Journal of Korean Vacuum Science & Technology; JKVST
Vol. 4, No. 1, March 2000, pp. 33~37

Electrical Breakdown In Flames

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(Received March 2, 2000)

Abstract – Properties of electrical discharge in flames and influence of plasma electrons on gas neutrals are investigated by making use of the ionization cross section of air. Frames have three distinctive features. They are hot, emit light and are weakly ionized. We investigate influence of these three characteristics of flames on the electrical breakdown. It is found that the breakdown electric field in flames is inversely proportional to the flame temperature T_g, thereby easily generating plasmas in flames. A swarm of low-energy electrons in flames would allow a significant population of electronically excited states of flame molecules to be formed. Therefore, the analysis shows that the electronic excitation of flame molecules may also considerably reduce the breakdown field. Plasma electrons generate atomic oxygen by the electron attachment of oxygen molecules in high-pressure flames. These oxygen atoms are the most reactive radicals in flames for material oxidation.

I. Introduction

According to Greek mythology, Prometheus helped Zeus to defeat Titan and established Zeus Kingdom, getting a highest honor from him. But, he stole fire from Zeus and gave it to human beings, making Zeus furious. So, Zeus chained Prometheus on a rock and tried to kill him. What was wrong to give fire to human beings? Zeus knew the side effects of fire, if the mankind is addicted to it. Even today, the major energy source for people is combustion. The high temperature of flames is the energy source. Most of the burning processes are exothermic oxidation. Oxygen molecules in air are relatively stable in comparison with oxygen atoms, which is one of the most reactive radicals. If the oxygen molecules are converted into atoms, the oxidation process becomes more dramatic, and combustion of materials will be more efficient and clean. One of the best ways to produce many of the free radicals including oxygen atoms is plasma generation. The electron-to-gas temperature ratio in a weakly-ionized plasma at high pressure is very high. Thus, collision of these electrons with gas neutrals leads the molecules to high excitation, often generating chemical radicals and even oxygen atoms. For example, the corona discharge system [1,2] in the atmospheric pressure has been investigated in connection with its applications to NO_x and SO_x reduction [3-7] from emission gas. The electrons in the corona-discharge plasma excite gas neutrals, which in turn carry out effective chemical reactions, thereby reducing emission of pollutants. Most of the pollutants contaminating the atmosphere are emitted from combustion devices, including coal-burning electric-power plants, factories, incinerators, and combustion engines. There are always flames at the core of these devices. Plasma generation in the flames may eliminate or reduce emission of air pollutants from these combustion devices. The plasma in the flame may also enhance the efficiency of these devices. One of the most common methods to generate plasma in air is the electrical discharge. In this context, we will investigate properties of electrical discharge in flames and investigate influence of the plasma electrons on gas neutrals in flames. Flames are hot (high temperature), visible (light emission) and pre-ionized. We, therefore, investigate particularly influence of these three characteristic features on discharge properties of flames.

II. Influence of Gas Temperature on Breakdown Field

One of the characteristics of flames is high gas temperature T_g. Energy gain of electrons in the electric field E is proportional to the product of λE. The electron mean free-path λ is inversely proportional to the neutral number density of n_0. In this regard, the most important parameter governing the electrical discharge is E/n_0, where the symbol n_0 represents the neutral number density in the flame. The parameter E/n_0 is therefore widely used in modern gas discharge physics. The system parameters of most discharge applications in flames follow the simple ideal gas law expressed as

$$\frac{p}{n_0 T_g}=const. \tag{1}$$

for a specified volume of flame. Here, p is the pressure inside the system and T_g is the gas temperature in Kelvin. Therefore, the essential parameter of the electrical discharge in an electric field is ET_g/p.

The simple analytical-description of an electrical discharge in flame at high pressure is based on the electron moment equation

$$\frac{\partial n_e}{\partial t}+\frac{\partial}{\partial R}(v_e n_e)=(\alpha-\beta)n_e-\frac{D}{\wedge^2}-\alpha_r n_e^2 \tag{2}$$

where n_e is the electron density, α and β are the ionization and attachment rates of neutrals by electrons. In Eq. (2), the term proportional to D is the diffusion loss of electrons where $\wedge$ is the plasma size, and the term proportional to α_r is the recombination loss of electrons. The characteristic ionization time of the first term in the right-hand side of Eq. (2) is on the order of nanoseconds. On the other hand, the characteristic time of recombination is on the order of milliseconds before breakdown. The plasma size in the flame for most applications is typically a few tens of cm or larger. In this context, we may neglect the electron loss by the diffusion and recombination before breakdown when the electron density is relatively low (typically 10^{10} electrons cm^{-3}). The ionization rate α of high-temperature gas is given by [8]

