

Study on the thermal decomposition reaction process and kinetics of SF₆ and tungsten

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Abstract The thermal reaction of SF₆ with tungsten powder was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC), combined with the characterization of solid decomposition products of SF₆ and tungsten by SEM, EDS, XPS and Raman. Based on above experiments, a two-stage decomposition process of SF₆ with tungsten was proposed: the first stage is the surface vulcanization reaction $W+SF_6 \rightarrow WS_2$, mainly taken place at 600 °C, with the activation energy valued at 152.8 kJ·mol⁻¹, according to Avrami-Erofeev equation; the second stage is the endothermic fluorination reaction $WS_2+SF_6 \rightarrow WF_6$, mainly taken place at 750 °C, with the activation energy valued at 126.0 kJ·mol⁻¹, according to the Avrami-Erofeev equation.

1 Introduction

SF₆ is a synthetic inert gas, colorless, tasteless, non-toxic, with excellent insulation performance, and has been applied in many important fields including gas insulated switchgear, semiconductor processing, aerospace etc [1]. On the other hand, SF₆ is a greenhouse gas, whose threat to the environment is 23900 times that of CO₂[2]. Therefore, its extensive use has attracted many researchers to understand its chemical properties. In contrast to the widely believed chemical inertia, SF₆ can react with some compounds like metal or low-valent complex under regular conditions. For example SF₆ can react with hot sodium film at 200 °C [3]. At -61 °C, SF₆ can be reduced with element Cs to CsS₂ in liquid ammonia [4]. Basta et al. found that the reaction of organotitanium and organozirconium complexes with SF₆ could react quickly at room temperature or even below room temperature [5]. Metal tungsten is a key material in electronic and electrical equipment, widely used in high voltage circuit breakers and plasma etching. Due to close contact of tungsten with SF₆ under these harsh conditions, decomposition of SF₆ inevitably taken place. For example, SF₆ corrodes copper-tungsten alloy and generates WF₆ under the action of arc[6]. SF₆-O₂ plasma corrodes refractory metal W to generate WF₆, WO₃, and WOF₄ [7], and Peignon et al. believed that WS₂ was an important intermediate for further oxidation or fluorination to obtain aforementioned decomposition products[8]. Fluorination, vulcanization and oxidation occur during tungsten and SF₆ plasma etching [8-11]. At present, although

researchers have basically confirmed the decomposition products of SF₆ caused by tungsten, the relevant decomposition processes are still unclear. Thermal decomposition reaction is a classical method to study the transformation of substances, which can reveal the thermodynamics and dynamics of the transformation process. However, the apparent activation energy and thermal decomposition kinetics of SF₆ reaction with tungsten powder have not been reported. Herein we adopt synchronous thermogravimetric/differential scanning calorimetric technique investigated thermal decomposition reaction of SF₆ and tungsten powder. Based on the principle of thermal analysis kinetics, the reaction temperature of W powder in SF₆ atmosphere was determined, the apparent activation energy of the reaction was calculated, and the kinetic equation of thermal decomposition reaction was obtained. Meanwhile, the decomposition product and the change of microstructure and composition at high temperature was determined by means of environmental scanning electron microscope (SEM), X-ray energy spectrum analysis (EDS), X-ray photoelectron spectrometer (XPS) and Raman spectroscopy characterization.

2 Experimental parts

2.1 The raw material

SF₆ gas purity 99.99% purchased Chengdu Kemet Special Gas Co., LTD., 4-6 μm tungsten powder.

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2.2 Thermal decomposition reaction of SF₆ and tungsten powder

The thermal decomposition behavior of SF₆ and tungsten was monitored by HCT-4 comprehensive thermal analyzer(Beijing Hengjiu Experimental Equipment Co., LTD.) to obtain the kinetic equation under following conditions: α-Al₂O₃ crucible was used as the reference, the gas flow rate was 100 mL·min⁻¹, sample dosage was 30-50 mg, the heating rate was 5, 10, 20 °C·min⁻¹, and the sample pool was α-Al₂O₃, the temperature range was 25~900°C, and the temperature is ventilated at room temperature for 60 min to ensure that the furnace is filled with SF₆ gas and then the samples are tested by TG and heat flow at different heating rates.

