An Investigation of Negative DC Partial Discharge Decomposition of SF$_6$ Under Different Metal Materials

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ABSTRACT For determine the influence of metal materials on the negative DC partial discharge (PD) decomposition of SF$_6$ and put forward for the method of SF$_6$ DC gas insulated equipment condition monitoring and fault diagnosis based on decomposed component analysis, this study investigates the decomposition characteristics of SF$_6$ under three common metal materials (Al, 304 stainless steel, and Cu) in gas insulated equipment by using SO$_2$, SOF$_2$, and SO$_2$F$_2$ as characteristic component gases under negative DC PD. Results show that the types of metal materials have substantial effects on the negative DC PD decomposition characteristics of SF$_6$. The simulation results based on the first principles confirm the phenomena observed in the experiment: the amounts and generation rates of SOF$_2$ were the most abundant, followed by SO$_2$F$_2$ and SO$_2$. The calculation based on free electron cloud and finite depth particle in a box model shows that the electron current density of field emission has the relationship with metal work function $\gamma$ and electrical field $E$: $j(0, E) \approx (BE^2/\gamma) \exp(-D\gamma^{3/2}/E)$, where B and D is constants. The electron current density by field emission is inversely proportional to the work function of metal with constant electric field. The metal material with smaller work function means the greater electron current density, further promoting the decomposition of SF$_6$ to generate more characteristic component gases. The results can well explain the phenomena observed in the experiment, that is, the decomposition of SF$_6$ is the most serious under Al electrode with lowest work function, followed by 304 stainless steel, and Cu.

INDEX TERMS Negative DC, metal materials, SF$_6$, first principle, work function.

I. INTRODUCTION

With the development and trial operation of key ultra-high voltage DC (UHVDCC) gas-insulated equipment, such as $\pm$ 800 and $\pm$ 1100 kV gas DC wall bushings [1]–[3], SF$_6$ DC gas-insulated equipment has been widely used in UHVDCC power transmission projects [4], [6]. DC gas-insulated equipment has great advantages, such as simple and compact structure, light weight, and good heat dissipation [7]. However, harmful metal protrusion defects are inevitably observed in the production, transportation, installation, and operation of gas-insulated equipment due to vibration, mechanical friction, collision, and other factors. Moreover, such defects cause partial discharge (PD). If defects is not handled in time, then the withstand voltage of the equipment considerably decreases [8], [9] and leads to a penetrating discharge accident. The method of SF$_6$ gas insulated equipment condition monitoring and fault diagnosis based on decomposed component analysis (DCA) have such advantages of immunity from the effects of electromagnetic interference, high sensitivity, and capacity to identify the fault type. Therefore, this method has become a focus of research [10]–[12]. The structure of gas-insulated equipment is complex and contains various components made of different metal...
materials. Previous studies have shown that metal materials directly influence the PD decomposition characteristics of SF$_6$ [13], [14]. Consequently, it is priority to study the DC PD decomposition characteristics of SF$_6$ under different metal materials, obtain the influence law of metal materials on the SF$_6$ DC PD decomposition characteristics, further to eliminate the adverse effects of metal material differences on the method and technology of insulation condition monitoring and fault diagnosis based on DCA.

Many scholars have studied the influence of metal materials on the decomposition characteristics of SF$_6$. Belmadan et al. [15], Vigh [16], and Hirooka et al. [17] studied the influence of metal materials on SF$_6$ decomposition under arc and found that the generation rate of metal fluoride is proportional to the electrode potential of metal, and metal plays a catalytic role. Tang et al. [19] studied the influence of metal materials on SF$_6$ decomposition under corona discharge and specified that the types of metal materials affect the decomposition characteristics of sulfur-containing decomposition gases, such as SF$_5$, SOF$_2$, and SO$_2$F$_2$; however, almost no correlation was observed with carbon-containing decomposition characteristic gases, such as CF$_4$. Tang et al. [19], [20] studied the influence of metal materials on SF$_6$ under positive DC PD; the difference in surface passivation film and metal halogenation resistance among metal materials resulted in different SF$_6$ decomposition characteristics. Little study on the effect of metal materials on the SF$_6$ decomposition characteristics under negative DC PD is currently available, but most unipolar HVDC transmissions use negative DC. Therefore, this study investigates the influence law of three common metal materials (Al, 304 stainless steel, and Cu) inside a gas-insulated equipment on SF$_6$ negative DC PD decomposition under the metal protrusion defect. Moreover, this study provides an experimental and theoretical foundation for method of SF$_6$ gas insulated equipment condition monitoring and fault diagnosis based on DCA.

