Analysis of Thermochemical Properties of three typical Manganese based thermite

Rui Zhu¹, Tao Guo*¹, Miao Yao¹, Xiaofeng Liu¹, Qiong Wang² and Wen Ding¹

¹College of Field Engineering, Army Engineering University of PLA, Nanjing, Jiangsu, 210007, China
²International Military Cooperation Office of the CMC, Beijing, Beijing, 100000, China
*Corresponding author’s e-mail: guotao3579@126.com

Abstract. In order to investigate the thermochemical and reactive properties of thermite composed of typical manganese oxides, three common manganese oxides meaning MnO₂, Mn₂O₃ and Mn₃O₄, are selected in this paper to form aluminothermic agent with Al powder, respectively. According to the chemical thermodynamics, the difference of Gibbs free energy among different components is calculated, and the reaction rate k is calculated according to Eyring equation, then the Gibbs free energy values of three thermite at different ambient temperatures are drawn. Furthermore, according to the theory of chemical reaction calorific value calculation, the reaction calorific values of three thermite at different temperatures are calculated. The results show that the Gibbs free energy of Al/MnO₂ system is the smallest at different temperatures, the reaction rate and the enthalpy of reaction of Al/MnO₂ are the fastest and the smallest at different temperatures and the heat release is the largest. The results of calculation provide theoretical guidance for experimental design and practice. Under the condition of the same mass of reactants, the discharge heat of MnO₂ is the largest, and the heat value of the MnO₂ is the highest.

1. Introduction

The high-energy combustion agent, also known as a high-heat agent, can also be understood as an aluminum-heat agent in a broad sense [1]. The main difference from the traditional thermite is that the reductant in the component is not limited to aluminum, but can also be other metal or non-metal with reduction ability, such as magnesium, calcium, boron. At the same time, oxides of the high-energy combustion agent are not less than one, but can participate in a variety of reactions together. The general formula of high-energy combustion agent reaction exothermic is as follows:

\[ A + BO \rightarrow AO + B + \Delta H \]

The biggest difference between high-energy combustion agent and ordinary pyrotechnic agent is that it can release huge heat (more than 2.31kJ/g, otherwise the reaction cannot be carried out), and the combustion temperature is above 2000K[2-3]. In view of the excellent properties of high-energy combustion agent, especially its high-energy density, small volume charge can also provide a large number of chemical heat energy, which is widely used in metallurgy, welding, cutting, unexploded ammunition destruction and other fields[4-5].

Thermites are mainly binary components, such as Al/Fe₂O₃[6], Al/CuO[7]. In recent years, because of the high oxygen content and large storage capacity of MnO₂, some scholars began to pay attention
to the thermite composed of MnO₂ and Al powder[8]. However, there are many valence states of Mn elements, and there are three kinds of common oxides: MnO₂, Mn₂O₃, and Mn₃O₄. On the other hand, in the process of TG/DSC thermogravimetric analysis of MnO₂, it is found that MnO₂ does not directly remove all O elements to form Mn, but gradually deoxidizes and is accompanied by two obvious endothermic processes[9-10]. These two endothermic peaks may have absorbed the heat generated in the aluminothermic reaction to some extent. Therefore, this paper considers that if Al/Mn₂O₃ and Al/Mn₃O₄ are directly used to prepare high-energy combustion agent, it may cross the process of endothermic reaction and thus improve the heat release per unit mass reaction. In this paper, from the point of view of Gibbs free energy and chemical reaction calorific value calculation, the thermochemical calculation of MnO₂, Mn₂O₃, and Mn₃O₄ metal oxides and Al is carried out, and the components with the largest reaction calorific value are found, which provides theoretical guidance for the following experimental practice.

2. Method and theories
In the chemical thermodynamic reaction, in order to judge the direction of the reaction process (negative, indicating that the reaction can be carried out), the thermodynamic function, that is, the Gibbs free energy[11-12] (Gibbs free energy), which is also known as Gibbs free energy, free enthalpy or free energy. Free energy is an important parameter in thermodynamics referring to the fact that some of the internal energy of the reactant system can be transformed into the energy of external work in a thermodynamic reaction process. G is commonly used to indicate that it is defined as:

\[ G = U - TS + pV = H - TS \]  \hspace{1cm} (1)

In this formula, U is the internal energy of the system, T is the absolute reaction temperature (K); S is entropy, p is pressure, V is volume, H is enthalpy.

The Eyring equation[13], also known as the Eyring-Polanyi equation, was proposed by Henry Eyring, Meredith Gwynne Evans and Michael Polanyi in 1935. This equation combines the transition state theory with the empirical Arenius equation, and the chemical reaction rate can be used to describe the difference of chemical kinetics. The expression is:

\[ k = \frac{k_B T}{h} e^\frac{\Delta S}{R} e^\frac{-\Delta H}{RT} \]  \hspace{1cm} (2)

As a further extension and generalization of Alenius formula, Eyring equation more intuitively expounds the relationship between chemical reaction rate constant k and each of the three physical quantity: Gibbs free energy value ΔG, reaction enthalpy change ΔH and reaction entropy change ΔS, that is, the reaction rate constant k is negatively correlated with Gibbs free energy value ΔG and reaction entropy change ΔS, and positively correlated with reaction enthalpy change ΔH under the premise that other conditions are equal and consistent[14].