2.3 Preparation of thermal decomposition reaction products

Solid decomposition products were obtained under constant temperature: under the atmosphere of SF₆, Al₂O₃ crucible was used as the reference, the flow rate was 100 mL·min⁻¹, and the furnace was ventilated at room temperature for 60 min to ensure that the furnace was filled with SF₆ gas, and the heating rate was 30 °C·min⁻¹ to 615 °C for 60 min, to make sure SF₆ and tungsten powder react completely. Solid samples were collected for further characterization after the reaction.

2.4 Characterization of solid decomposition products

The morphology and size of decomposition products were characterized by Quanta 200 environmental scanning electron microscope and EDS spectroscopy, with the parameter accelerating voltage at 20 kV and accelerating current at 2 μA. The chemical composition and element binding state of the products were analyzed by Axis UltraDLD X-ray photoelectron spectroscopy (Shimadzu, Japan), and the energy reference was stained carbon C1s (Eb=284.6 eV). The chemical composition was identified by a Reflex laser Raman spectrometer with a transmittance efficiency greater than 30%, scanning range 100-4000 cm⁻¹, signal to noise ratio of silicon third-order peak was better than 22:1 and spectral resolution as visible full spectrum ≤1 cm⁻¹.

3 Discussion of results

3.1 Thermal decomposition reaction of SF₆ and tungsten powder

High voltage circuit breaker contacts are mainly composed of tungsten, but the research on the chemical reaction of tungsten in SF₆ atmosphere is not clear, and current research mainly focuses on the plasma etching of SF₆ and tungsten. In order to study the reaction mechanism of SF₆ and tungsten at high temperature, a thermal decomposition reaction model of SF₆ and

tungsten powder was established to study the reaction process.

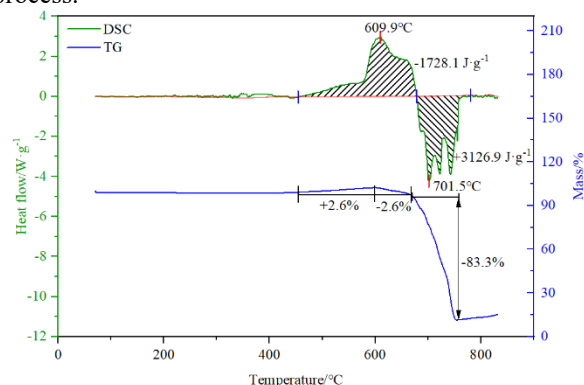


Fig.1 Thermal decomposition reaction of W powder in SF₆ atmosphere

It can be seen from Fig 1 that under SF₆ atmosphere, when heated at a heating rate of 5 °C·min⁻¹, the weight gain of the substance occurs in the range of 457-598 °C with a weight gain rate of 2.6%, and the weight loss of the substance occurs in the range of 598-678 °C with a weight loss rate of 2.6%. The weight gain rate is basically the same as the weight loss rate. The maximum exothermic peak appears on the DSC curve at 609 °C, which may be due to the sulfide reaction $W+SF_6 \rightarrow WS_2$ on the surface, and the heat release is 1728.1 J·g⁻¹. Substantial weight loss occurs at 678-754 °C, with a loss rate of 83.3%. At 702 °C, an endothermic peak appears on the DSC curve, which may be caused by surface fluoridation $WS_2+SF_6 \rightarrow WF_6$, the heat absorption is 3126.9 J·g⁻¹.