II. PD DECOMPOSITION PROCESS OF SF$_6$

According to the plasma chemical model proposed by Van Brunt and Herron [21], [22], SF$_6$ decomposes into low-fluorinated sulfides, such as SF$_5$ and SF$_4$, and F atoms in the nearby glow area because of high-energy electrons, as indicated by Reaction (1).

$$e + SF_6 \rightarrow SF_{6-x} + xF + e \quad x = 1, \ldots, 5$$ (1)

However, the vast majority of low-fluorinated sulfides and F species to form SF$_6$ quickly. Only low levels of primary decomposition products react with the generated metal vapor (it is represents by M in Reaction (2)–(7)), trace amounts of H$_2$O, and O$_2$; as shown in Reaction (2)–(14).

$$nF^* + M \rightarrow MF_n$$ (6)

$$SF_3 + M \rightarrow MF + SF_4$$ (7)

$$SF_6 + O \rightarrow SOF_4 + 2F$$ (8)

$$SF_5 + OH \rightarrow SOF_4 + HF$$ (9)

$$SF_4 + H_2O \rightarrow SOF_2 + 2HF$$ (10)

$$SF_2 + O \rightarrow SOF_2$$ (11)

$$SF_2 + O_2 \rightarrow SOF_2F_2$$ (12)

$$SOF_4 + H_2O \rightarrow SOF_2F_2 + 2HF$$ (13)

$$SOF_2 + H_2O \rightarrow SO_2 + 2HF$$ (14)

In addition, there are organic solid insulation material, such as epoxy, in the gas-insulated equipment, carbon-containing gas would be generated in the PD process, as shown in Reaction (15), and (16).

$$\text{epoxy} + F \rightarrow CF_4$$ (15)

$$\text{epoxy} + 2S \rightarrow CS_2$$ (16)

Reaction (2)–(14) show that under the action of PD, metal materials play a catalytic role in the primary decomposition products generation by SF$_6$ decomposition; on the other hand, the primary decomposition products will react with metal vapor to generate metal fluorides. The different of metallic materials lead to varying amounts and rates of the primary decomposition products of SF$_6$. Such variation further affects the generation of SF$_6$ decomposition components.

III. EXPERIMENTAL PLATFORM AND PROCEDURES

A. EXPERIMENTAL PLATFORM

The SF$_6$ decomposition under negative DC PD setup in this study is shown in Figure 1. A needle–plate electrode model is used to simulate typical metal protrusion insulation defects in gas-insulated equipment; a diagram is shown in Figure 2.

The spacing between needle and plate was 2 mm, the curvature radius of the needle was approximately 0.25 mm, and the cone angle of the needle was approximately 30°. The ground electrode was 100 mm in diameter and 10 mm in thickness. The needle and plate electrodes were made of Cu, Al, and 304 stainless steel, which are common in DC gas-insulated equipment. Because the laboratory equipment pressure generally ranges from 0.10 to 0.40 MPa [23] and to ensure the comparability of experimental data, gas chamber

FIGURE 1. Partial discharge decomposition experimental devices under the negative direct current (GC represents gas chromatograph, DSO represents oscilloscope).
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FIGURE 2. Diagram of the protrusion defect model.

pressure (absolute pressure), ambient temperature, and relative humidity were constant (0.35 MPa, 25 °C, and 50%, respectively). Water vapor content was less than 10 µL/L, and oxygen content was less than 100 µL/L. The SF₆ decomposition products were measured by Shimadzu GC-2010 Pro gas chromatograph (GC) (99.999% purity helium gas was used as carrier gas, with a flow rate of 2 mL/min, column temperature of 40 °C, injection volume of 1 mL, and diversion ratio of 10:1).

