

CALCULATION OF ADIABATIC TEMPERATURE THROUGH COMPUTER PROGRAM IN PROCESS OF COMBUSTION SYNTHESIS^①

Hu, Wenbin Liu, Weiwei^② Liu, Yexiang Wang, Huazhang Zheng, Ziqiao
Central South University of Technology, Changsha 410083, China

ABSTRACT

The adiabatic temperature in the process of self-propagating high temperature synthesis is calculated through FOXBASE language program on the base of establishing thermodynamic data pool concerned. The adiabatic temperature of some common self-propagating high temperature synthesis has been calculated, and the computed results are compared with the adiabatic temperature reported. At the same time, the curve about the influence of preheating temperature and adding diluent on T_{ad} is drawn as an example.

Key words: self-propagating high temperature synthesis adiabatic temperature preheating temperature diluent calculation through computer program

1 INTRODUCTION

In the study of SHS, one finds that reaction systems must satisfy certain thermodynamic condition, so that the reaction can propagate itself. The basic thermodynamic parameters of the reaction is adiabatic temperature, which is the highest temperature that the reaction system can reach, provided that all the released heat is used to increase the temperature of reaction system after reactants are initiated. The adiabatic temperature is a theoretical result. The study shows that if the self-propagating reaction can be self-sustaining, it must satisfy the following formula:

$$T_{ad} \geq 1800 \text{ K}^{[1 \sim 4]}$$

At the same time, preheating reactant

and adding diluent (Du) can directly influence the T_{ad} of SHS reaction, and the value of reaction temperature directly influences both the phase state of product and the mechanism of SHS reaction. Therefore, the quantitative calculation of T_{ad} in the system is absolutely necessary in the study of SHS reaction. The previous study was mainly concentrated on evaluating T_{ad} under the condition that simple elements compose simple compound at room temperature. But no systematic literature can provide the information about the influence of initial condition (preheating, adding diluent) on T_{ad} and about the calculation of T_{ad} in complex reaction. Considering the influence of initial condition on T_{ad} and great many of thermodynamic

① Manuscript received June 13, 1993;

② Works in the Computation Center of the Department of Coal in Hunan

data, great amount of calculating work would be involved if product had phase state transformation. This study creates a FOXBASE language program on the base of establishing a data pool. Provided that the equation of SHS reaction and the preheating temperature (T_0) are input, the computer can calculate the ultimate T_{ad} of SHS reaction rapidly and accurately under certain initial conditions. And it can decide whether the product will cause solid phase transformation or melt, and calculate solid phase transformation rate and melted rate of itself. At last, it can make use of calculation results and draw the curve of $T_0 - T_{ad}$ and $Du\%$ — T_{ad} as an example. This study has greatly instructive meaning to the theoretical and applied study of SHS.

2 CALCULATING METHOD AND PROGRAMMING

Suppose that molar heat capacity at constant pressure is:

$$C_p = A_1 + A_2 10^{-3} T + A_3 10^5 T^{-2} + A_4 10^{-6} T^2 + A_5 10^8 T^{-3} \\ (\times 4.18 \text{ J/K} \cdot \text{mol}) \quad (1)$$

The thermodynamic data pool of some common substances is established. It induces the name of the substance, the coefficient of C_p at different phase state, the solid phase transformation point (T_{tr}), the solid phase transformation heat (ΔH_{tr}), the melting point (T_m), the heat of fusion (ΔH_m) and the standard heat content of the formation (H_{298}^0). According to the first law of thermodynamics, one can obtain:

$$C_p = dH/dT \quad (2)$$

Integrating this equation between normal temperature and T , one gets:

$$H_T^0 - H_{298}^0 = \int_{298}^T C_p dt \quad (3)$$

Equation (3) is the basic computing equation of this study, but it can only satisfy the condition that there is no solid state phase change in the studied temperature interval. If there is any solid phase change ($T \geq T_{tr}$), then the calculating equation of relative heat content is

$$H_T^0 - H_{298}^0 = \int_{298}^{T_{tr}} C_p dT + \Delta H_{tr} + \int_{T_{tr}}^T C_p' dT \quad (4)$$

where C_p' is the molar heat capacity at constant pressure.