3.2 Characterization of solid products of thermal decomposition of SF₆ and tungsten powder

The morphology and elements of raw materials of tungsten powder and solid products after thermal decomposition reaction of SF₆ and tungsten powder were analyzed by environmental scanning electron microscopy (SEM) energy spectrum analyzer. The results are shown in Fig 2. Fig 2a shows the raw material of 4-6 μm tungsten powder, which is distributed in irregular polygons. Fig. 2b shows the scanning electron microscopy of solid decomposition products of 4-6 μm tungsten powder at 615 °C for 60 min. Compared with unprocessed tungsten powder, smaller particles in μm magnitude are generated on the surface, indicating that tungsten powder has undergone chemical reaction with SF₆. Fig. 2c shows the EDS spectra of 4-6 μm tungsten powder raw material, containing only W element. Fig. 2d shows the EDS diagram of tungsten powder at 615 °C for 60 min, which shows that the measured sample contains W, S and O elements, and their mass ratios are 76.91%, 17.06% and 6.03%, respectively. It is speculated that oxides and sulfides may be generated.

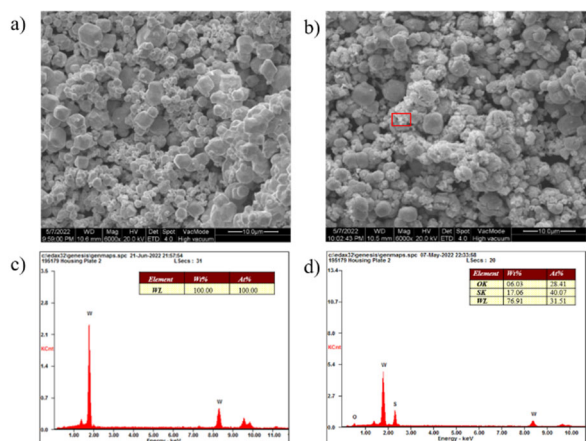


Fig.2 SEM-EDS of tungsten powder raw material, solid products after thermal decomposition reaction of SF₆ and tungsten powder

(**Fig. 2a** raw material of 4-6 μm tungsten powder; **Fig. 2b** SEM images of the solid decomposition products of 4-6 μm tungsten powder at 615 °C for 60 min. **Fig. 2c** EDS spectra of 4-6 μm tungsten powder raw materials. **Fig. 2d** EDS diagram of tungsten powder at 615 °C for 60 min.)

Fig. 3 shows the typical Raman spectra of the solid products of SF₆ reacting with W powder under 532 nm laser excitation in the frequency range of 100-800 cm⁻¹. WS₂ has 10 Raman modes, labeled as first-order modes of LA(M), LA(K), E_{2g}(Γ) and A_{1g}(Γ), second-order modes of 2LA(M) and some combined modes [12-15]. E_{2g}(Γ) and A_{1g}(Γ) are two optical phonon modes in the center of the Brillouin region. E_{2g}(Γ) corresponds to the in-plane optical mode, and A_{1g}(Γ) corresponds to the out-of-plane vibration of the sulfur atom. LA(M) is a longitudinal acoustic mode at point M, which is the collective motion of atoms in the lattice in the plane, similar to sound waves. The additional peaks correspond to the multiphonon modes combined with these first-order modes. Three peaks with good resolution can be observed in Fig. 2, which are 174.1, 350.9 and 420.1 cm⁻¹ corresponding to the first modes LA(M), E_{2g}(Γ) and A_{1g}(Γ), respectively.

In order to determine the surface chemical composition and elemental valence of SF₆ reacting with tungsten powder, X-ray photoelectron spectroscopy (XPS) was performed on the solid decomposition products, and the results are shown in Fig 4. It can be seen from Fig. 4A that there are four elements: C, W, O and S after SF₆ reacts with tungsten powder. The C1s peak at 284.6 eV is derived from vacuum pollution. Fig 4b is the high-resolution map of W4f, where the characteristic peaks at 32.4 eV and 34.5 eV correspond to W4f 7/2 and W4f 5/2 of W⁴⁺ in WS₂, respectively. The characteristic peaks at 35.5 eV and 37.8 eV correspond to W4f 7/2 and W4f 5/2 of W⁶⁺ in WO₃, respectively. Fig 4c is the high-resolution diagram of S 2p, where the characteristic peaks at 35.5 eV and 37.8 eV correspond to W4f 7/2 and W4f 5/2 of W⁶⁺ in WO₃, respectively. Fig 4c is the high-resolution diagram of S2p, where the characteristic peaks