B. EXPERIMENTAL PROCEDURES

(1) The electrode and the gas chamber wall were wiped with absolute alcohol to remove residual impurities.

(2) After electrode installation, the circuit was connected, as shown in Figure 1. The gas chamber was pumped to vacuum using a vacuum pump, filled with new SF₆ (the purity is 99.999%) to the atmosphere, and then pumped to vacuum. The above process was repeated twice to discharge the gaseous impurities in the gas chamber fully. Afterward, the gas chamber was pumped into vacuum and set aside for 12 h to check the gas tightness of the gas chamber.

(3) The gas chamber was filled with SF₆ at an absolute pressure of 0.35 MPa. The amounts of H₂O and O₂ in the gas chamber were measured using GE600 precision dew point meter and HY-YF oxygen analyzer, respectively, to ensure that their amounts were in line with IEC 60480-2004 [24]. Then, they were set aside for 12 h.

(4) Voltage U = 25.00 kV was applied to the electrode for 96 h. About 20 mL decomposition sample gas was sampled every 12 h. Then, the volume fraction of each decomposition components of gas sample gas was measured.

(5) Turn off the power, replace the metal protrusion defect made of other metal materials, and repeat the above steps.

IV. INFLUENCE OF METAL MATERIALS ON THE PD DECOMPOSITION OF SF₆

Numerous studies have indicated that SF₆ decomposes under PD through a series of chemical reactions by which the low-fluorinated sulfur species react with metal vapor, trace H₂O, and O₂. The reaction products include SO₂F₂, SOF₂, CF₄, SO₂, SOF₄, HF, CS₂, and SF₄ [25]-[27]. However, HF is a corrosive acid that can react with metal and organic solid insulating materials. SOF₄ is labile toward hydrolysis [28] and easily influenced by trace H₂O in equipment. The chemical properties of H₂S are stable, but minimal H₂S is produced under PD. On the other hand, the three decomposition components, SO₂, SO₂F₂, and SO₂F₄, are relatively inert, and the proportion of their contents can determine the discharge intensity [14]. Hence, this study focuses on the role of the three decomposition products of SF₆, namely, SO₂F₂, SOF₂, and SO₂.

A. GENERATION LAW OF THREE DECOMPOSITION COMPONENTS UNDER DIFFERENT METAL MATERIALS

The amounts of SO₂F₂ varies with time under different metal materials is shown in Figure 3. Specifically, the amounts of SO₂F₂ under the Al protrusion model was the largest, followed by 304 stainless steel, and the amounts of SO₂F₂ under the Cu protrusion model was the smallest. In addition, the formation rate of SO₂F₂ decreased with time under the Al condition. The amounts of SO₂F₂ varies with time under different metal materials is shown in Figure 4. Overall, the amounts

FIGURE 3. Curves of SO₂F₂ with time under DC PD.

FIGURE 4. Curves of SO₂F₂ with time under DC PD.
and generation rates of SO$_2$F$_2$ under three kinds of metal protrusions were less than those of SOF$_2$ by the action of negative DC PD. Similar to SOF$_2$, the amounts of SO$_2$F$_2$ under Al protrusion was the most abundant, followed by 304 stainless steel protrusion, and the amounts of SO$_2$F$_2$ under copper protrusion was least.

The amounts of SO$_2$ varies with time under different metal materials is shown in Figure 5. Similarly, the amounts of SO$_2$ under Al protrusion was the most abundant, followed by 304 stainless steel and Cu protrusion. The phenomenon could be attributed to the following: The reaction rates of the main generation reaction of SOF$_2$ were much higher than those of SO$_2$F$_2$ and SO$_2$. The main generation reaction of SOF$_2$ was Reaction (10) and (11), and the main generation reaction of SO$_2$F$_2$ are the Reaction (12) and (13). SF$_6$ only needs to break two S–F bonds to generate SF$_4$, the reactant in Reaction (10), but SF$_6$ needs to break four S–F bonds to generate SF$_2$, the reactant in Reaction (12). Therefore, SF$_4$ is more easily produced. In addition, the reaction rate of Reaction (10) and (11) was approximately two orders of magnitude of that of Reaction (13) [12]. Consequently, the amounts and generation rates of SOF$_2$ were greater than those of SO$_2$F$_2$. SO$_2$ was mainly hydrolyzed by SOF$_2$, which was constrained by the amounts of SOF$_2$, as shown in Reaction n (14). The chemical properties of SOF$_2$ were relatively inactive, and its hydrolysis reaction rate was only $1.2\pm10^{-23}$ cm$^3$s$^{-1}$ [28]; the reaction rates of Reaction (10) – (13) were an order of magnitude greater than that of Reaction (14) [22]. Therefore, the amounts and generation rates of SO$_2$ were the smallest among the three kinds of characteristic decomposition components.