If there are both solid phase transformation and melt ($T \geq T_m$) in the studied temperature interval, one should calculate relative heat content according to the following equation:

$$H_T^0 - H_{298}^0 = \int_{298}^{T_{tr}} C_p dT + \Delta H_{tr} + \int_{T_{tr}}^{T_m} C_p' dT + \Delta H_m + \int_{T_m}^T C_p'' dT \quad (5)$$

where C_p'' is the molar heat capacity at constant pressure under the liquid state. If there is no solid phase transformation but there is melt ($T \geq T_m$), then

$$H_T^0 - H_{298}^0 = \int_{298}^{T_m} C_p dT + \Delta H_m + \int_{T_m}^T C_p'' dT \quad (6)$$

the final equation of T_{ad} is

$$\sum_i m_i H_{T_0}^0 (\text{reactant} + \text{diluent}) = \sum_j n_j H_{T_{ad}}^0 (\text{product} + \text{diluent}) \quad (7)$$

where m_i, n_j are mole fractions of the substance in the equation. This is an equation concerning T_{ad} . Cycle pilot calculation method is used to solve T_{ad} with the consideration of the accuracy of 1 K of the relevant thermodynamic data. Suppose pilot calculation function is:

$$f(T_{ad}) = \sum_i n_i H_{T_{ad}}^0 - \sum_j m_j H_{T_0}^0 \quad (8)$$

First, suppose $T_{ad'} = 1000 \text{ K}$, if $f(T_{ad'}) < 0$, one should define cycle pilot calculation

tion step as $+100$, assign $(T_{ad'} + 100)$ to $T_{ad'}$ and continue pilot calculation until $f(T_{ad'}) \geq 0$. Then, one changes cycle step to -10 , $T_{ad'} = T_{ad'} - 10$, and continue pilot calculation until $f(T_{ad'}) \leq 0$. After that, one changes cycle step to $+1$, $T_{ad'} = T_{ad'} + 1$, and continues the calculation until $f(T_{ad'}) \geq 0$. The final value of T_{ad} is $(T_{ad'} - 0.5) \pm 0.5$ K. If the final result of cycle pilot calculation is $T_{ad'} = T_{ir}$ or T_m , then whether there is phase state transformation should be decided, and solid phase transformation rate and melted rate should be calculated. The equation of phase transformation rate (U_m) is

$$U_m = \left(\sum_i m_i H_{T_0}^0 - \sum_j n_j H_{T_{ad'}}^0 + n_j \Delta H \right) / (n_j \Delta H) \quad (9)$$

where n_j is a mole factor, and ΔH is phase transformation heat.

If $U_m > 0$, then there really exists phase transformation, output $U_m, T_{ad} = T_{ad'}$.

If $U_m = 0$, then there is no phase transformation, $T_{ad} = T_{ad'}$.

If $U_m < 0$, then the temperature of the phase transformation has not been reached, $T_{ad} = (T_{ad'} - 0.5) \pm 0.5 < T_{ir} \text{ (or } T_m)$.

3 THE CALCULATION OF T_{ad} OF SOME COMMON SHS REACTIONS

This program adopts the way of man-machine interaction in English. Input preheating temperature and reaction equation, it can read the relevant thermodynamic data in the data pool automatically, and calculate the final T_{ad} of SHS reaction conveniently, rapidly and accurately. The T_{ad} of some common SHS reactions calculated by this program is shown in Table 1.

From Table 1, one can find that the T_{ad} calculated by this program approach roughly that of ref. [1]. The main reasons

causing the difference are as follows: on the one hand, different authors employ different thermodynamic data; on the other hand, up to now, all the T_{ad} reported are estimated values, which can be found from the T_{ad} quoted from ref. [1] in Table 1. Generally speaking, the accuracy of the reported value is 100 K or 10 K, the estimated value is comparatively rough, and to say nothing of reflecting the condition of the phase state transformation of product. Whereas program can calculate the T_{ad} of SHS reaction conveniently, rapidly and accurately. In addition, if there is phase transformation, it can give the relevant condition of the phase transformation.

By this program, T_{ad} of SHS reaction under certain condition (preheating and adding diluent) can be calculated. Fig. 1 shows the relationship of T_{ad} with preheating temperature as an example. Fig. 2 shows the relationship between diluent content and T_{ad} under different preheating conditions for the SHS reaction $10\text{Al} + 3\text{TiO}_2 + 3\text{B}_2\text{O}_3 + x\text{Al}_2\text{O}_3$ (or TiB_2) = $5\text{Al}_2\text{O}_3 + 3\text{TiB}_2 + x\text{Al}_2\text{O}_3$ (or TiB_2). From Figs. 1 and 2, one can see that the T_{ad} of SHS reaction under certain initial condition be obviously known. T_{ad} of SHS reaction can be used to help investigate the process, mechanism and the state of the product of SHS reaction.

4 CONCLUSIONS

(1) T_{ad} of SHS reaction can be calculated conveniently, rapidly and accurately by inputting preheating temperature and SHS reaction on the base of establishing data pool;

(2) Using the calculation results, one can draw the curve about the influence of certain initial condition (preheating, adding diluent) on T_{ad} of SHS reaction, and the T_{ad} can be seen obviously.

