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Composition of a thermal plasma formed from PTFE with copper in non-oxidant atmosphere.
Part II: Comparison of a test case with nitrogen

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Abstract

The aim of this work is to compare the main characteristic of good dielectric gas defined in our previous paper with nitrogen gas. We study the molar fraction of chemical species in PTFE, N₂ and Cu mixture for several proportions and pressures. We show that the nitrogen gas does not satisfy the characteristic of good dielectric leading to the manufacturer to modify entirely the electrical isolating set up.

Key Words: circuit breakers, nitrogen, PTFE, carbon formation, copper, dielectric gas, plasma composition.

Introduction

In our previous paper we have define a test case with the SF₆, PTFE and Cu to choose the better insulating compounds [1]. As a matter of fact the SF₆ gas is widely used for electrical insulating and in high voltage circuit breakers [2-6]. The environmental impact and the life cycle cost are, at the present time, keys for new markets. So the competition between industries is high for their image and for the purchasers to find alternatives.

Studying the electrical breakdown strength of nitrogen and SF₆ with Pashen curves [7], one can think that playing with the pressure we can obtain the same breakdown strength. That is to say with a higher pressure the electrical breakdown strength of nitrogen is the same as the electrical breakdown strength of SF₆. For the test case with SF₆, PTFE and Cu we have shown that we have to avoid the production of condensed matter and have a good proportion of electronegative species decreasing the electrons mobility [1]. The composition results can give available indications. Consequently, the study of the composition for N₂, PTFE and Cu with a pressure of 1 to 30 bars is useful.

First we explicit the chosen chemical species and the massic enthalpy calculation with condensed phase. Secondly, we study the results for three mixtures case 1: 1% (C₂F₄)ₙ, 98% N₂, 1% Cu; case 2: 50% (C₂F₄)ₙ, 49% N₂, 1% Cu and case 3: 98% (C₂F₄)ₙ, 1% N₂, 1% Cu in weight percentage and for the case 2 with three pressure 1, 10 and 30 bars. Finally, we give a conclusion.

Chemical species and enthalpy calculation

In our calculation, for the N₂, PTFE, Cu mixtures, 11 monatomic species are taken into account: C, C⁺, C₂⁺, Cu, Cu⁺, Cu²⁺, F, F⁺, F²⁺, N, N⁺ and electrons, 17 diatomic species: C₂, C₂⁺, CF, CF⁺, CN, CN⁺, CN²⁺, Cu₂, CuF, F₂, F₂⁺, F²⁺, FN, N₂, N₂⁺ and 25 polyatomic species: C₂F₂, C₂F₃N, C₂F₄⁺, C₂F₅, C₂N₂, C₃, C₄, C₄N₂, C₅, CF₂, CF₂⁺, CF₃, CF₃⁺, CF₄, CFN, CNN, CuF₂, F₂N, F₂N₂-C, F₂N₂-T, F₃N, F₄N₂, N₃, NCN. For solid and
liquid phase we take the carbon solid, liquid copper and solid copper into account. As in our previous paper, the thermodynamic properties versus temperature are taken from [8] for solid and liquid copper. The thermodynamic properties for solid carbon are those of the graphite taken from [8]. For the gaseous polyatomic species data are taken from [8]. For the monatomic and diatomic species the thermodynamic properties are calculated from the partition functions [9]. The enthalpies of formation are taken in [8].

To determine the composition we used the numerical method as described in [1, 10]. Concerning the enthalpy since we have solid and liquid phase we calculated it by unit of mass.

\[ H = \left( \frac{\sum_{i=1}^{N} x_i h_i + \Delta H}{\sum_{i=1}^{N} x_i m_i} \right) \]

Where \( x_i \) the molar fraction, \( h_i \) the specific enthalpy of chemical species, \( m_i \) the molar weight and \( \Delta H \) the enthalpy correction due to Debye effect that is very low in our temperature range.

II. \( \text{N}_2, (\text{C}_2\text{F}_4)_n, \text{Cu} \) mixtures

II.1 Influence of stoichiometric parameters.

**Figure 1.a:** Molar fraction versus temperature at 1 bar for a mixture of 1% \((\text{C}_2\text{F}_4)_n\), 98% \(\text{N}_2\), 1% Cu in weight percentage.
Figure 1.b: Molar fraction versus temperature at 1 bar for a mixture of 50% \((\text{C}_2\text{F}_4)_n\), 49% \(\text{N}_2\), 1% \(\text{Cu}\) in weight percentage.

