D.C.—ARC PLASMA GENERATOR FOR NONEQUILIBRIUM PLASMACHEMICAL PROCESSES[1)]

KVALTIN, J.[2)], Prague

The conditions for nonequilibrium plasmachemical reactions are discussed, especially those for high threshold synthesis. The analysis of conditions for the generation of the nonequilibrium plasma is made and the design of the d.c.–arc plasma generator is suggested on the basis of a chosen criterion. The measured E–I–u characteristics of atmospheric pressure Ar arc are presented as well as the positive plasma column potentials of that generator.

I. INTRODUCTION

The vibrational energy of molecules E_v is the most effective energy in realizing the endothermic high threshold reactions, e.g. the simple reactions of the type:

$$A + BC \rightleftarrows \mathrm{AB} + \mathrm{C} \tag{1}$$

The translational energy of the particles E_t contributes to the energy E_v during the collision if the exchange of atoms occurs (see [1]). Macheret et al. suggested to determine the reaction rate coefficient $K(T_g, T_v)$ by integration of the crossection function $\sigma[E_t, E_v]$, which depends on both these energies. For a given energy distribution functions $f_t(E_t)$, $f_v(E_v)$ [1] then is

$$K(T_g, T_v) \sim \iint\limits_{E_t = F(E_v)}^{\infty} \sigma(E_t, E_v) E_t^{1/2} f_t(E_t) f_v(E_v) \mathrm{d}E_t \mathrm{d}E_v . \tag{2}$$

The effective threshold of reaction is defined by a threshold curve $E_t = F(E_v)$, not only be the activation energy of reaction E_a. From the analysis of (2) it follows [1] that the reaction threshold as well as the value of the reaction rate coefficient $K(T_g, T_v)$ depends on values of the gas temperature T_g and on the nonequilibrium degree T_v/T_g simultaneously. The efficiency of reaction is connected with the excess of all energy $\sim (T_g + T_v)$ over the reaction enthalpy Q, and also with the excess of vibrational energy $\sim (T_v/T_g)$ if the reaction and relaxation runs.

[1)] Contribution presented at the 8th Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma, STARÁ LESNÁ, May 28 - June 1, 1990

[2)] Institute of Plasma Physics, 182 11 PRAGUE, CSFR

The nonequilibrium conditions in the discharge can be reached by the free electron excitation of the vibrational levels (e–V). The Treanor up-pumping mechanism (V–V) can lead to the dissociation if the gas temperature T_g is sufficiently low. Of course, the energy electrons can dissociate the molecules directly ($e-D$).

Coupling between the electron distribution function EDF and the vibrational distribution functions of the ground N_v or the electronically excited N_v^* states occurs in the low-energy ($0.5 < \bar{\varepsilon} < 3\,\mathrm{eV}$) discharges. The second-kind collisions tend to equalize the electron temperature T_e to a vibrational T_v. This mechanism can enlarge the relaxation process by an order of magnitude. Capitelli et al. [2] estimate the value of T_v in the afterglow of this low-pressure discharge by the criterion $q = (E/N)n_e\tau/p$, where τ is the residence time of particles in the discharge and p ~~is the pressure~~.

The vibrational energy E_v is dispersed mainly by its conversion on the translational one (V–T). An increase of the gas temperature T_g progressively eliminates the nonequilibrium effects and shifts the Treanor distribution (or the similar nonequilibrium one) to the Boltzman distribution. The gas temperature $T_q \simeq 6\,\mathrm{kK}$ is the upper limit by some authors [2] when the relaxation (V–T) overcomes the up-pumping processes (V–V) in the low pressure system. Moreover, this limit can be lower for the reactions of polyatomic molecules [3].

The dissociation rate constants K_d are described in some cases by the dependence on the reduced electric field E/N or E/p only. For nitrogen gas N_2 e.g., the pure vibrational mechanism (PVM) runs up to the value of $E/N \simeq 6\times10^{-16}\,\mathrm{Vcm}^2$, for the higher values of E/N the direct electron impact mechanism (DEM) can prevail. Moreover, the small amount of hydrogen H_2 can strongly reduce the importance of PVM [4].

The importance of keeping a low gas temperature T_g is seen also from the equilibrium calculations of systems in which the condensed phase appears [5, 6]. Solids originate at the gas temperature T_g much lower than that for the dissociation of the reagent molecules.