**B. GENERATION LAW OF THE TOTAL AMOUNTS OF CHARACTERISTIC DECOMPOSITION COMPONENTS**

The S atoms in SOF$_2$, SO$_2$F$_2$, and SO$_2$ may only come from SF$_6$. Therefore, the total amounts of the three kinds of characteristic components could characterize the discharge intensity and the insulation deterioration of SF$_6$. The total amounts of SOF$_2$, SO$_2$F$_2$, and SO$_2$ varies with time under different metal materials is shown in Figure 6. The total amounts of the three characteristic components followed the order Al $>$ 304 stainless steel $>$ Cu. Therefore, the deterioration of SF$_6$ by Al was the most serious under PD, followed by 304 stainless steel and Cu.

**C. SIMULATION ANALYSIS OF CHARACTERISTIC DECOMPOSITION COMPONENT GENERATION REACTIONS**

The main generation reactions of SOF$_2$, SO$_2$F$_2$, and SO$_2$ were simulated by Materials Studios 7.0 software based on density functional theory (DFT) to analyze the generation mechanism of SF$_6$ PD characteristic decomposition components. Structural optimization and energy analysis were performed using the Dmol$^3$ module. DFT is a theory that describes the ground state energy of the system as a function of electron density to solve the problem of multiparticle system in the first principle calculation. The basic premise is that the ground state property of the system is only determined by the distribution of electron density [29]. The material microstructure can be obtained by solving the Schrodinger equation via DFT, and the data of the material microstructure can be obtained without empirical calculation, which can provide the basis for the judgment of its physical and chemical properties.

During simulation, all structures were optimized in Geometry Optimization task of Dmol$^3$ by using the generalized gradient approximation (GGA) of the Perdew-burke-Ernzerhof (PBE) functional was utilized to deal with the electron exchange and correlation [30]. GGA is an empirical description function, which can well describe the thermodynamic properties of molecular system. The double numerical plus polarization (DNP) was as the atomic orbital basis set, that is, all non-hydrogen atoms are polarized by d orbital function, while all hydrogen atoms are polarized by s orbital function during simulation, which makes the results of simulation more accurate. Otherwise, select electron spin was unrestricted. The Brillouin zone was sampled by $1\times1\times1$ k-points.
TABLE 1. Selected characteristic decomposition component generation reaction and their reaction heat.

| No. | Generation reaction equation | Reaction heat (kcal/mol) |
|-----|-----------------------------|-------------------------|
| 1   | SF$_2$+O→SOF$_2$             | -136.98                 |
| 2   | SF$_4$+H$_2$O→SOF$_2$+2HF   | -21.46                  |
| 3   | SOF$_4$+H$_2$O→SO$_2$F$_2$+2HF | -51.89             |
| 4   | SF$_3$+O$_2$→SOF$_2$      | -90.16                  |
| 5   | SOF$_2$+H$_2$O→SO$_2$+2HF  | 1.6142                  |

![Molecular geometric structures by optimization.](image)

**FIGURE 7.** Molecular geometric structures by optimization.

via the Monkhorst–Pack method; precision choose “fine”. In addition, to ensure the high accuracy of convergence calculation in all structural optimization processes, the gradient, convergence threshold on energy, and displacement were $4 \times 10^{-3}$ Ha/Å, $2 \times 10^{-3}$ Ha, and $5 \times 10^{-3}$ Å, respectively [31]. On the basis, the length and bond angle of each optimized molecule and reaction heat were determined.

