Theoretical calculation of self-propagating high-temperature synthesis (SHS) preparation of AlB_{12}

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Abstract: Although experimental results of preparing AlB_{12} by self-propagating high-temperature synthesis using Mg-B_2O_3-Al_2O_3 as raw material has been studied, the theoretical calculations for the preparation of AlB_{12} have not been examined as thoroughly. In this article, for the first time, we report on the study of theoretical calculation and the adiabatic temperature, calculated, and compared with the actual reaction temperature. The Gibbs free energy for each level of reaction is also calculated. The calculation results show that the adiabatic temperature is 2789.5 K, the standard Gibbs free energy of each reaction is less than 0, and the reaction can proceed spontaneously, which is consistent with the results of the experiment.

Keywords: AlB_{12}, SHS, Theoretical calculations, Adiabatic temperature, Standard Gibbs free energy

Introduction

In the process of SHS synthesis reaction research, the reaction system must meet certain thermodynamic conditions so that the reaction can self-sustain the combustion reaction process (1-3). Among them, the most basic thermodynamic parameter is the Adiabatic Temperature of the reaction (4-7). Self-propagating high-temperature synthesis (or SHS) is a chemical reaction under special conditions (8-11). Thermodynamic analysis mainly discusses the feasibility of the reaction, such as how to judge whether a chemical reaction can proceed under given conditions, to what extent, and what effect the reaction will have after changing the conditions (12-14).

Thermodynamic analysis of the combustion system is the basis for studying the SHS process (15-17). The main task of thermodynamic analysis is to calculate the combustion temperature and product balance under adiabatic conditions, that is, when all the heat released by the reaction is used to heat the product synthesized during the reaction (18, 19). The calculation is based on the minimum principles of conservation of mass and energy and chemical potential (Gibbs free energy) (20, 21). Thermodynamic calculation is a very effective method for studying the SHS process, as it helps to control the temperature and composition of the process products (22-25).

Previous studies have shown that AlB_{12} can be prepared by the self-propagating method (26-28), and the reaction temperature is higher than 2300 °C. However, the self-propagating reaction has not been calculated theoretically. In this article, the basic principle of self-propagating reaction is explained, the theoretical calculation of self-propagating preparation of AlB_{12} is studied, and the calculated results are compared with the actual test results.

Principle of self-propagating reaction

Adiabatic temperature is an important thermodynamic parameter describing the characteristics of combustion synthesis (SHS) reaction . Merzhanov et al. put forward the following empirical criterion, that is, only when $T_{ad} > 1800K$, the SHS response can be self-sustained (25). Munir found that the ratio of the heat of formation of some compounds below their melting point to the heat capacity at 298K has a linear relationship with $\Delta H^{\theta}_{298} / \Delta Cp_{298}$ and T_{ad} (29, 30). It can be concluded that the reaction can maintain itself only when $\Delta H^{\theta}_{298} / \Delta Cp_{298} \geq 2000K$ (corresponding to $T_{ad} \geq 1800K$). Otherwise, only the outside world can supplement energy into the system, such as by using a "preheating", "chemical furnace" or the use of "thermal explosion" methods to maintain self-reaction.

$$A(s) + B(s) \rightarrow AB(s) + \Delta H \tag{1}$$

Taking the enthalpy of the system as the state function, the heat released during the reaction is:

$$\Delta H = \Delta H^{\theta}_{298} + \int_{298}^{Tad} \Delta Cp dT \tag{2}$$

in which ΔH^{θ}_{298} is the standard enthalpy for formation of the product at a temperature of 298K, and ΔCp is the heat capacity of the product.