3. Results and discussion

3.1 Calculation of Gibbs free energy value
According to the theory and method analysis, the Gibbs free energy ΔG of the three groups formed with Al powder and each of MnO₂, Mn₂O₃, and Mn₃O₄ metal oxides at different temperatures are calculated. After calculating the reaction rate k value according to Eyring equation, the Gibbs free energy values of three kinds of thermite at different ambient temperatures are drawn, as shown in Fig.1.
From Fig. 1, the Gibbs free energy value of Al/MnO2 is the smallest at different temperatures, followed by Al/Mn2O3 and Al/Mn3O4, so the reaction rate of Al/MnO2 is the fastest, Al/Mn2O3 is slower, Al/Mn3O4 is the slowest, which accords with the experimental phenomenon. On the other hand, the mass ratios of oxygen elements in MnO2, Mn2O3 and Mn3O4 molecules were 36.8%, 30.3% and 27.9%, respectively. Although the overall reaction ratio is strictly in accordance with the chemical equation, because the oxygen content in the latter two molecules is lower, the chemical bond is shorter and the bond is closer, the activation energy is higher. For this kind of reaction, the faster the reaction rate is, the easier it is to transfer heat without detonation.

3.2 calculation of reaction heat

According to the calculation theory and method analysis of chemical reaction calorific value, the reaction calorific values ΔH between three group of Al powder and each of MnO2, Mn2O3 and Mn3O4 at 0℃ to 1500℃ were calculated, and the picture were drawn according to the chemical reaction calorific values changes of the three thermite at each temperature, as is shown in Fig. 2.

From Fig. 2, the reaction enthalpy of Al/MnO2 is the smallest at different temperatures, followed by Al/Mn2O3 and Al/Mn3O4, so the heat release of Al/MnO2 is the largest, Al/Mn2O3 is the second, Al/Mn3O4 is the smallest, which accords with the experimental phenomenon. According to the TG/DSC curve of MnO2 [10], it can be seen that the heat release of MnO2 is the smallest under the same molar amount, but the calorific value of MnO2 is the highest under the condition of the same mass reactant, and it can be seen that the calorific value of MnO2 is the highest.
4. Conclusion
In this paper, MnO$_2$, Mn$_3$O$_4$, and Mn$_2$O$_4$ are selected as three typical manganese oxides. According to the theory of chemical thermodynamics and the calculation theory of calorific value of chemical reaction, the energy of thermite system formed by Al powder and three typical manganese oxides, severally, is calculated and studied, and the Gibbs free energy and reaction calorific value of the system at different temperatures are calculated emphatically. The calculated results show that the Gibbs free energy value of Al/MnO$_2$ system is the smallest and the reaction rate is the fastest at different temperatures, and the reaction enthalpy of Al/MnO$_2$ is the smallest at different temperatures, and its reaction heat release is the largest. From the results of theoretical calculation, the combustion efficiency of Al/MnO$_2$ system may be optimal, which provides theoretical guidance for experimental design and practice.

References
[1] Yan, S., Jian, G., Zachariah, M.R. (2012) Electrospun nanofiber-based thermite textiles and their reactive properties. Acs. Applied Materials & Interfaces., 4: 6432–6435.
[2] Zheng, B.H., Wang, P.S., Guan, L., et al. (2015) Reaction Properties of Super Thermites. Chinese Journal of Energetic Materials., 23: 1004–1009.
[3] Shimojo, F., Nakano, A., Kalia, R.K., et al. (2008) Electronic processes in fast thermite chemical reactions: a first-principles molecular dynamics study. Physical Review E Statistical Nonlinear & Soft Matter Physics., 77:066103.
[4] An, T., Zhao, F.Q., Yi, J.H., et al. (2011) Preparation, Characterization, Decomposition Mechanism and Non-Isothermal Decomposition Reaction Kinetics of the Super Thermite Al/CuO Precursor. Acta Physico-Chimica Sinica., 27: 281–288.
[5] Ouyang, D., Pan, G., Guan, H., et al. (2011) Effect of different additives on the thermal properties and combustion characteristics of pyrotechnic mixtures containing the KClO$_4$/Mg–Al alloy. Thermochimica Acta., 513: 119–123.
[6] Duraes, L., Costa, B.F.O., Santos, R., et al. (2007) Fe$_2$O$_3$/aluminum thermite reaction intermediate and final products characterization. Materials Science & Engineering A., 465: 199–210.
[7] Petrantoni, M., Rossi, C., Salvagnac, L., et al. (2010) Multilayered Al/CuO thermite formation by reactive magnetron sputtering: Nano versus micro. Journal of Applied Physics., 108: 84323.
[8] Zhao, N.N., Cui-Cui, H.E., Liu, J.B., et al. (2012) Preparation and Characterization of Superthermite Al/MnO$_2$ and Its Compatibilities with the Propellant Components. Chinese Journal of Explosives & Propellants., 35: 32–36.
[9] Song, J. X, Fang, X., Guo, T., Bei, F.L., Ding, W., Yu, H.J., Zhang, X.N. (2018) A Novel Process of Thermal Decomposition of MnO$_2$ Nanorods. Russian Journal of Physical Chemistry A., 92: 1742–1747.
[10] Ghodbane, O., Pascal, J.L., Fraisse, B., et al. (2011) Structural in Situ Study of the Thermal Behavior of Manganese Dioxide Materials: Toward Selected Electrode Materials for Supercapacitors. Acs. Applied Materials & Interfaces., 2: 3493–3505.
[11] Liu, Shirong. (1992) Gibbs free energy and chemical equilibrium. Central South University of Technology Press, Changsha.
[12] Zhang, Juncai. (1999) Calculation and application of Gibbs free energy variation. Journal of Xianyang normal University., 3: 49–53.
[13] Bonnet, L., Rayez, J.C. (2010) Dynamical derivation of Eyring equation and the second-order kinetic law. International Journal of Quantum Chemistry., 110: 2355–2359.
[14] Huang, L., Hwang, A., Phillips, J. (2011) Effect of Temperature on Microbial Growth Rate–Mathematical Analysis: The Arrhenius and Eyring–Polanyi Connections. Journal of Food Science, 76: E553–E560.