Literature [22] showed that the main formation reactions of SOF$_2$ were Reaction (10) and (11), those of SO$_2$F$_2$ were Reaction (12) and (13), and that of SO$_2$ was Reaction (14). The geometrically optimized stable molecular structure model, including the bond length and bond angle for the reactants and products involved in the above five reactions, is shown in Figure 7. The unit of bond length is Å. The simulation results of this study are similar to those reported in literature [32]–[34]. On this basis, the reaction heat of the main reaction of three decomposition component gases were calculated as shown in Table 1.

If the reaction heat is negative, then the reaction is an exothermic reaction; otherwise, it is an endothermic reaction. In addition, if the reaction is spontaneous, the smaller the reaction heat is, the more easily the corresponding reaction occurs [33]. Five reactions in Table 1 can be spontaneously achieved [35] because the reaction heat of SOF$_2$ and SO$_2$F$_2$ are far less than that of SO$_2$. Therefore, SOF$_2$ and SO$_2$F$_2$ are easier to generate compared with SO$_2$; this finding is consistent with the experimental results in this study.

Compared with SOF$_2$ and SO$_2$F$_2$, the reaction heat of generation reaction 1 of SOF$_2$ was much less than that of generation reactions 3 and 4 of SO$_2$F$_2$. From this reaction pathway, SOF$_2$ was easier to generate, but the reaction heat of generation reaction 2 of SOF$_2$ was greater than that of generation reactions 3 and 4 of SO$_2$F$_2$, it seems that SOF$_2$ is more difficult to generate from this reaction pathway, however. The reaction heat of SF$_6$ generated SF$_4$, SF$_2$ and SOF$_4$ were endothermic, and that of SF$_6$ to SF$_4$ is much less than that of SF$_2$ and SOF$_4$. For example, the reaction heat of SF$_6$ to SF$_4$ is 128.71 kcal/mol, while that of SF$_6$ to SF$_2$ is 364.2 kcal/mol [36]. Consequently, in terms of the total reaction process of SF$_6$ generating to SOF$_2$ or SO$_2$F$_2$, the reaction heat of SOF$_2$ is lower and easier to generate than that of SO$_2$F$_2$, which is also consistent with the experimental results in this study.

**V. COMPUTATIONAL STUDY AND THEORETICAL ANALYSIS OF THE EFFECT OF METAL MATERIALS ON THE NEGATIVE DC PD DECOMPOSITION OF SF$_6$**

If the external environment provides a certain amount of energy to the electrons inside the metal, then the electrons may break away from the metal bond and enter the gas phase only when the kinetic energy facilitates the decomposition of more SF$_6$. In theory, more electrons and kinetic energy facilitate the decomposition of more SF$_6$ and further generate more stable characteristic decomposition components.

Based on the free electron cloud and finite depth particle in a box model [37], the field emission of different metal materials was described in this study.

Assuming the work function of electrons $\gamma = W_\infty - W_{FM}$, $W_\infty$ is the potential energy of electrons at an infinite distance outside the particle on a box, $W_{FM}$ is the Fermi energy of electrons, and $W_0$ is the potential energy of electrons inside the metal. When the temperature is $T$, electrons can leave the metal surface and enter the gas phase only when the velocity of electrons $v_0$ along the vertical direction of the metal surface (set as the x-axis direction) is greater than the threshold velocity $v_T$. At this point, the electron energy is zero.

$$W(\vec{A}) = \frac{\hbar^2(\vec{A})^2}{2m} = \frac{mv^2}{2} \quad (17)$$

Thus, the number of states in the region $d \vec{A} = dA_x dA_y dA_z$ of the unit crystal wave vector space can be obtained.