When adiabatic, the thermal effect of the system is $\Delta H = 0$, and the adiabatic temperature T_{ad} can be calculated in the following situations:

a. When $T_{ad} < T_{mp}$:

$$-\Delta H^{\theta}_{298} = \int_{298}^{Tad} \Delta Cp dT \tag{3}$$

b. When $T_{ad} = T_{mp}$:

$$-\Delta H^{\theta}_{298} = \int_{298}^{Tad} \Delta Cp dT + \gamma \Delta H_m \tag{4}$$

in which ΔH^{θ}_{298} is the enthalpy of the product in the molten state, and ΔCp_{298} is the heat of fusion of the product.

c. When $T_{ad} > T_{mp}$:

$$-\Delta H^{\theta}_{298} = \int_{298}^{Tad} \Delta Cp dT + \Delta H_m + \int_{Tmp}^{Tad} \Delta Cp dT \tag{5}$$

It can be calculated approximately with the following equation:

$$Cp = a + b \times 10^{-3} \times T + c \times 10^{5} T^{-2} + d \times 10^{-6} T^{2} \tag{6}$$

Calculation of Gibbs free energy

The Gibbs free energy change ΔG is a criterion for determining whether a chemical can proceed spontaneously under constant temperature and pressure conditions (31). The Gibbs free energy in the standard state can roughly reflect the possibility of a reaction or reaction trend. If $\Delta G^{\theta}<0$ in the system, the reaction process is irreversible and proceeds spontaneously. If it is $\Delta G^{\theta}=0$, the reaction process is reversible and spontaneous. And if it is $\Delta G^{\theta}>0$, the reaction cannot proceed spontaneously.

$$V_1B_1 + V_2B_2 + ... \rightarrow V_jB_j + ... \quad (7)$$

In equation (7), Vi is the measurement coefficient of the element or compound Bi.

The calculation equation for the change of its standard free energy is:

$$\Delta G^{\theta} = \sum v_i G_i T \quad (8)$$

In the equation (8), G_i, T is the free energy of the element or compound B at temperature T.

In the Al_2O_3-B_2O_3-Mg system, the following chemical reactions generally occur:

$$Al_2O_3 + 3Mg \rightarrow 2Al + 3MgO \quad (9)$$

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \quad (10)$$

$$Al + 12B \rightarrow AlB_{12} \quad (11)$$

$$Al_2O_3 + 12B_2O_3 + 39Mg \rightarrow 2AlB_{12} + 39MgO \quad (12)$$

Table 1 shows the free energy changes. A more systematic study of the thermodynamics of related reaction systems, prediction of the phases that may exist and appear in the reactants and products from the perspective of thermodynamics, provides a theoretical basis for the regulation of the self-propagating high-temperature synthesis process.

Table 1 The relation between free energy and temperature of different reactions

Equation	$\Delta G^{\theta}=A+BT$ (kJ/mol)	Temperature range/K
$Al_2O_3 + 3Mg \rightarrow 2Al + 3MgO$	-128.01584+0.00792T	273-893
	-139.08535+0.01888T	893-2303
$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$	-262.37839+0.07233T	2303-2573
	-532.60705+0.05814T	273-723
	-559.15828+0.0947T	723-853
$Al + 12B \rightarrow AlB_{12}$	-600.18482+0.13789T	853-2353
	-505.72672+0.09833T	2353-2573
$Al_2O_3 + 12B_2O_3 + 39Mg \rightarrow 2AlB_{12} + 39MgO$	-220+0.00745T	933-2473
	-825.48067+0.23708T	2473-2789.5
	-1219.78117+0.16076T	273-933
	-1707.37528+0.21488T	933-2573

Result of calculation

The adiabatic temperature was calculated using HSC6.0 software, and the adiabatic temperature of the reactions is 2789.5 K. Previous studies have shown that the reaction temperature of self-propagating preparation of AlB_{12} exceeds 2300 °C (2573 K). This tested result matches the calculation result. Since =2789.5 K>1800K, self-propagation can proceed smoothly. Note that the reaction always has $\Delta G^{\theta} < 0$ in table 1, so the reaction can proceed spontaneously.

Summary

The calculation results of preparing AlB_{12} using Mg, Al_2O_3 and B_2O_3 as the raw materials shows that the adiabatic temperature of the system is 2789.5K, which meets the self-propagating reaction conditions. The calculated results are consistent with the actual test results. The Standard Gibbs free energy of the reaction formula is less than zero, which also proves the possibility of self-propagating reactions.

Notes

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