$$\alpha=3.5\times10^3 v_e\frac{pT_r}{T_g}\exp\left(-1.65\times10^5\frac{pT_r}{ET_g}\right) \tag{3}$$

for an ionization cross section of air. The experimental data of numerical numbers for Eq. (3) has been obtained at room temperature of $T_g = T_r = 300$°K. Similarly, the attachment rate β in Eq. (2) is expressed as [8]

$$\beta=1.5v_e\frac{pT_r}{T_g}\exp\left(-2.5\times10^4\frac{pT_r}{ET_g}\right) \tag{4}$$

for high-temperature gas, and is in units of sec^{-1}.

The breakdown field for hot air in the flame is obtained from $\alpha = \beta$ in Eqs. (3) and (4), and is given by

$$\frac{E}{p}=25.7\frac{T_r}{T_g}\ (kV/cm\cdot atm) \tag{5}$$

where $T_r = 300$°K is the room temperature and T_g is the gas temperature in flame. The temperature dependence of breakdown parameter in Eq. (5) is an obvious outcome from the electrical discharge parameter E/n_0 in the discharge community. We remind the general audience the importance of gas temperature on electrical breakdown in Eq. (5). The required breakdown field in the flame is inversely proportional to the flame temperature T_g. Therefore, the electrical power for plasma generation by electrical breakdown in a flame is inversely proportional to the square of the flame temperature. Similar properties have been reported for the microwave breakdown in a hot chamber gas [9]. We can produce plasma very easily by focusing relatively-low power microwaves into a high temperature flame. The microwave power density required for electrical breakdown and plasma generation is inversely proportional to the square of the flame temperature. Properties of the corona discharge in hot gas in a cylindrical device [10] have also been investigated and they are similar to Eq. (5). Plasma can easily be generated in flames between electrodes with a relatively-low voltage.

III. Electronic Excitation of Gas Molecules

Flames already contain a high concentration of plasma species. Ion concentrations found in the reaction zones of unseeded premixed hydrocarbon and air flames at pressures between 2 and 760 Torr lie in the range of 10^9~10^{12} ions cm^{-3}. The concentration is highest when acetylene is the fuel. A typical ion concentration in flame is about 10^{10} ions cm^{-3}. The ion concentration also has a relatively-long density tail in the burned gas downstream. The ionization process most favored by experimental evidence is chemi-ionization,

$$CH + O \rightarrow CHO^+ + e^- \tag{6}$$

the reaction that is exothermic with release energy of 20 kcal per mole. The ionization process in Eq. (6) can also be called one of the associative ionizations. Electrons are lighter than ions in the flame plasma, having high mobility. Therefore, some electrons in the flame plasma move out, leaving ions behind. This process is called the ambipolar diffusion resulting in the net positive charge of the flame. In this regard, a flame with a positive potential usually bends toward the cathode. Making use of these properties, we can enhance or suppress a flame with an electric field. As mentioned above, flames are already weakly-ionized plasma with a typical plasma density more than 10^{10} ions cm^{-3}. These high-density electrons will easily initiate electrical breakdown and discharge in the presence of an electric field, one of the characteristic features of flames.

The electron temperature at the breakdown in the flame is about $T_e = 2.3$ eV, even for a high temperature gas, and that the mean electron energy is $<\varepsilon> = 3.45$ eV. We remind the reader that electrons in flame plasma gain energy in the presence of an electric field and their mean energy is about 3 eV or more. This would allow a significant population of both electronically and vibrationally excited states of nitrogen to be formed. Remember that a majority of the neutrals in a flame are still nitrogen molecules. The previous study has shown that the cross sections for formation of many of these excited states are large, on the order of 10^{-16} cm^2. There are two favorable excited states in nitrogen molecules in flame. The first is the negative ion state of nitrogen at excited level of 2.3 eV. The second, with an onset above 6 eV, is associated with the $A^3\Sigma_u^+$ state, which is the lowest electronically excited state of the nitrogen molecules. Many excited states have relatively long lives allowing the steady state concentration to build up to high population level. For example, the $A^3\Sigma_u^+$ state of nitrogen molecules has a lifetime of 2 seconds. Thus, it is easily shown that the steady state population of such states can reach very high levels.