Some first conclusions about the effective running of the high-threshold, high-pressure synthesis can be made on the basis above-mentioned notes (condensation of solid we will demand): 1. high nonequilibrium degree T_e/T_g (or T_v/T_g) of generated plasma is demanded; 2. sufficiently low gas temperature T_g is necessary; 3. quick mixing of the proper chosen reagents in afterglow is required to utilize the short relaxation time.

Plasma nonequilibrium degree in the atomic gas discharges is estimated for example by the Finkelnburg criterion. For the elastic collisions in the weak electric field there is [7, 8]

$$(T_e - T_g)/T_e = (M/4m_e)[\bar{\lambda}_e eE/(3/2)kT_e]^2, \tag{3}$$

where $\bar{\lambda}_e$ is the mean free path of electrons, m_e is the mass of the electron. The relative value of the nonequilibrium degree is determined mainly by the fraction of electron energies, i.e. the one obtained from the electric field, and of the thermal energy. This formula also shows the way how to increase the nonequilibrium degree in the case of prevailing inelastic collisions in the molecular gases, i.e. to increase mainly E. Maximal electric field intensity E was measured in the linear type of a d.c.–arc generator. The field intensity $E = 250\,\mathrm{V/cm}$ was reached in the air or nitrogen type discharge if the transpirational channel wall was used, in contrast to the value of $E = 60\,\mathrm{V/cm}$ only in the smooth wall channel [9, 10].

Panasenko et al. [11] studied the breaking of LTR on the atmospheric pressure argon arc. Nonequilibrium $\Delta T = T_e - T_g \simeq 1\,\mathrm{kK}$ exists on the arc axis and also on the whole radius R for the current $I = 5\,\mathrm{A}$. We can see from the model results that magnification of the nonequilibrium degree T_e/T_g is possible also by decreasing the discharge current I. Elongation of the nonequilibrium zone along the z axis in the afterglow is caused due to the increase of the gas flow rate g as well.

II. CRITERION OF NONEQUILIBRIUM

Estimation of the nonequilibrium degree, or at least estimation of the conditions under which the nonequilibrium in the plasma appears, can be useful.

Pfender states that the value assumed for thermal plasmas can be $E/p = 10\,\mathrm{V/mkPa}$, while this value in nonequilibrium plasmas can exceed $10^4\,\mathrm{V/mkPa}$ [12]. Another simple criterion is cited in the mentioned work of Panasenko. From the values obtained in the Lelevkin measurement it follows that the nonequilibrium exists on the axis of the atmospheric pressure argon arc for $I/d < 100\,\mathrm{A/cm}$ [11].

The gas T_g and the electron T_e temperatures strongly influence the flow of the cold gas through the discharge. While T_g decreases monotonically with the rise of the gas velocity u (we assume a sufficiently large channel radius R), the electron temperature T_e increases with the rise of u only. Then we can estimate the nonequilibrium degree by the formula:

$$T_e/T_g \sim f[(E/p)(u/I)]. \tag{4}$$

This formula is in agreement with the previous ones. It can be also in agreement with the results of model [11] if some dependence between the gas flow rate g, the discharge channel diameter d, and the gas velocity u is assumed, though the model is a simple one. The dependence can be valid also for molecular gases and it can be linear in some interval of electron energies. The value of $q^e = (E/p)(u/I) \simeq (10^{-3} + 10^{-2})\Omega/\mathrm{s\,Pa}$ is estimated for the origin of the nonequilibrium degree $T_e/T_g > 1$ on the argon arc axis.

III. EXPERIMENTAL

The best conditions for the nonequilibrium UHF synthesis exist if the thermalization of the generated plasma is minimal, further if the given device operates at the lowest power [13]. The power or enthalpy cannot characterize sufficiently the plasma generated for the aim of nonequilibrium synthesis [14]. The described type of the d.c.–arc atmospheric pressure plasma generator can enable to study these conditions.

The generator design issues from the mentioned criterion. First, we endeavoured to get maximal values of the electric field intensity E by a maximal velocity u of the cold gas. The gas has to influence the discharge along all its length, thus the transpirational wall of the channel is suitable to be used. Secondly, the minimal current I was required for the atmospheric pressure arc discharge ($p \simeq$ const). Of course, stable burning is also required. The radius $R = 0.4$ cm of the discharge channel was chosen (approximately 1/2 of the characteristic diffusion length), to further the increase of the field intensity E. The length of the arc is $l = 6.5$ cm.