Figure 1.c: Molar fraction versus temperature at 1 bar for a mixture of 98% \((\text{C}_2\text{F}_4)_n\), 1% \(\text{SF}_6\), 1% \(\text{Cu}\) in weight percentage.

In figure 1, the molar fraction has been plotted for three mixtures based on \(\text{N}_2\), PTFE and copper. In the case 1, 1% \((\text{C}_2\text{F}_4)_n\), 98% \(\text{N}_2\), 1% \(\text{Cu}\) in weight percentage, the main chemical
species is the Nitrogen $N_2$. We observe condensed phase liquid and solid copper and carbon solid in the considered temperature range. The $N_2$ molecules does not dissociate at a high rate in the considered temperature range. The carbon solid sublimates in Cyanogen CN around 2890K. The solid copper sublimes in CuF before to be liquefied. For temperature higher than 3000K the main species are $N_2$, N and F. For the charged particles, the electrical neutrality is reached between $e^-$ and $Cu^+$. 

In the case 2, 50% $(C_2F_4)_n$ 49% $N_2$ 1% Cu, the main chemical species are $N_2$, CF$_4$, solid carbon and solid copper. The CF$_4$ molecules dissociate in CF$_2$ and F at a temperature around 2500 K. Equilibrium is reach between CF$_2$ molecules, F and carbon solid until 3480K when carbon sublimes. For this temperature the CF$_2$ molecules dissociates in CF and F. The solid copper sublimates in CuF and CuF$_2$ at a temperature of 1350 K. For the higher temperature at 6000 K the main chemical species are $N_2$, F, C, N, CN, CF, Cu and C$_2$. The electrical neutrality is reach between $Cu^+$ and F$^-$ for the temperature lower than 4250 K and $e^-$ and $Cu^+$ for the higher temperature in the considered temperature range.

In the case 3, 98% $(C_2F_4)_n$ 1% $N_2$ 1% Cu, the main chemical species are solid carbon, CF$_4$, Nitrogen $N_2$ and solid copper at low temperature. The CF$_4$ molecules dissociate in CF$_2$ and F at a temperature around 2650K. CF$_2$ molecules dissociate in solid carbon and F between 3050 K and 3700 K. Thus the molar fraction of solid carbon is stable in this temperature range. At 3685 K, when solid carbon sublimes in CF and C$_3$, the CF$_2$ molecules dissociate in CF and F. Around 4470 K, CF dissociates in C and F. The solid copper sublimes in CuF and CuF$_2$ at a temperature of 1418 K 1350 K. For the higher temperature 6000 K the species are monatomic F, C, CF, CN, C$_2$ and Cu. The electrical neutrality is reach between $Cu^+$ and F$^-$ for the temperature lower than 4500 K and $e^-$ and $Cu^+$ for the higher temperature in the considered temperature range.

Comparing the three considered cases, we observe that in each case the carbon solid and the solid copper are presents. Modifying stoichiometric coefficients does not allow the creation of gaseous species with carbon avoiding the carbon solid. The CF$_4$ molecules are present in each considered cases. The neutrality in gas phase is made at low temperature between F$^-$ and $Cu^+$ and between $e^-$ and $Cu^+$ for the higher temperature in the considered temperature range.

### II.2 Influence of the pressure

In figure 2, in the case of 50% $(C_2F_4)_n$, 49% $N_2$ , 1% Cu in weight percentage for two pressures 10 bars and 30 bars, the molar fraction are plotted versus the temperature. The dissociation of CF$_4$ in CF$_2$ and F is made at 2540 K for 1 bar, 2790 K for 10 bars and 2920 K at 30 bars. The carbon solid sublimes of at 3475 K for 1 bar, at 3630 K for 10 bars and at 3670 K for 30 bars. The CF$_2$ dissociates in CF and F around 3460 K at 1 bar, 3560 K at 10 bars and 3830 K at 30 bars. CF dissociates in C and F around 4100 K for 1 bar, 3940 K at 10 bars and 4220 K at 30 bars. The solid copper sublimes and liquid copper vaporized in CuF and CuF$_2$ at a temperature of 1340 K at 1 bar, 1470 K at 10 bars and 1545 K for 30 bars. For the higher temperature 6000 K, we observe that the higher the pressure the higher the molecule molar fractions. So the main species for 6000 K at 1 bar are F, $N_2$, C, N, CN, CF, Cu and C$_2$ and for 30 bars $N_2$, F, C, CF, CN, N, C$_2$N, C$_2$, and Cu. The electrical neutrality is reach between $Cu^+$ and F$^-$ for the temperature lower than 4250 K and $e^-$ and $Cu^+$ for the higher temperature in the considered temperature range at 1 bar. For 10 bars, the electrical neutrality is reach between $Cu^+$ and F$^-$ for the temperature lower than 5230 K and $e^-$ and $Cu^+$ for the higher temperature. For 30 bars, the electrical neutrality is made between F, CF$^+$ and Cu$^+$. 
Figure 2.a: Molar fraction versus temperature at 10 bars for a mixture of 50% (C$_2$F$_4$)$_n$, 49% N$_2$, 1% Cu in weight percentage.