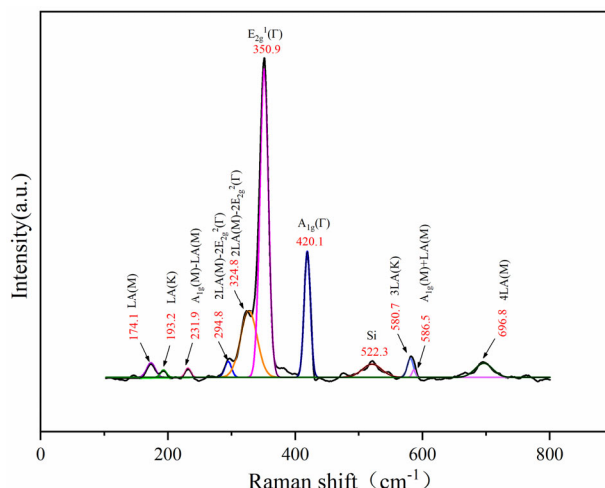


Fig. 3 Raman spectra of solid products of W powder in SF₆ atmosphere

at 162.0 eV and 163.3 eV correspond to S2p3/2 and S2p1/2 of S²⁻ in WS₂ respectively [16-18]. It is speculated that the formation of WS₂ is caused by the reaction between W and SF₆, and a small amount of WO₃ may be caused by the reaction between solid decomposition products and O₂ in the air during the cooling process, but F element is not detected, which is speculated to be caused by the volatilization of WF₆.

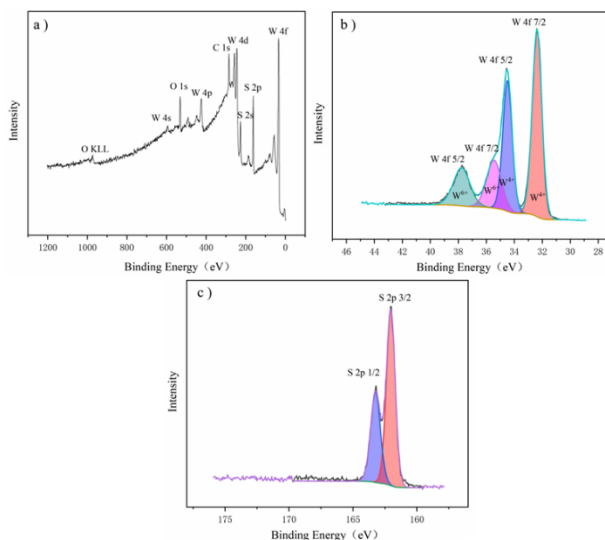


Fig. 4 XPS spectra of solid products of W powder in SF₆ atmosphere a) Full spectrum; b) W4f; c) S2p

3.3 Kinetic analysis of thermal decomposition reaction between SF₆ and tungsten powder

In order to further study the thermal decomposition reaction between SF₆ and tungsten powder and determine the most probable mechanism function F(α), the non-isothermal thermal decomposition kinetics of tungsten powder under SF₆ atmosphere was analyzed on a comprehensive thermal analyzer with different heating rates. The kinetic parameters of thermal decomposition of SF₆ with tungsten powder were calculated by using the Kissinger equation and the Flynn-Wall-Ozawa equation.

Table 1 shows the kinetic parameters of the thermal decomposition of SF₆ and tungsten powder calculated at different heating rates (β). It can be seen from Table 1 that the activation energy of the first stage of the sulfurization reaction of SF₆ and tungsten powder is 152.8 kJ·mol⁻¹, and the activation energy of the second stage of the fluoridation reaction is 126.0 kJ·mol⁻¹.

Ti was obtained from DSC curves of thermal decomposition reaction between SF₆ and tungsten powder at different heating rates (β), and the apparent activation energy E_a corresponding to the reaction fraction α was calculated by Ozawa equation. α and E_a were used to draw α~T and E_a~α curves, and the results were shown in Fig.5.