The beginning of the arc is carried out between the cathode and the assistance anode by high-frequency, high-voltage circuits. The arc is then switched-over on the anode [15]. The potentials are picked-up along the channel by metallic rings which introduce the gas flow into the channel simultaneously. The discharge has been studied in the argon gas up to this time. The schematic diagram of the generator is in Fig. 1.

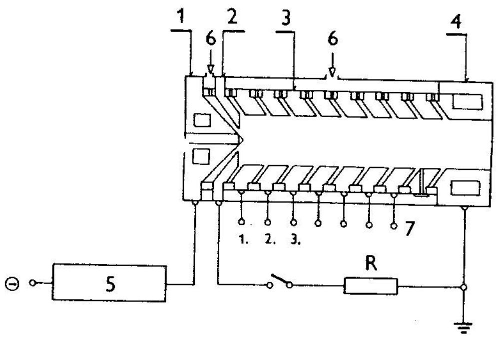

Fig. 1. Arrangement of the d.c.–arc plasma generator. 1 — cathode, 2 — assistance anode; 3 — ring section (metal and insul. rings); 4 — anode; 5 — H.F.–H.V. circuits; 6 — gas inlets; 7 — ring potential terminals

IV. RESULTS

Obtained E–I–u characteristics for the argon arc are illustrated in Fig. 2.

The electrode voltage drop was assumed $\Delta U_A = \Delta U_C = 5$ V [see 13]. The characteristic gas velocities u in the slots of the metalic rings were evaluated from the gas flow rate g. The picked-up plasma column potentials ΔU between the metalic rings are recorded in Tab. 1 (the rings are numbered from the cathode). The obtained values of field intensity E are in agreement with those obtained on the pore-like transpirational wall plasma generator [see 10]. The graph of potentials for the current $I = 30$ A is in Fig. 3. The temperatures of the plasma T_e, T_g have not been measured.

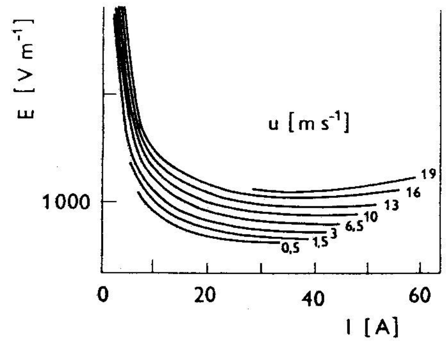

Fig. 2. The E–I–u characteristics of the argon arc ($p \simeq 10^5$ Pa). u — velocity in slots of rings

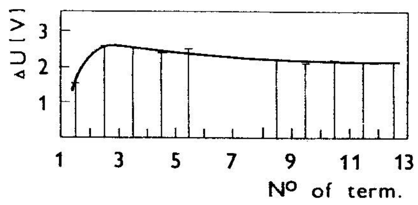

Fig. 3. Potentials ΔU between the metallic rings. Terminals of rings are numbered from cathode. ($I = 30$ A, $g = 0.9$ g/s, $u = 3$ m/s)

Table 1
Potentials ΔU and electric field intensity E on the plasma column

N^o of term	1.–3.	3.–5.	5.–9.	9.–13.	Cond.
ΔU [V]	8.75	9.75	19.40	20.30	1
E [V/m]	975	1080	1080	1120	
E [V/m]	$\simeq 600$				2

Conditions -1 : $I = 48$ A; $g = 2.2\,\mathrm{gs}^{-1}$; $2R = 8 \times 10^{-3}$ m; $L/2R = 8$
-2 [11]: $I = 60$ A; $g = 1.1\,\mathrm{gs}^{-1}$; $2R = 10 \times 10^{-3}$ m; $L/2R = 5$

V. CONCLUSIONS

If we use the Polanyi–Semenov rule $E_a = 46.12 + 0.75Q$ [16] to estimate the activation energy of the equilibrium reaction, we can obtain really high quantities (extreme for the silicon nitride enthalpy $Q = 7.5 \times 10^2$ kJ/mol [17]). The primary interest is to get the lower synthesis threshold and magnify the reaction rate coefficient $K(T_g, T_v)$. The use of the d.c.–arc generator can bring some advantages with respect to the UHF synthesis, but a minimal gas temperature T_g and a high nonequilibrium degree T_v/T_g (or T_e/T_g) of the plasma are necessary. Another problem is to choose proper reagents and mix them in the anode to utilize the short relaxation times. The study of new conditions for nonequilibrium plasma generation can also be useful.