Table 1 Calculation results of T_{ad}
of Some Common SHS Reaction

SHS reaction equation	T_{ad} /K	phase transition condition	T_{ad} in rel. [1]
$Ti+2B=TiB_2$	3 193	melted, melting rate 27.0%	3 190
$Ti+C=TiC$	3 290	melted, melting rate 16.4%	3 210
$Si+C=SiC$	1 858.5		1 800
$4B+C=B_4C$	1 038.5		1 000
$2Ti+N_2=2TiN$	4 908.5	all melted	4 900
$Zr+2B=ZrB_2$	3 323	melted, melting rate 78.2%	3 310
$Nb+2B=NbB_2$	2 317.5		2 400
$W+C=WC$	1 161.5	melted, melting rate 97.3%	1 000
$Ta+C=TaC$	2 711.5		2 700
$2Ta+N_2=2TaN$	3 363		3 360
$2Nb+N_2=2NbN$	3 474.5		3 500
$Nb+2Si=NbSi_2$	2 013.5		1 900
$5Ti+3Si=Ti_5Si_3$	2 547.5		2 500
$Mo+2Si=MoSi_2$	1 942.5		1 900
$V+C=VC$	2 228.5		
$5Zr+3Si=Zr_5Si_3$	2 755.5		2 800
$Zr+C=ZrC$	3 757.5		
$Ni+Al=NiAl$	1 912	melted, melting rate 11.8%	
$Ti+3Al=TiAl_3$	1 516.5		
$4Al+3TiO_2=3Ti+Al_2O_3$	1 805.5		
$4Al+3TiO_2+3C=3TiC+2Al_2O_3$	2 303.0	Al_2O_3 melted, melting rate 99.5%	
$10Al+3TiO_2+3B_2O_3=5Al_2O_3+3TiB_2$	2 531.5	Al_2O_3 all melted	
$2Al+B_2O_3=Al_2O_3+2B$	2 303	Al_2O_3 melted, melting rate 71.1%	
$5Mg+TiO_2+B_2O_3=5MgO+TiB_2$	3 098	MgO melted, melting rate 21.5%	
$2Al+Fe_2O_3=Al_2O_3+2Fe$	3 148.5	all melted	

* Relevant thermodynamic data come from rel. [5].

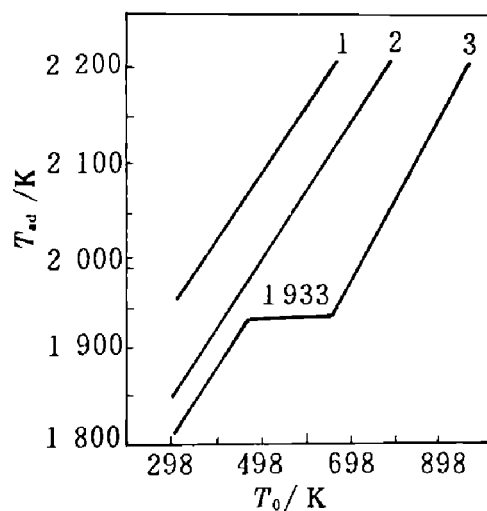


Fig. 1 Plots of T_{ad} vs T_0

1— $Mo+2Si=MoSi_2$; 2— $Si+C=SiC$;
3— $4Al+3TiO_2=3Ti+2Al_2O_3$

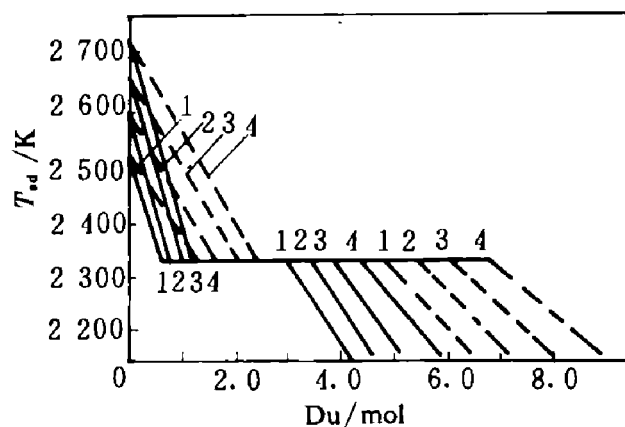


Fig. 2 Plots of T_{ad} vs Du

1— $T_0=298$ K; 2— $T_0=400$ K; 3— $T_0=500$ K; 4— $T_0=600$ K; solid line—Diluent is Al_2O_3 ; dash line—Diluent is TiB_2

REFERENCE

- 1 Munir, Z A. Am Ceram Soc Bull, 1988, 67 (2); 342—349.
- 2 Munir, Z A; Anselmi—Tamburini, U. Mater Sci Rep, 1989, 3, 277—365.
- 3 Frankhouser, William L. Advanced Processing of Ceramic Compounds. Park Ridge, Noyes Data Corp., Jersey, U S A, 1987.
- 4 Crider, I F. Ceram Eng Sci Proc, 1982, 3(9—10); 519—528.
- 5 Barin, I et al. Thermo-Chemical Properties of Inorganic Substances, 1973, 1977.