There are also electronic excitations of other species in flame. Carbon monoxide displays a similar behavior to that observed in nitrogen, including the low-energy (1.7 eV) excitation. The onset of the $a^3\pi$ *electronic excitation in CO occurs at 6 eV similar to* the $A^3\Sigma_u^+$ state of nitrogen molecules. As another example, flames of carbon monoxide and oxygen show a band spectrum superposed on a strong continuum that extends from the visible light into the ultraviolet. The band spectrum is chiefly attributable to excited CO_2 formed in the reaction

$$CO + O + M \rightarrow CO_2{}^* + M \tag{7}$$

where $CO_2{}^*$ represents the electronically excited state of carbon dioxide and M is a third party. The excited carbon dioxide decays to ground state later, emitting a photon. There is also an evidence that the OH radical is also electronically excited during the reaction of

$$O + H \rightarrow OH^* \tag{8}$$

which decays later to the ground state, emitting a photon. Most of the visible and ultraviolet radiations from flame are clear evidence of electronic excitation of some flame molecules.

Molecular species of the flame and their electronic excitation depend on the flame and fuel conditions. These parameters must be independently determined according to experimental conditions. Once the atoms or molecules are electronically excited as mentioned above, transfer of energy from an excited electronic state of a molecule to ionized state of other molecule can be accomplished. One of these examples is the associative ionization mentioned in Eq. (6). The ionization by collision of excited molecules may take place. The other example is the penning ionization. If the excited energy of one molecule is equal or exceed the ionization potential of the other molecule and the excited molecule is in a metastable state, the other molecule is ionized by contact of the excited molecule. The penning ionization is the most important because the cross section of penning ionization is very large and the metastable molecular density can be significant in many discharge experiments. Another ionization of the electronically excited molecules is the stepwise ionization, which may be less important than the penning ionization. We therefore conclude that the electronic excitation of flame molecules may reduce the breakdown field considerably due to the associative, stepwise and penning ionizations.

One of the issues to be investigated is microwave propagation through flames. The dielectric constant of a weakly-ionized plasma in flames is expressed as

$$\kappa = 1 - i\frac{\omega_p^2}{\omega\nu} \quad (9)$$

where ω_p is the electron plasma frequency, ν is the collisional frequency of electrons with neutrals in the flame, and ω is the microwave frequency. Equation (9) is valid only for the case of $\nu >> \omega$, which is the case of most applications in experiments. The scattering cross section of electrons by air molecules is 1.3×10^{-15} cm^2. Thus, the collisional frequency ν in the flame is given by

$$\nu = 1.36\times10^{12}\frac{T_r}{T_g}\sqrt{T_e} \quad (10)$$

where $T_r = 300°K$ is the room temperature, T_g is the gas temperature in units of Kelvin and T_e is the electron temperature in units of eV. Assuming that the ion density is $n_p = 10^{10}$ cm^{-3} before breakdown, it is shown that the dielectric constant in Eq. (9) is very close to unity with the imaginary value less than 1 percent for microwave frequency of $\omega = 1.54\times10^{10}$ rad/sec corresponding to a wave frequency of 2.45 GHz. We therefore conclude that the weakly ionized flame before breakdown is reasonably transparent for microwaves. However, the flame plasma with density more than 10^{12} cm^{-3} after breakdown is impenetrable by microwaves. The microwave will be reflected at flame surface with high density plasma and will breakdown other flames with low density plasma.

The conductivity σ of the plasma is defined by

$$\sigma = \frac{\omega_p^2}{4\pi\nu} \quad (11)$$

The electric field produced by the electrodes penetrates the flame located inside before breakdown. On the other hand, the conductivity of the flame plasma in Eq. (11) is large enough to push the electric field out of the flame after breakdown. Usually, the electric field is generated by a voltage difference between electrodes with a fixed distance. Whenever a flame inside the electrodes breaks down, generating high plasma density, the electric field in the remaining space increases, thereby breaking down the rest of flame. Therefore, the initiation of the breakdown is the most difficult part for microwave or electrical breakdown. Once the breakdown is initiated at any part of the flame, rest of the flame may also break down in a domino effect.

