties of semiconductors at their curling or flexion. For long-live work of the electrodes it is of especial importance that carbon nanotubes have high emission of electrons, they are chemically inert at high electric field intensity (107 - 108 V/m) and residual gas ions bombardment. All these properties indicate that nanotubes and the composites on their base are ideal material to protect the plasmatron electrodes and as a consequence to prolong their life. Thus the cathode condensate is produced in accordance with propane/butane pyrolysis in conditions of high-accuracy arc discharge with magnet focusing without use of rare gas (argon or helium).

Beside Raman spectroscopy investigation the electrode condensate was examined using atomic power microscope (Fig. 5) scanning electron microscope (SEM) (Fig. 6) and transmission electron microscope (TEM) (Figs. 7 and 8). As it is seen the basic mass of the carbon sample (about 80 %) is represented as film and band graphite particles collected to aggregates of various size and density. Basal cleavage spacing of these particles is a little more than one of "ideal" graphite. It is $d_{002} = 3.45$ -

3.55 Å, in contrast to $d_{002} = 3.35$ Å of “ideal” graphite. Width of the bands varies from 4 to 40 nm.

Sometimes film and band particles collected into stratified packages.

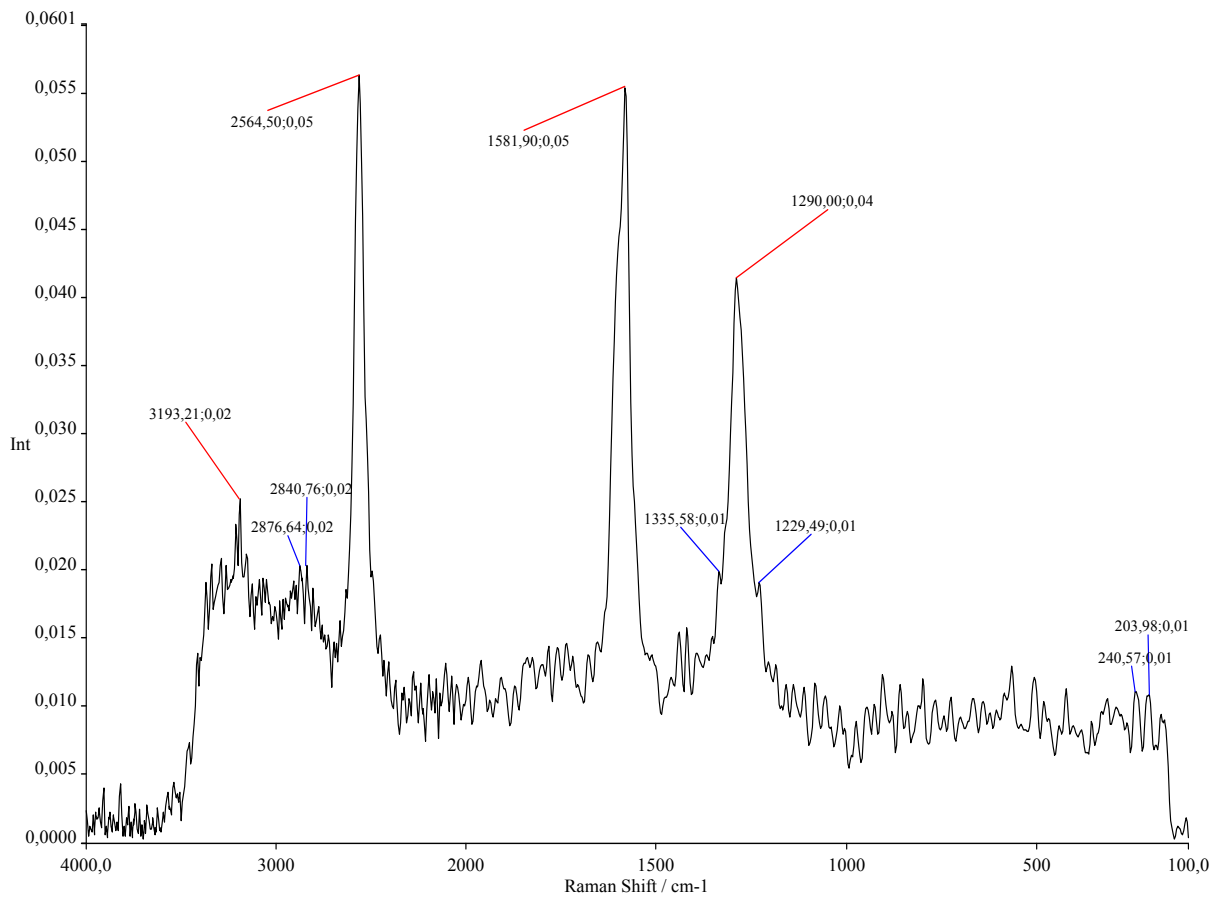


Figure 4 – Raman-spectrum of the carbon condensate from copper cathode of the plasmatron fulfilled using Fourier spectrometer SPECTRUM GX (PerkinElmer, USA). The spectrum registration conditions: $\lambda = 1.064$ mkm, 100 scans, 1500 mW.