Table 1. Apparent activation energy of tungsten powder in SF₆ atmosphere at different heating rates

Stage	β / (°C·min ⁻¹)	T _p / °C	E _k / (kJ·mol ⁻¹)	lg(A / (k / s ⁻¹))	r _k	E _o / (kJ·mol ⁻¹)	r _o
First stage	5	60	149.2	6.16	0.97	156.3	0.98
	10	62					
	20	66					
Mean: E _o =(149.2+156.3)/2=152.8 kJ·mol ⁻¹							
Second stage	5	70	120.9	3.67	0.93	131.0	0.94
	10	71					
	20	77					
Mean: E _o =(120.9+131.0)/2=125.95 kJ·mol ⁻¹							

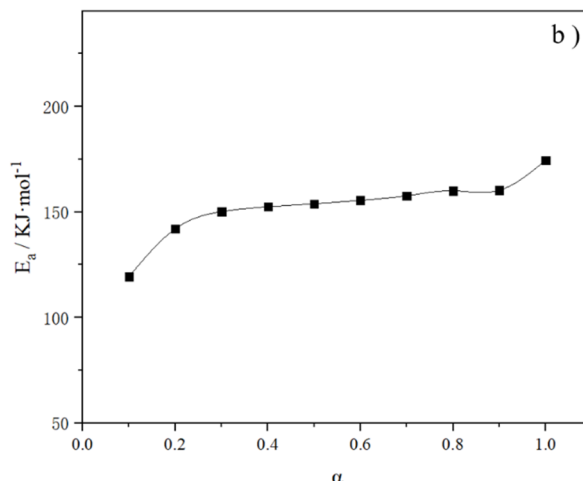
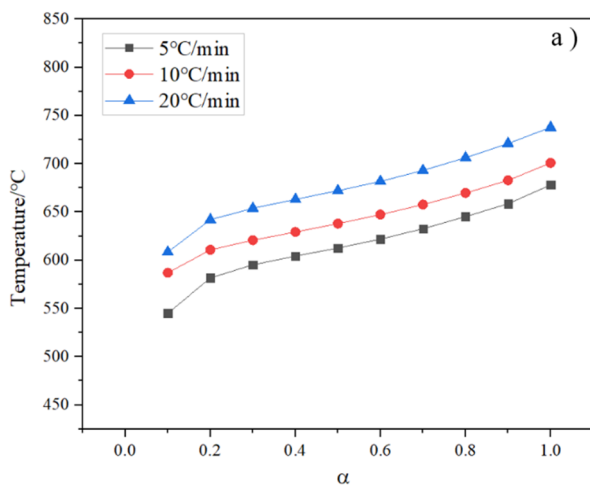


Fig. 5a) T~α curves of SF₆ and W powder at different heating rates in the first stage of thermal reaction obtained by Ozawa method

b) E~α curve of the first stage of the thermal reaction between SF₆ and W powder obtained by Ozawa method

Table 2. calculated values of kinetic parameters for the first stage of SF₆ and W powder thermal reaction

β / (K/min)	Eq.	E/kJ·mol ⁻¹	Log (A/s ⁻¹)	r	Q
5	General Integral	148.13	5.93	0.999	1.63e ⁻⁴
	Mac-Callum-Tanner	155.37	6.46	0.999	3.03e ⁻⁵
	Statava-Sestak	154.87	6.44	0.999	3.03e ⁻⁴
	Agrawal	148.13	5.93	0.999	1.63e ⁻⁴
	General Integral	152.30	6.22	0.999	2.03e ⁻⁴
	Mac-Callum-Tanner	159.99	6.78	0.999	3.78e ⁻⁵
10	Statava-Sestak	159.25	6.73	0.999	3.78e ⁻⁴
	Agrawal	152.30	6.21	0.999	2.03e ⁻⁴
	General Integral	158.08	6.51	0.999	1.61e ⁻⁴
	Mac-Callum-Tanner	153.501	6.78	0.999	2.89e ⁻⁵
20	Statava-Sestak	153.112	6.78	0.999	3.00e ⁻⁵
	Agrawal	158.08	6.50	0.999	1.61e ⁻⁴
	Mean	154.42	6.44		