$$d \vec{A} / 8\pi^3 = (m/\hbar)^3 d\vec{v} \quad (18)$$

The number of electrons $dn$ among $d\vec{v} + d\vec{v}$ can be expressed as

$$dn = 2\frac{m^3}{\hbar^3} \times \frac{d\vec{v}}{\exp[(\vec{v}^2 / 2m) - W_{FM})/kT] + 1} = n(v_x, v_y, v_z)dv_x dv_y dv_z \quad (19)$$
In Formula (17), (18), and (19), $m$ is the electronic mass, $K$ is the Boltzmann constant, $T$ is the temperature, $h$ is the Planck constant, $e$ is the electron charge, and $n(v_x, v_y, v_z)$ is the distribution of electron velocity. According to quantum mechanics theory, electrons do not necessarily detach the metal when they reach the metal surface, but need to be multiplied by the transmission factor $\delta(v_x)$ of the electron wave penetrating the metal surface barrier to calculate the probability of the electron leaving the metal [38]. Consequence, at temperature $T$, the value of current density $J(T)$ per unit time due to electrons detaching from the metal surface barrier can be expressed as

$$j(T) = e \int_{0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x n(v_x, v_y, v_z) \delta(v_x) dv_x dv_y dv_z$$

(20)

where $e$ is the electric charge. Then, the polar coordinate system is used to make $p^2 = v_x^2 + v_y^2$ dy dv_x, where the integral limit of $\varphi$ is $0 \sim 2\pi$. At the same time, make:

$$v_x^2/m - W_{FM} = \theta, \quad mv_x dv_x = d\theta$$

(21)

$$m\rho^2/2kT = \sigma, \quad \rho d\rho = d\sigma$$

(22)

where the integral limit of $\sigma$ is $0 \sim \infty$; the integral limit of $\theta$ is $\gamma \sim \infty$. As a result:

$$j(T) = 4\pi m e kT/h^3 \int_{\gamma}^{\infty} \delta(\theta) \ln(\exp(-\theta/kT) + 1) d\theta$$

(23)

Formula (23) is a strict Sommerfeld model [38], which can characterize and quantitatively explain the thermal emission of electrons. However, it remains unable to explain how the electrons detach from the metal surface and enter the gas phase when field emission. According to quantum mechanics, electrons can penetrate the metal surface barrier and leave the metal under the action of applied electric field even if the energy of the electrons inside the metal is below the maximum potential energy. In other words, if the velocity of electron along the x-axis $v_x > 0$, field emission can be generated under the action of applied electric field [38]. In addition, the field emission current density of electrons can also be estimated theoretically by thermal emission current, but the lower limit of integration should be determined by the condition of $v_x = 0$, as a result,

$$j(T, E) = 4\pi m e kT/h^3 \int_{-W_{FM}}^{\infty} \delta(\theta) \ln(\exp(-\theta/kT) + 1) d\theta$$

(24)

In addition, when the applied electric field is $E$, the potential energy $W(x)$ of the electron outside the metal is defined as

$$W(x) = W_{\infty} - W_0 - eEx$$

(25)

Under the action of applied electric field, the electron transmissivity is closely related to energy. Therefore, WKB (G. Wentzel, H. A. Kramers, L. Brillouin, WKB) method is used to estimate approximately the electron transmissivity [39].

$$\delta(W_e) = \exp[-2/h \int_{0}^{x_0} 2m(W(x) - W_e)^{1/2} dx]$$

(26)

where the kinetic energy of the electrons perpendicular to the metal surface is $W_e = v_x^2/2m$. The upper limit of integral $x_0$ in Formula (26) is determined by $W(x) = W_e$, so Formula (27) can be obtained by calculating Formula (26).

$$\delta(W_e) = \exp[-8m/3e\hbar E(W_{\infty} - W_0 - W_e^3/2)]$$

(27)

Because the calculation of field emission made here, considering the situation $T \approx 0$ K to simplify the model and facilitate calculation. At this point, $\theta = v_x^2/2m - W_{FM} < 0$, namely, there is no electrons would occupy the state in which $\theta$ is greater than 0. The integral limit of $\theta$ is $-\infty \sim 0$. In addition, $\ln[\exp(-\theta/kT) + 1] \approx -\theta/kT$ when $T \approx 0$ and $\theta < 0$. Therefore, Formula (24) can be simplified at $T \approx 0$ K as follows:

$$j(0, E) = 4\pi m e kT/h^3 \int_{-W_{FM}}^{\infty} \delta(\theta) \ln(\exp(-\theta/kT) + 1) d\theta$$

$$\approx 4\pi m e kT/h^3 \int_{-W_{FM}}^{\infty} \delta(\theta) \cdot (\theta/kT) d\theta$$

$$= 4\pi m e/h^3 \int_{0}^{\infty} \delta(\theta) \cdot \theta d\theta$$

(28)

