Screening of the best formula for flame type high energy burner

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Abstract. In order to explore the best formula of flame-type high-energy burner, this paper selects 7 groups of flame-type high-energy burners with good stability, high energy and a wide range of raw materials based on the existing literature and patents. The Gibbs free energy values of 7 groups of formulations at different temperatures were calculated by using the chemical thermodynamic formula, and the changes in Gibbs free energy values of 7 groups of formulations were drawn, which provided a basis for the calculation of reaction rate k value by Eyring equation. Then, according to the calculation theory of chemical reaction calorific value, the heat of reaction of 7 different formulations at different temperatures was calculated. The results show that the Gibbs free energy value of Al/MnO₂ in the seven groups of formulations is much smaller than that of the other groups in the same reaction temperature environment, and decreases with increasing temperature. According to the Arrhenius formula and the Eyring equation, the reaction rate of Al/MnO₂ is the fastest in each group. When the other conditions are constant, the reaction enthalpy of Al/MnO₂ is the smallest in each group, therefore the heat released by the reaction is the most. In summary, under the same quality conditions, the Al/MnO₂ flame type high energy burner formulation has the fastest reaction rate and the most heat release, which provides theoretical guidance for experimental design and practice.

1. Introduction

High-energy combustion agents, also known as high-heating agents, can also be understood as a broad range of aluminothermy [1]. As one of the traditional high-energy materials, the thermite stores a large amount of chemical energy, which can be quickly released by a redox reaction called aluminothermic reaction. The aluminothermic reaction is believed to generate molten metal and release a large amount of heat from the exothermic aluminothermic mixture or composite. In view of the excellent properties of high-energy combustion agents, especially their high energy density, smaller volumes of drugs can also provide a large amount of chemical heat energy, which is widely used, for example, in the fields of metallurgy, welding, cutting, and destruction of unexploded ordnance [2-3].

There are certain requirements for the selection of various components in high-energy combustion agents. First, it is not suitable to select scarce raw materials, such as Be. Second, it is not applicable to select highly toxic or corrosive components, such as Ca, PbO₂, Ni₂O₃, etc. Third, it is unfavorable to choose the substance that is difficult to obtain elemental substance or extremely easy to denatured in air, such as K, B, etc. Fourth, try to choose the components with better compatibility. Fifth, it is not appropriate to choose components with less heat of combustion, such as C, S, etc. At present, many reducing metals used are Al, Mg, etc., and oxidizing agents include Mn, Fe, and Cu.
In addition to conventional slag type high energy combustion agents, flame type high energy combustion agents are currently available and have more advantages. However, there are few studies on flame-type high-energy burners, and further research is needed. Song [4] pointed out some defects in the destruction of ammunition by traditional slag-type high-energy combustion agents, and prepared flame-type high-energy combustion agents with different doses of Al/MnO2 to carry out the ammunition shell penetration test of the simulated projectile materials. The theoretical calculation of the combustion temperature is based on the experiment. Lv Huiping and Pan Gongpei et al [5]. used different types of flame-type high-energy combustion agents as experimental objects to determine the thermodynamic characteristics of each group, and provided different sets of different thermal parameters of flame-type high-energy combustion agents. At present, there are few pieces of research on flame-type high-energy combustion agents. In this paper, the flame-type high-energy burner formula is screened, and the best flame-type high-energy burner formula is calculated according to the thermochemical theory.