Stage 1: The conversion rate of 0.4-0.6 interval is different heating rate β corresponding to the thermodynamic data into the equation after the non-isothermal calculation method to obtain the activation energy Mean E_o =154.42 kJ mol⁻¹, through the Kissinger method and Ozawa method equation to calculate the activation energy Mean E_o=152.80 kJ mol⁻¹, and the activation energies are close. Table 2 shows that each G(α) and F(α) in 41 mechanism functions [19] are substituted

into the General Integral, Mac-Callum-Tanner, Statava-Sestak and Agrawal equations [20]. The kinetic parameters of thermal decomposition reaction between SF₆ and tungsten powder were determined by linear regression and logical selection. By comparison and analysis of the value of activation energy E₀, the most possible mechanism functions can be obtained as the No. 15 function. The differential formula of the mechanism function of No. 15 is $f(\alpha)=4/3[-\ln(1-\alpha)]^{1/4}$. $E_k=149.20$ kJ·mol⁻¹ and $A=10^{6.16}$ s⁻¹ calculated by Kissinger equation were substituted into equation $d\alpha/dt=(1/\beta)Af(\alpha)e^{-E_k/RT}$. The kinetic equation of the first stage thermal decomposition of SF₆ with tungsten powder is obtained as $d\alpha/dt=10^{6.16}(1/\beta)4/3[-\ln(1-\alpha)]^{1/4}\exp(-1.492\times 10^5/RT)$.

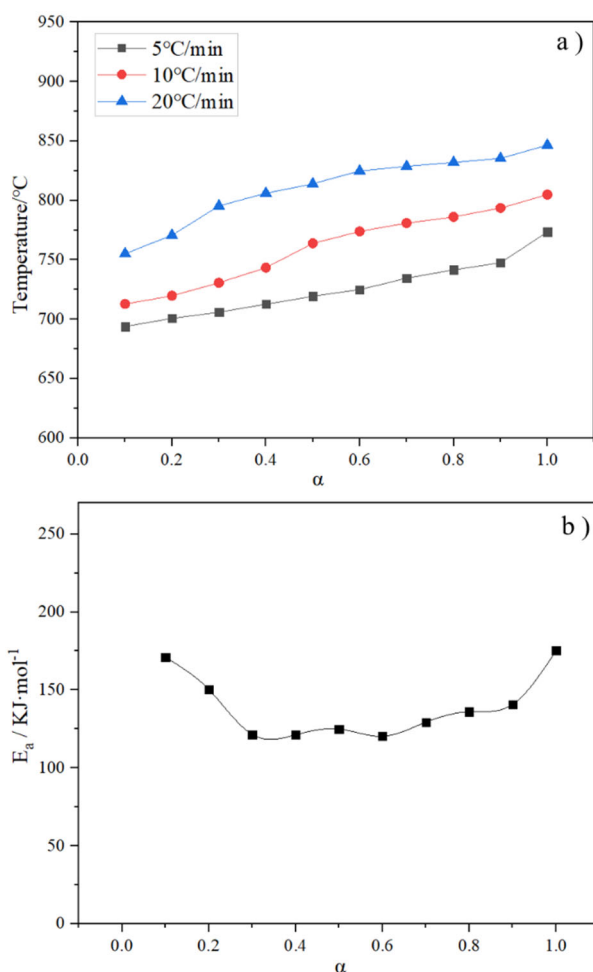


Fig. 4 a) T~α curves of SF₆ and W powder at different heating rates in the second stage of thermal reaction obtained by Ozawa method; **b)** Ozawa method obtained the E~α curve of the second phase of the thermal reaction between SF₆ and W powder

Table 4 Calculated values of kinetic parameters for the second stage of SF₆ and W powder thermal reaction