Figure 2.b: Molar fraction versus temperature at 30 bars for a mixture of 50% (C$_2$F$_4$)$_n$, 49% N$_2$, 1% Cu.
III. Massic Enthalpy

In figure 3, we have plotted the massic enthalpy versus temperature for the three considered case the nitrogen and SF6 gas and three pressures for case 2. The nitrogen gas is considered as a reference gas with enthalpy of formation equal to zero [8] due to the fact that it is stable in atmosphere. The enthalpy of the SF6 gas has a variation of enthalpy between 1800K and 4000 K due to dissociation of SF6, SF4, and SF2 [11, 12]. This variation of enthalpy is useful to extinguish an electrical arc since the electrical energy from the electrical circuit is consumed by the chemical reaction in the gas. Unlike the variation of enthalpy for the nitrogen gas monotonically increases in the considered temperature range. As a matter of fact no dissociation occurs. The same conclusion can be made for the mixture of the case 1, 1% (C2F4)n, 98% N2, 1% Cu due to the fact that the main chemical species is the nitrogen (Fig 1. and 2). For the case 2 and case 3, the variation in enthalpy in the temperature range is due to the sublimation of solid carbon and to the dissociation of CF4 and CF2. (Fig 1 and 2).

The increase in the enthalpy is due to the chemical reaction. The higher the pressure the higher the temperature when the chemical reaction occurs. In figure 3 b, we have plotted the massic enthalpy versus temperature in the case 2, SF6 and nitrogen for three pressures 1, 10 and 30 bars. The variation of enthalpy in SF6 gas is due to the dissociations of gaseous species SF6, SF4, and SF2, so since the pressure increase the dissociation reactions are made at higher temperature. Concerning the case 2 the increases in enthalpy is due to the carbon sublimation and to dissociation of gaseous species CF4 and CF2. Even the sublimation is abrupt (Fig 1 and 2) no sharks increases in enthalpy is observed. As a matter of fact around the same temperature # 4000K the gaseous dissociation occurs. With the increase of pressure the enthalpy increases at higher temperature. Since no dissociation occurs in the temperature range 1000 to 5000 K no variation in enthalpy for nitrogen plasma is observed in this temperature range.

Figure 3.a: Massic enthalpy versus temperature at 1 bar for several mixtures, SF6 and N2
**Figure 3.b:** Massic enthalpy versus temperature for case 2, SF$_6$ and N$_2$ at tree pressures (1, 10 and 30 bars)

**Conclusion**

We have presented the molar fraction and massic enthalpy of mixture of PTFE, N$_2$ and Cu for several proportions and pressures versus temperature. The industries since the SF$_6$ have large environmental impact wish to replace the SF$_6$ gas for their system (electrical insulating, circuit breakers). In our previous paper we have shown that a good proportion (stoichiometric variables) of SF$_6$ in the mixture avoids the condensed phase [1 see also 13]. With nitrogen the condensed phase are always present. The system with nitrogen has to use a high pressure to clean and push the polluted gas far from the electrodes avoiding restriking. The energy gained by the gas flow can be similar between SF$_6$ gas and nitrogen gas. This energy in the first case is due to the dissociation of SF$_6$, SF$_4$ and SF$_2$ for SF$_6$ gas and CF$_4$ and CF$_2$ and in the second case to sublimation of condensed carbon for mixture of N$_2$, PTFE and Copper. The electronegative ions molar fraction is low due to the fact that the N$^-$ is unstable. Nevertheless, the electronegative ions are mainly due to the species from wall ablation. Finally, it seems that the nitrogen is not a god gas for electrical insulating in the existing system. To use the nitrogen, manufacturers have to change their electrical isolating set up.

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