2. Principle and analysis

2.1. Formula screening

In the chemical thermodynamic reaction, in order to judge the direction of the reaction process According to the literature and patents [6-7], the common high-energy burner adiabatic flame temperature value [8] can be seen in Table 1 below.

| Reaction equation                  | Adiabatic flame temperature / K | phase change                  |
|-----------------------------------|---------------------------------|-------------------------------|
| 2Al+ 3NiO = Al2O3+ 3Ni            | 3773                            | Ni vaporization,              |
| Ti+ 2B = TiB2                      | 3193                            | Evaporation rate: 6.37%       |
| Zr+ 2B = ZrB2                      | 3323                            | Melting, melting rate: 14.13% |
| 2Al+ B2O3: Al2O3+ 2B              | 2315                            | Al2O3 solid, B fusion         |
| Ti+ C = TiC                        | 3290                            | Melting, melting rate: 11%    |
| 2Al+ Fe2O3: Al2O3+ 2Fe            | 3622                            | Fe Vaporization,              |
| Si+ C = SiC                        | 1858.5                          | Evaporation rate: 14.24%      |
| Ta + C = TaC                       | 2711.5                          | Solid                         |
| Ti+ 0.5N2 = TiN                    | 4908.5                          | Fully melted in liquid form   |
| Nb + 0.5N2 = NbN                   | 3474.5                          | Fully melted in liquid form   |
| Ta+ 0.5N2 = TaN                    | 3363                            |                               |
| Ti+ 2B = TiB2                      | 3350                            | Fully melted in liquid form   |
| 2Al+3CuO=Al2O3+3Cu                | 2777                            | Gaseous                       |
| Nb + 2B = NbB2                     | 2317.5                          | Solid                         |
| Zr+ C = ZrC                        | 3400                            | Fully melted in liquid form   |
| 2Ta + C = Ta2C                     | 2600                            | Solid                         |
| TiO2+10/3B = TiB3+2/3B2O3          | 1400                            | No self - propagating reaction|
| 4Al+ 3Ti2O3= 2Al2O3+ 3Ti           | 1805.5                          | Are all solid state           |

From the above table, according to the following principles, the following 7 formulas are selected: 1. The adiabatic flame temperature is higher 2. Ensure that it can’t react with other components in the air at room temperature 3. The raw material storage conditions are easy to control 4. Non-toxic. See Table 2 below for details.
Table 2. Flame type high energy burner formula to be studied.

| No | Component   | Mass ratio | No | Component   | Mass ratio |
|----|-------------|------------|----|-------------|------------|
| 1  | Al/CuO      | 20/80      | 5  | Al/Ni2O3/PTFE | 27/30/42/3 |
| 2  | Al/CuO/SiC  | 20/80/2    | 6  | Al/MnO2     | 29.5/70.5  |
| 3  | Al/CuO/SiC  | 20/80/5    | 7  | Al/NiO      | 24.5/75.5  |
| 4  | Al/PbO2     | 13/87      |

2.2. Method and theory
For the chemical combustion performance of various formulations, the chemical reaction rate and the total reaction exotherm of the reagent are the decisive factors determining the thermal performance of the reaction. The relationship between the reaction rate and concentration of the chemical reaction measured by the experiment is represented by the rate equation:

\[
\frac{dc}{dt} = -kc
\]

(1)

Where \(c\) is the concentration; \(t\) is the time; and \(k\) is the ratio constant.

For the isothermal reaction process at different temperatures, Arrhenius carried out a large number of confirmatory experiments, and found that there is the following relationship between the chemical reaction rate constant \(k\) and the chemical reaction temperature \(T\):

\[
k = A e^{\frac{E_a}{RT}}
\]

(2)

Where \(k\) is the chemical reaction rate constant; \(A\) is the Arrhenius factor; \(R\) is the gas constant; \(T\) is the reaction temperature;

A thermodynamic function is introduced, namely Gibbs free energy [9-11].

\[
G = U - TS + pV = H - TS
\]

(3)

Where \(U\) is the internal energy of the system; \(T\) is the absolute reaction temperature (K); \(S\) is the entropy; \(P\) is the pressure; \(V\) is volume; \(H\) is the enthalpy.