β/ (K/min)	Eq.	E/kJ·mol ⁻¹	Log (A/s ⁻¹)	r	Q
5	The General Integral	124.57	3.65	0.991	2.01 e ⁻³
	Mac-Callum-Tanner	133.44	4.25	0.993	3.75 e ⁻⁴
	Statava-Sestak	134.17	4.38	0.993	3.75 e ⁻⁴
	Agrawal	124.57	3.64	0.991	2.01 e ⁻³
10	The General Integral	121.82	3.28	0.990	6.90 e ⁻³
	Mac-Callum-Tanner	131.25	3.90	0.992	1.30 e ⁻³
	Statava-Sestak	132.10	4.05	0.992	1.30 e ⁻³
	Agrawal	121.82	3.27	0.990	6.90e ⁻³
20	The General Integral	118.49	3.30	0.992	1.68e ⁻³
	Mac-Callum-Tanner	128.86	3.98	0.994	3.17e ⁻⁴
	Statava-Sestak	129.84	4.14	0.994	3.17e ⁻⁴
	Agrawal	118.49	3.29	0.992	1.68e ⁻³
	Mean	126.62	3.76		

The conversion rate is 0.3-0.7 in the interval of different heating rate β corresponding to the thermodynamic data into the equation after non-isothermal calculation method to obtain the activation energy Mean E₀=126.62 kJ·mol⁻¹, through the Kissinger method and Ozawa method equation calculated the activation energy Mean E₀=125.95 kJ·mol⁻¹, and the activation energies are close. Compared with the value of activation energy E₀ calculated by 41 mechanism functions, it can be found that the most possible mechanism functions are No. 12 function. The differential formula of mechanism function No. 12 is $F(\alpha)=5/2[-\ln(1-\alpha)]^{3/5}$. $E_k=120.90$ kJ·mol⁻¹ and $A=10^{3.76}$ s⁻¹ calculated by Kissinger equation were substituted into equation $d\alpha/dt=(1/\beta)Af(\alpha)e^{-E_k/RT}$. The kinetic equation of the first stage thermal decomposition of SF₆ with tungsten powder is obtained as $d\alpha/dt=10^{3.76}(1/\beta)5/2[-\ln(1-\alpha)]^{3/5}\exp(-1.209\times 10^5/RT)$.

4 Conclusion

In summary, thermal decomposition reaction of tungsten powder with SF₆ was studied through synchronous thermogravimetric/differential scanning calorimetric technique. In addition, environmental scanning electron microscope (SEM), X-ray energy spectrum analysis (EDS), X-ray photoelectron spectrometer (XPS) and Raman spectroscopy characterization was carried out for solid breakdown products under the condition of high temperature, obtaining the change of microstructure,

elements, chemical composition and structure. Based on the principle of thermal analysis kinetics, the reaction temperature of W powder in SF₆ atmosphere was determined, the apparent activation energy of the reaction was calculated, and the kinetic equation of thermal decomposition reaction was obtained. The main conclusions are as follows:

(1) Tungsten powder will interact with SF₆ at 600 °C, and will interact with SF₆ to form WS₂ and WO₃ at 615 °C. When the temperature reaches 750 °C, that is, before reaching the melting and boiling point, it will evaporate completely in the form of gas WF₆.

(2) The reaction between SF₆ and tungsten can be divided into two stages. The first stage is exothermic reaction, W+SF₆ → WS₂, ΔH = -1728.1 J · g⁻¹. The thermal decomposition kinetic equation of sulfide reaction is as follows: $\frac{d\alpha}{dt}=10^{6.16}(1/\beta) 4/3[-\ln(1-\alpha)]^{1/4} \exp(-1.492 \times 10^5/RT)$. The second stage is endothermic reaction, reaction equation: WS₂+SF₆→WF₆, ΔH =+3126.9 J · g⁻¹. The kinetic equation of thermal decomposition of fluorination reaction is: $\frac{d\alpha}{dt}=10^{3.76}(1/\beta)5/2[-\ln(1-\alpha)]^{3/5}\exp(-1.209 \times 10^5/RT)$.

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