IV. Dissociation of Oxygen Molecules

Whenever electrical breakdown occurs in flame, flame molecules are ionized, producing significant concentrations of ions and electrons. The plasma density generated by the electrical breakdown in a flame can be on the order of 10^{13} ions cm^{-3} or more. Once a considerable concentration of electrons exists in flame, all kinds of radicals will be generated by electrons. The prime candidates for the most reactive free radicals are oxygen atoms. As will be seen later, electrons in the flame create an abundance of oxygen atoms. The oxidation process of materials by oxygen atoms can easily be a million times faster than that by oxygen molecules. For example, the oxidation of methanol by oxygen molecules is a bimolecular reaction and is expressed as[11]

$$CH_3OH + O_2 \rightarrow CH_2OH + HO_2 \quad (12)$$

with the reaction constant of

$$k_{O2} = 3.4\times10^{-11}\exp\left(-\frac{22600}{T_g}\right) \quad (13)$$

which predicts $k_{O2} = 10^{-18}$ at a gas temperature of $T_g = 1300°K$. The bimolecular reaction of methanol with oxygen atoms is expressed as [11]

$$CH_3OH + O \rightarrow OH + Other\ Products \quad (14)$$

with the reaction constant of

$$k_O = 10^{-12}\left(\frac{T_g}{300}\right)^{2.5}\exp\left(-\frac{1550}{T_g}\right) \quad (15)$$

which predicts $k_O = 10^{-11}$ at a chamber temperature of $T_g = 1300°K$. As shown in Eqs. (13) and (15), the oxidation of methanol by oxygen atoms is 10 million times faster than that by oxygen molecules at the gas temperature of $T_g = 1300°K$. We also note from Eqs. (13) and (15) that the ratio k_O/k_{O2} increases drastically as the gas temperature decreases. The reaction constant may not explain everything in gas kinetics. However, it is obvious that abundant oxygen atom generation may be most beneficial to the oxidation and may provide clean burns. Most of the particulate is a collection of unburned carbons. This unburned carbon-collection may disappear in the environment of abundant oxygen atoms.

The most dominant ionization process is the electron impact ionization of oxygen and nitrogen molecules. That is

$$O_2 + e^- \rightarrow O_2^+ + 2e^-$$
$$N_2 + e^- \rightarrow N_2^+ + 2e^- \qquad (16)$$

generating oxygen and nitrogen molecular ions. One mechanism to lose these diatomic ions in a large volume plasma is the dissociative recombination, which is expressed as

$$O_2^+ + e^- \rightarrow O + O \qquad (17)$$

Equation (17) is the process of oxygen atom generation. The other mechanism of oxygen atom generation in a high-pressure weakly-ionized plasma is the dissociation of molecules by energetic electrons. That is

$$O_2 + e^- \rightarrow O + O + e^- \qquad (18)$$

The most-dominant oxygen atom generation in high-pressure weakly-ionized gas is the electron attachment of oxygen molecules. That is

$$O_2 + e^- \rightarrow O^- + O \qquad (19)$$

which has the attachment rate β in Eq. (4). We emphasize that all the oxygen atom generations in Eqs. (17), (18) and (19) are carried out by electrons. Therefore, the plasma plays a pivotal role in atomic oxygen generation. The oxygen atom generation by electron attachment process in Eq. (19) is at least two orders of magnitude larger than the other two processes in high-pressure weakly-ionized plasmas generated by electrical discharge.

V. Conclusions

The properties of electrical discharge in flames and the influence of plasma electrons on gas neutrals were investigated in this article by using the ionization cross section of air. Influence of gas temperature on electrical discharge properties was investigated in Sec. II by making use of the electron energy-gain in the electric field. The energy gain is inversely proportional to the gas neutral density. Electrical breakdown occurs whenever ionization of neutrals dominates electron attachment of oxygen molecules. It was found in Sec. II that the breakdown electric field in flames is inversely proportional to the flame temperature T_g. Therefore, we can produce plasma very easily by focusing relatively-low power microwave into the high temperature flame. The plasma can also easily be generated in flames between electrodes with a relatively-low voltage.

Flames are already a weakly ionized plasma with typical density more than 10^{10} ions cm^{-3}. Influence of preexisting electrons in flames on electrical discharge properties was investigated in Sec. III. A swarm of electrons with the mean electron energy of $\langle\varepsilon\rangle = 3.45$ eV would allow a significant population of both electronically and vibrationally excited states of flame molecules to be formed. Flame molecules can also be excited electronically by chemical energies released by exothermic reactions. The analysis in Sec. III shows that the electronic excitation of flame molecules may reduce the breakdown field considerably. Plasma electrons generate an abundance of various chemical radicals. We investigated dissociation of oxygen molecules in Sec. IV. The most-dominant oxygen atom generation in high-pressure weakly-ionized gas is the electron attachment of oxygen molecules. Oxygen atoms are the most reactive radicals in flames, oxidizing materials.

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