Eyring Equation (Eyring-Polanyi equation) was proposed by Henry Eyring, Meredith Gwynne Evans and Michael Polanyi in 1935. Combining the transition state theory with the empirical Arrhenius equation, the chemical reaction rate can be used to describe the differences in chemical kinetics.

\[
k = \frac{k_B T}{h} e^{\frac{\Delta G}{RT}}
\]

(4)

Where \(T\) is the adiabatic reaction temperature; \(h\) is the Planck constant; \(Bk\) is the Boltzmann constant; \(k\) is the reaction rate constant; \(R\) is the gas constant; \(\Delta H\) is the reaction enthalpy; \(\Delta S\) is the reaction entropy change; \(\Delta G\) is the Gibbs free energy. As a further extension and extension of the Arrhenius formula, the Eyring equation more intuitively illustrates the relationship [12] between the chemical reaction rate constant \(k\) and the Gibbs free energy value \(\Delta G\) and the reaction enthalpy change \(\Delta H\) and the reaction entropy change \(\Delta S\).

According to the derivation of the first law of thermodynamics, when the chemical reaction is subjected to an irreversible chemical reaction under constant temperature constant temperature or constant temperature and constant pressure, and no useful work is performed (the chemical reaction undergoes a thorough irreversible reaction):

\[
Q_p = \Delta H
\]

(5)

Where \(QP\) is the constant pressure thermal effect; \(\Delta H\) is the enthalpy difference before and after the reaction.

3. Results and discussion

3.1. Gibbs free energy calculation
According to the above theoretical method, the Gibbs free energy $\Delta G$ value of the above seven groups of formulas at different temperatures is obtained, and then the reaction rate $k$ value can be calculated according to the Eyring equation. The figure 1 shows the Gibbs free energy values for seven different formulations at different ambient temperatures.

![Figure 1. Calculation results of each group of Gibbs free energy values.](image1)

It is not difficult to observe from the data in the chart. Under certain other conditions, the Gibbs free energy value of Al/MnO2 is much smaller than that of other groups in the same reaction temperature environment, and decreases with increasing temperature. According to the Arrhenius formula and the Eyring equation, the reaction rate of Al/MnO2 is the fastest in each group.

3.2. Reaction heat calculation

The first law of thermodynamics:

$$\Delta H = H_1 - H_2$$

Where $H_1$ is the calorific value of the state reflected; $H_2$ is the calorific value of the state at the end of the reaction. It can be seen that the smaller the reaction enthalpy value, the greater the heat release reaction, and the reaction exotherm value is opposite to the reaction enthalpy change value.

![Figure 2. Calculation results of each group of reaction enthalpy changes.](image2)

As shown in figure 2, the reaction enthalpy values of each group are calculated. When the other conditions are constant, the reaction enthalpy of Al/MnO2 is the smallest in each group, and the heat released by the reaction is the most. Especially at temperatures below 1200 °C, it releases far more heat than the other groups. When the temperature exceeds 1200 °C, the exotherm of No. 1-3, the Al/CuO group is also approaching to Al/MnO2. The reaction enthalpy of Al/MnO2 also slightly increased around 700 °C, and slightly decreased around 1300 °C, but the overall fluctuation was not large. As far as the calculation results are concerned, Al/MnO2 has the largest heat release and is relatively stable, which provides theoretical guidance for experimental design and practice.

4. Conclusion

In this paper, MnO2, Mn2O3 and Mn3O4 are selected as three typical manganese oxides. This paper searches for literature and patents, including flame-type high-energy burner formulations in existing studies, and screens and obtains seven groups of components to be tested according to the conditions of adiabatic flame temperature, wide source of materials, and harsh storage conditions. According to the theory of chemical thermodynamics and the calculation of calorific value of chemical reaction, the energy of the aluminothermic system composed of Al powder and Al powder and the Gibbs free
energy and reaction calorific value of the system at different temperatures were calculated. The results show that the Gibbs free energy value of Al/MnO2 system is the smallest at different temperatures, and the reaction rate is the fastest. The reaction enthalpy of Al/MnO2 is the smallest at different temperatures, and the reaction heat release is the largest. From the theoretical calculation results, the combustion efficiency of Al/MnO2 system may be the best, which provides theoretical guidance for experimental design and practice.

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