When $\theta \approx 0$, namely, $W_{FM} = W_e$, the probability of electrons penetrating the metal barrier is the greatest. In other words, $\theta = 0$ is the most important contribution to the field emission electron flow. Consequently, Taylor expansion of $\delta(\theta)$ is performed at $\theta = 0$ and obtains

$$\delta(\theta) = \exp[-8m/3e\hbar E(\gamma - 3/2\theta^2 + \cdots)]$$

(29)

Formula (29) is brought into Formula (24).

$$j(0, E) \approx \frac{BE^2}{\gamma} \exp(-D\gamma^3/2E)$$

(30)

where $B = e^3/8\pi \hbar$, $D = 8m/3e\hbar$, and they are all related constants.

Formula (30) shows the electron current density of field emission, which is determined by the applied electric field and metal work function. When the applied electric field is constant, the electron current density is inversely proportional to the metal work function.

### TABLE 2. Work function of three kinds of metal.

| Metallic elements | Work function(eV) |
|-------------------|-------------------|
| Al                | 4.25              |
| Fe                | 4.31              |
| Cu                | 4.40              |
The size parameters and applied voltage of the three kinds of metal protrusion defects are the same; thus, the electric fields $E$ generated under different metal material protrusions are the same. Al has the least escape work, followed by 304 stainless steel and Cu (The Fe content in 304 stainless steel is much higher than that of other metal elements; thus, Fe plays a decisive role in the current density of field emission in 304 stainless steel). The work function of three metals is shown in Table 2 [37]. Therefore, some electrons in conduction band of Al are easier to “pass through” the barrier away from the metal surface than those in 304 stainless steel and Cu. Consequently, the electron current density of Al is higher than that of other two metal material, namely, the electron current density of Al, 304 stainless steel and Cu are $5.787E^2 \exp(-1.261/E)$, $5.707E^2 \exp(-1.288/E)$ and $5.59E^2 \exp(-1.329/E)$ via Formula (30), respectively, which promotes SF$_6$ decomposed more easily under the strike of high-energy electrons by Reaction (1) and generate more characteristic components gases under Al protrusion.

**VI. CONCLUSION**

In this study, the influence of three common metal materials on the decomposition of SF$_6$ in gas-insulated equipment under negative DC PD was investigated, which improve the research of SF$_6$ decomposition mechanism, and provide a scientific and theoretical basis for the method of SF$_6$ DC gas insulated equipment condition monitoring and fault diagnosis based on DCA. The following conclusions were drawn:

1. There is a significant correlation between the types of metal materials and the negative DC PD decomposition of SF$_6$. The amounts of SO$_2$F, SO$_2$F$_2$, and SO$_2$, which were generated by the decomposition of SF$_6$, were the most abundant under Al, followed by 304 stainless steel, and Cu. In addition, the amounts and generation rates of SOF$_2$ are the largest under the same metal, followed by SO$_2$F$_2$ and SO$_2$.

2. The reaction heats of five main formation reactions of decomposition components (SOF$_2$, SO$_2$F$_2$, and SO$_2$) were calculated by DFT simulation. The smaller the reaction heat is, the more easily the corresponding reaction occurs. The observation on the generation rates of decomposition components via the simulation is consistent with the actual measurement results.

3. Based on the free electron cloud and finite depth particle in a box model, the electron current density of field emission has the relationship with metal work function $\gamma$ and electrical field $E$: $j(0, E) \approx \frac{BE^2}{3} \exp(-D\gamma^{3/2}/E)$. The electron current density of field emission is inversely proportional to the metal work function with constant electric field. Consequently, SF$_6$ decomposition components gases are more abundant via Reaction (1)–(16) under the metal electrode with lower work function. The results can well explain the phenomena observed in the experiment. The influence of metal materials on the decomposition of SF$_6$ needs to be fully considered when putting forward for the method of SF$_6$ DC gas insulated equipment condition monitoring and fault diagnosis based on DCA.

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