The previous results confirmed the conception based on the stronger criterion of the nonequilibrium. From the E–I–u characteristics we can see the growth of the electric field intensity E depending on the growth of the gas velocity u. The field intensity E grows also with the drop of the current I if the pressure p is held constant. The mutual dependence of quantities exists due to the plasma conductivity, thus some deviation in the course of the characteristic can be measured. The sum of potentials ΔU is smaller also in comparison with the between-electrode potential, owing to the thickness of the metallic rings.

It will be necessary to carry out in future the measurement of temperatures on the argon gas (or chosen gas mixtures). The knowledge of the electron concentration can be useful also, because decrease of the discharge current can cause an increase of the reaction gain [9, 18, 19].

REFERENCES

[1] Macheret, S.O., Fridman, A.A., Elkin, A.A.: In: *Plasmachemistry-89*. Vol. I., Dokl. Akad. Nauk, Moscow 1989, p. 163.

[2] Capitelli, M., Gorse, C., Ricard, A.: In *Nonequilibrium Vibrational Kinetics*, ed. by M. Capitelli. Springer-Verlag. Berlin 1986, p. 315.

[3] Rusanov, V.D., Fridman, A.A., Sholin, G.V.: In Ibid. [1], p. 295:.

[4] Cacciatore, M., Capitelli, M., De Benedictis, S., Dilonardo, M., Gorse, C.: In Ibid. [2], p. 5.

[5] Chang, Yl., Pfender, E.: Plasma Chem. Plasma Process. *7* (1987), 275.

[6] Chang, Yl., Young, R.M., Prender, E.: Ibid. [5], 299:.

[7] Mehmetoglu, M.T., Gauvin, W.H.: AIChEJ. *29* (1983), 207.

[8] Dautov, G.Ju.: IFZ. *53* (1987), 966.

[9] Pustogarov, A.V., Slovetsky, D.I., Karabut, A.B., Sharshakov, V.N., Vischnjevsky, V.Ju.: IFZ. *57* (1988), 576.

[10] Zhukov, M.F., Anschakov, A.C., Zasypkin, I.M., Kurotchin, Ju.V., Lukashov, V.P., Pustogarov, A.V. *The Arc – Generators with Between electrode Sections. Nauka. Moscow. 1981, p. 177.:.*

[11] Panasenko, L.N., Sevastjanjenko, V.G.: IFZ. *52* (1987), 611.

[12] Pfender, E.: Pure & Appl. Chem. *52* (1980), 177.

[13] Baddour, R.F., Timmins, R.S. *The Application Of Plasmas To Chemical Processing*. (In Russian). Mir. Moscow 1970, p. 108:.

[14] Slovetsky, D.I. *The mechanisms Of Chemical Reactions In Nonequilibrium Plasma*. Nauka. Moscow 1980, p. 284:.

[15] Kvaltin, J.: Int. Rep. IX/88, IPP, CS. Acad. Sci. (1988).

[16] Suris, A.L. *Plasmachemical Processes And Devices*. Kchimija Moscow 1989, p. 112:.

[17] Gnesin, G.G. *Oxideless Ceramic Materials*. Tekhnika. Kiev 1987, p. 11:.

[18] Kurotchkin, Ja.V., Polak, L.S., Pustogarov, A.V., Slovetsky, D.I., Ukolov, V.V.: TVT. *16* (1978), 485.

[19] Kurotchkin, Ju.V., Polak, L.S., Pustogarov, A.V., Slovetsky, D.I., Ukolov, V.V.: TVT. *16* (1978), 1167.

Received October 18th, 1990

Accepted for publication September 16th, 1991

ДУГОВОЙ ГЕНЕРАТОР ПЛАЗМЫ ПОСТОЯННОГО ТОКА ДЛЯ НЕРОВНОВЕСНЫХ ПЛАЗМОХИМИЧЕСКИХ ПРОЦЕССОВ

В работе обсуждаются условия в неровновесных плазмохимических процессов с целю изучения высокопорогового синтеза. Анализ условий генерации неровновесной плазмы используется при конструкции генератора плазменной дуги постоянного тока. Проведено измерение E-I-u и также потенциала плазменного пнутя генератора при атмосферическом давлении Ar.