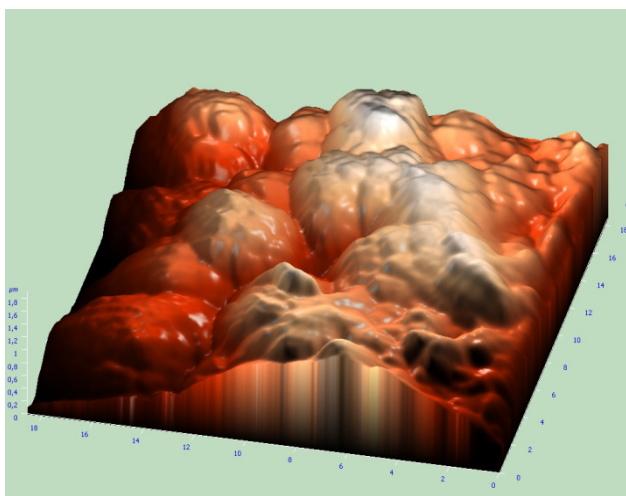


Figure 5 – Image of a sample of the cathode condensate through atomic power microscope.

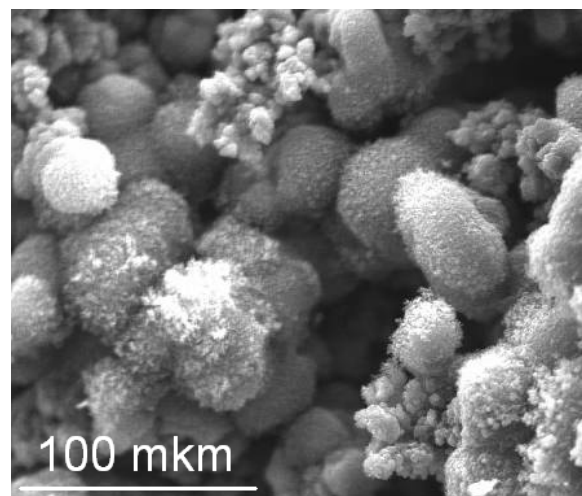


Figure 6 – SEM image of a sample of the cathode condensate.

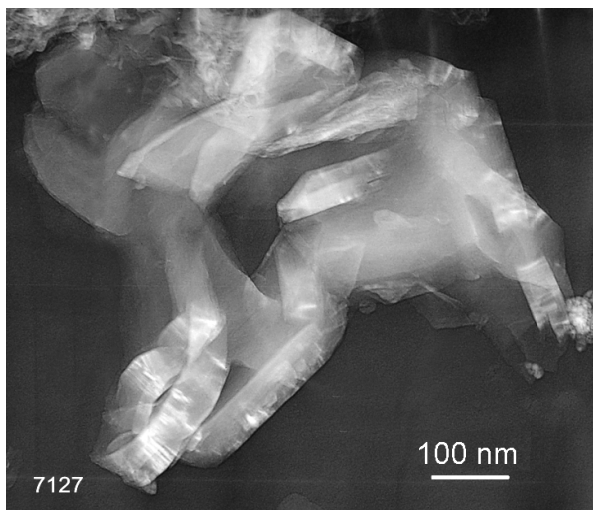


Figure 7 – 02TEM image of a sample of the cathode condensate.

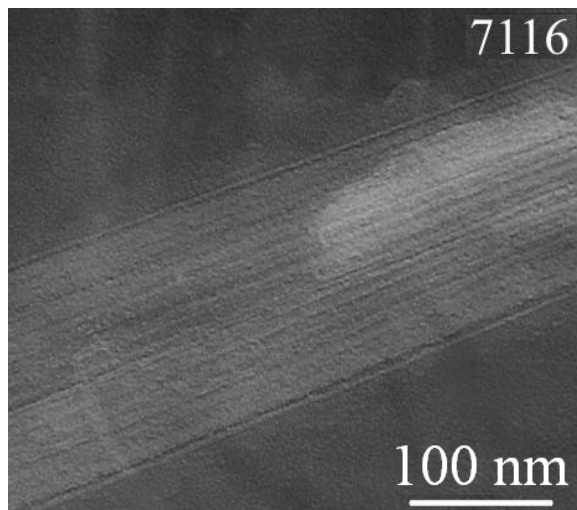


Figure 8 – TEM image of a sample of the cathode condensate.

4 Conclusions

On the base of atomic microscopy, SEM, TEM and the Raman-spectroscopy investigation, it can be concluded that the cathode condensate is composite carbonic stuff made of carbon nano-clusters which consists mainly of single and multi-walled carbon nanotubes and other carbonic forms including some quantity of the copper

atoms intercalated to the carbonic matrix. In the regimes with overflow of propane/butane the soot contained 10 % of composite material in the form of nanotubes was received.

Lifelong of the cathode totals more than 500 hours. The experiments confirmed principal possibility for unlimited long-life of the cathode filmed with carbon nanostructural material.

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